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Exchange of nutrients and oxygen across
the sediment–water interface below a
Sparus aurata marine fish farm in the
north-western Mediterranean Sea

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Abstract

Purpose This study analyzes the effects of aquaculture activities in open seawater in the north-western coastal waters of the Mediterranean Sea. It is the first of its kind to be based on benthic flux data gathered in situ below fish farms for this particular area.

Materials and methods Samples were collected on four sampling campaigns over a 1-year cycle under a *Sparus aurata* fish farm facility where benthic fluxes were measured in situ using light and dark benthic chambers. Bottom water and sediment samples were also collected. Data were compared to those for a nearby control station.

Results and discussion Significant differences were found (ANOVA, $p < 0.05$) between concentrations of organic matter (OM), total phosphorus and redox potentials in sediments located under the cages and those of the control station. The consumption of dissolved oxygen (DO) by sediment and positive ammonium (NH_4^+) fluxes was stimulated by OM content, with correlations of $r = -0.60$ ($p < 0.01$) and $r = 0.70$ ($p < 0.01$), respectively. The OM content of sediments was found to be consistently higher under the cages than at the control station, with the highest value (1.8 ± 0.7 %) under the cages observed during the early summer; values of DO and NH_4^+ fluxes were -64 ± 17 and 12.7 ± 1.0 $\text{mmol m}^{-2} \text{ day}^{-1}$, respectively. PO_4^{3-} fluxes were consistently higher in the fish farm sediments (between 0.58 and 0.98 $\text{mmol m}^{-2} \text{ day}^{-1}$) than those observed at the control station. Nitrate (NO_3^-) fluxes were found to be consistently negative due to denitrification occurring in the sediments and were related to the concentration of NO_3^- in bottom waters ($r = 0.92$, $p < 0.01$). Si fluxes were shown to be associated with water temperature ($r = 0.59$, $p < 0.05$).

Conclusions The results imply that sediments located below cages accumulate organic matter originating from aquaculture activities, especially

during summer months when this activity increases. Sediments undergo biogeochemical changes that mainly affect fluxes of DO, NH_4^+ and soluble reactive phosphorus, although these do not seem to have a significant impact on the quality of the water column due to the hydrodynamic characteristics of the area.

Keywords Aquaculture impacts. Benthic. Fish farm. Fluxes. Sediment.

1. Introduction

World aquaculture production increased dramatically from 0.6×10^6 t in 1950 to 68.4×10^6 t in 2008. Spain's aquaculture production is the highest of all EU member countries and was 249,070 t in 2008 (19.5 % of total EU production); followed by France and Italy (APROMAR 2010). It is a growing economic activity which unfortunately brings with it environmental consequences (Belias et al. 2007; Borja et al. 2009).

There is growing concern in many countries, both among citizens and the scientific community, regarding the sustainability of this growing industry (Hargrave 2005). The magnitude of its ecological impact depends on the physical and oceanographic conditions of the fish farm site, water temperature and ecosystem absorption capacity. In addition to this, fish farm management and size, cultivation density, duration of cultivation operations, fish feed digestibility and fish health are all significant factors that need to be taken into account (Molina and Vergara 2005).

Studies of the environmental effects of aquaculture activities have focused on a number of aspects, including: changes occurring in the water itself (Maldonado et al. 2005) and in the sediment layers of fish farm facilities Karakassis et al. 1998; Aksu and Kocatas 2007); disturbances in *Posidonia oceanica* meadows (Pergent-Martini et al. 2006); anoxic conditions of the sediment layer below cages Hargrave et al. 1997); and the influence of current velocities (Black and McDougall 2002). Some studies have analysed

metals and pigments found in sediments as well as bacteria and multiple stable isotopes as indicators of environmental impact (Mazzola et al. 2000; Kaymakci et al. 2010). Others have focused on the environmental impact of aquaculture activities on nutrients and plankton (Neofitou and Klaoudatos 2008); on nutrients and benthic community structure (Mazzola et al. 2000; Yucel-Gier et al. 2007); and on the geochemistry of sediments and benthic organisms (Mazzola et al. 2000).

The enrichment in organic matter produced in the sediments below cages causes high rates of decomposition, which can modify the quality of the water around the facility. This can lead to a decrease in oxygen in the water column, promote eutrophication and turn the sediments anoxic, with the result that the organic matter decomposes anaerobically. It can also seriously affect the structure of the benthic community (Jackson et al. 2004). Sediment plays a crucial role in the cycling of nutrients and can operate as the main source of nutrients in the water column, especially in coastal ecosystems (Warnken et al. 2002). A greater understanding of the above processes would help to predict impacts and adopt practices in aquaculture activity geared towards a sustainable use of the marine environment. By measuring oxygen and nutrient fluxes, it is possible to identify the main mechanisms in the mineralisation process and quantitatively determine the importance of sediments in the global cycles of nutrients on fish farms (Riise and Roos 1997).

Thus, this study should be seen in the context of the widespread preoccupation which exists with the release of waste from aquaculture and its potential to cause great harm to the ecosystem through changes in the nutrient load. More specifically, the study focuses on the effects of gilthead sea bream (*Sparus aurata*) farming activities on benthic metabolism over a 1-year farming cycle. These activities involve the use of floating cages located in

open seawater in the north-western waters of the Mediterranean Sea. Oxygen and nutrient fluxes at the sediment–water interface were determined via in situ incubations using benthic chambers. All the data were compared with that collected at a control station.

It is worth pointing out that at the international level, there have been few in situ studies into benthic fluxes at fish farms (e.g. Holby and Hall 1991, 1994; Hall et al. 1992; Freitas et al. 2008; Ferrón et al. 2009), or ex situ studies (e.g. Heilskov and Holmer 2001; Nizzoli et al. 2007). Just one study of north-western Mediterranean waters has been completed to date and this involved ex situ experiments (Belias et al. 2007).

2. Materials and methods

2.1. Study area

The study area is located in the north-western waters of the Mediterranean Sea, off the coastal town of Burriana (Spain), on the site of an intensive fish farm (UTM X: 752170; UTM Y: 4414096) located about 2 km from the coast at a depth of 19 m. The area is characterised by sandy sediments. The fish farm comprises 15 cages, and all measurements were taken from an area below a cage located at the centre of the fish farm. This farm produces 500 t annually and measurements were taken below a cage with a biomass of between 30 and 47 t. The sea breams were fed on commercial feed (conversion factor, 1.8 to 2), which was unequally distributed throughout the year as the feed rate varied according to temperature.

2.2. Sampling and sampling points

Measurements were taken from two sampling points: the first was located below a fish farm cage (I) and the other, which was used as a control area (C), was located 100 m north of the fish farm, up-current from dominant

sea currents. Samples were collected during four sampling campaigns: the first in autumn (25 November 2008, I-1; 01 December 2008, C-1); the second in winter (23 February 2009, I-2; 28 February 2009, C-2); the third in spring (28 April 2009, I-3; 02 May 2009, C-3); and the fourth in early summer (17 June 2009, I-4; 19 June 2009, C-4). Control station sediments were similar to those found below the fish farm cages. The control station was not influenced by nutrients released by the fish farm activities and the 100-m distance was deemed sufficient as various authors (e.g. Karakassis et al. 1998; Yucel-Gier et al. 2007; Borja et al. 2009) have shown that the environmental effects of fish farm activities are limited to areas immediately beneath the cages.

2.3. Benthic chamber experiments and analysis

To study nutrient and oxygen fluxes at the sediment–water interface, measurements were taken in situ using benthic chambers, similar to those used by Freitas et al. (2008). Light and dark chambers were used for each incubation, with three replicate samples being taken for each chamber type to minimise the effects of spatial heterogeneity. The measurements were taken using semi-spherical methacrylate chambers with a diameter of 40 cm and a volume of 16.7 l, covering a sediment surface area of 0.125 m². The chambers contained a manual stirrer to minimise concentration gradients (Niencheski and Jahnke 2002).

The chambers were placed in the sediment manually by scuba divers, and the total incubation period was 6 h. Samples of water were taken from inside the chambers every 2 h using 60-ml plastic syringes inserted through openings controlled by a valve. Ammonium (NH₄⁺), nitrates (NO₃⁻), soluble reactive phosphorus (PO₄³⁻), silicate (Si) and dissolved oxygen (DO) concentrations were analysed. Benthic fluxes were estimated from the slope of a linear regression of the time series results and the chamber volume (Niencheski and Jahnke 2002) and Eq. (1), as used by Nizzoli et al. (2007):

$$F = (C_t - C_o) \cdot (1/(A \cdot t)) \cdot V \cdot 24$$

where F (millimoles per square metre per day) is the estimated flow; C_t and C_o (millimoles) are the final and initial concentrations obtained in the linear fit; A (square metre) is the area of incubation; t (hours) is the total incubation time; and V (l) is volume of incubated water.

2.4. Bottom water and sediment

At the start of each sampling day, the transparency of the water column was measured using a Secchi disk (Secchi depth), and salinity (Sal), pH and temperature (Temp) of bottom water were measured using a WTW Multi 340i multiparameter probe. Water samples were taken using a Niskin bottle at a depth of 0.5 m from the bottom to analyse DO and nutrients. Samples were also taken every 2 m from the water column to analyse for chlorophyll-a (chl-a).

Scuba divers visually inspected the sea bottom for signs of *Beggiatoa* spp. and phytobenthic assemblages. During each sampling session, three samples of unaltered sediment layers were taken from the fish farm and control area using corers with a length of 30 cm and an internal diameter of 6.5 cm in order to examine physical and chemical parameters such as redox potential (Eh), organic matter (OM), water content, porosity, granulometry and total phosphorus (TP). When the corers were brought up to the surface, their Eh was measured and 1 cm of sediment was removed from the uppermost layer of the sample for analysis of the various parameters.

2.5. Parameters considered and analytical methods

The DO samples were fixed immediately and analysed in situ using the Winkler iodometric method (Baumgarten et al. 1996). For the analysis of dissolved nutrients, the samples were filtered using a cellulose acetate

membrane filter with a pore size of 0.45 μm . The NH_4^+ was determined on the same day and the remaining samples were frozen for later analysis. The nutrients were analysed using the methods described by Aminot and Chaussepied (1983) and adapted by Baumgarten et al. (1996). The chl-*a* was determined using the methodology described in APHA, AWWA and WEF (2005). The intensity of light at the bottom (I_z) was calculated following Lorenti and De Falco (2004) using the Secchi depth and solar radiation data provided by the Valencian Institute of Agricultural Research. Sediment Eh was measured at a depth of 0.5 cm using a Crison PH25 potentiometer. Sediment water content was calculated as the difference between wet and dry weight and expressed as a percentage. Sediment porosity was determined according to Dell'Anno et al. (2002). To determine sediment TP, digestion was performed following Arocena and Conde (1999). OM was analysed using the combustion method (Dell'Anno et al. 2002). Granulometry was performed for the sediment samples using the Wentworth scale (Shepard 1954).

3. Results

3.1. Bottom water and sediment

Table 1 lists the values for DO, nutrients, salinity, pH and temperature of bottom water, Secchi depths and the I_z values were calculated for the fish farm and the control station. The temperature varied between 12.9 °C in winter and 20.3 °C at the beginning of summer. Salinity ranged from 37.0 to 38.0 ‰. DO concentrations at the fish farm were found to be consistently lower than those observed at the control station. The highest concentration of NH_4^+ was observed in autumn at the fish farm, with a value of 3.1 μM , and the highest concentrations of NO_3^- were observed in autumn and winter. PO_4^{3-} concentrations were very low and there were no great differences among the four sampling campaigns: the values oscillated

between 0.10 and 0.26 μM . The maximum Si value of 5.4 μM was found in the bottom water of the control station in the early summer.

No differences in transparency were found between the fish farm and the control station, except for a control station sample taken in early summer, which had a higher value and resulted in a greater I_z . As can be seen from Table 1, the I_z value was quite low except for the early summer sample just mentioned, which was 12.3 W m^{-2} . In fact, the I_z below the cages may have been overestimated as Secchi depths were taken next to the cage and the shade they generated over the sediment was not taken into account.

Table 1 Parameters measured in bottom water of the fish farm (I) and the control station (C) in the four sampling campaigns

| Parameters | Autumn | | Winter | | Spring | | Early Summer | |
|--------------------------------------|--------|------|--------|------|--------|------|--------------|------|
| | I | C | I | C | I | C | I | C |
| Temp ($^{\circ}\text{C}$) | 16.0 | 15.0 | 12.9 | 12.9 | 16.0 | 16.1 | 20.3 | 18.6 |
| Sal (‰) | 37.8 | 37.9 | 37.9 | 38.0 | 37.0 | 37.4 | 37.4 | 37.4 |
| pH | 8.1 | 8.1 | 8.2 | 8.1 | 8.1 | 8.1 | 8.0 | 8.0 |
| DO (mg l^{-1}) | 4.4 | 7.1 | 8.4 | 8.7 | 7.9 | 9.4 | 7.8 | 9.0 |
| NH_4^+ (μM) | 3.1 | 0.5 | 0.4 | <0.1 | <0.1 | <0.1 | 0.5 | 0.9 |
| NO_3^- (μM) | 4.0 | 0.7 | 3.9 | 2.0 | 0.3 | 0.1 | 0.2 | 0.0 |
| PO_4^{3-} (μM) | 0.23 | 0.13 | 0.12 | 0.11 | 0.22 | 0.26 | 0.10 | 0.10 |
| Si (μM) | 2.6 | 1.7 | 2.1 | 2.9 | 1.8 | 2.0 | 1.1 | 5.4 |
| Secchi depth (m) | 6.0 | 5.0 | 4.9 | 4.6 | 6.7 | 6.0 | 6.7 | 13.0 |
| I_z (Wm^{-2}) | 0.2 | 0.2 | 0.2 | 0.1 | 1.0 | 0.6 | 2.4 | 12.3 |

Both the fish farm and the control station were characterised by sandy sediments with a grain size mode of between 0.125 and 0.063 mm and an average grain size corresponding to very fine sand. At both locations, water content was approximately 25 % and porosity was 0.46. Differences were found only in the percentage of shell content (12.1 ± 4.0 % under the fish

farm and 0.3 ± 0.2 % at the control station). The value was 37 times higher under the cages due to anti-fouling activity (cleaning of cages).

Significant differences (ANOVA, $p < 0.05$) were found between fish farm and control station sediments in OM content, TP concentrations and Eh measurements. In the four sampling campaigns, OM content and TP concentrations were found to be greater at the fish farm than at the control station (Fig. 1a, b). The highest OM content (1.8 ± 0.7 %) and TP ($1,350 \pm 411$ mg kg^{-1}) and greatest negative values for Eh (-207 ± 90 mV) were found in the early summer samples taken from below cages. Reducing conditions were observed under the cages throughout the year; Eh values were found to be consistently negative and much lower than those observed at the control station (see Fig. 1c). Visual inspections did not reveal *Beggiatoa* spp.; however, microphytobenthic assemblages were observed in the control station sediments in the spring.

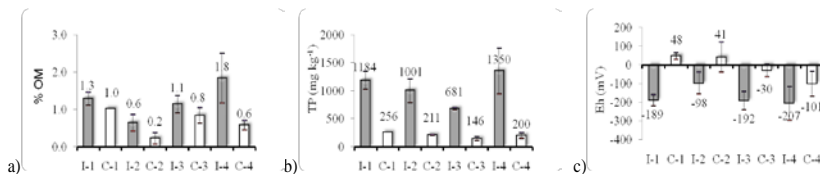


Fig. 1 a–c Values of organic matter (OM), total phosphorus (TP) and Eh in sediments under the fish farm (I) and the control station (C) in the four sampling campaigns.

3.2. Benthic fluxes

Analysis of all samples revealed no significant differences between the dark and light benthic chambers for the fluxes measured. In general, DO fluxes were negative (Fig. 2a), which indicates DO consumption by the

sediment. These values were found to be more negative at the fish farm than at the control station, and the highest consumption value was found under the cages in the early summer (up to $-71 \pm 20 \text{ mmol m}^{-2} \text{ day}^{-1}$). Significant differences (ANOVA, $p < 0.05$) between the fish farm and the control station were only observed in spring and early summer. It was during these seasons when a positive flux was also observed in the light benthic chambers at the control station (up to $17 \pm 10 \text{ mmol m}^{-2} \text{ day}^{-1}$, in spring). All the chambers showed positive fluxes in NH_4^+ from the sediment to the water column (see Fig. 2b). Significant differences (ANOVA, $p < 0.05$) were found between NH_4^+ fluxes measured at the fish farm and at the control station in the autumn, spring and early summer. The latter sampling campaign showed the greatest differences, with the highest flux found under the fish farm ($13.6 \pm 1.0 \text{ mmol m}^{-2} \text{ day}^{-1}$).

PO_4^{3-} fluxes were generally positive, i.e. phosphorus from the sediment was released to the water column, and were consistently greater below the fish farm than at the control station (see Fig. 2c); however, significant differences were only found (ANOVA, $p < 0.05$) in autumn and early summer. NO_3^- fluxes were negative, i.e. NO_3^- from the water column was consumed by the sediment. These fluxes were found to be more negative at the fish farm in autumn, winter and spring than those observed at the control station (see Fig. 2d), although significant differences (ANOVA, $p < 0.05$) were only found in autumn. Si fluxes were positive (see Fig. 2e), except for the samples taken in winter at the control station, which showed negative fluxes in both the light and dark benthic chambers. Significant differences (ANOVA, $p < 0.05$) between Si fluxes at the fish farm and control station were only observed in the winter. The highest and most positive Si fluxes were found in spring and early summer.

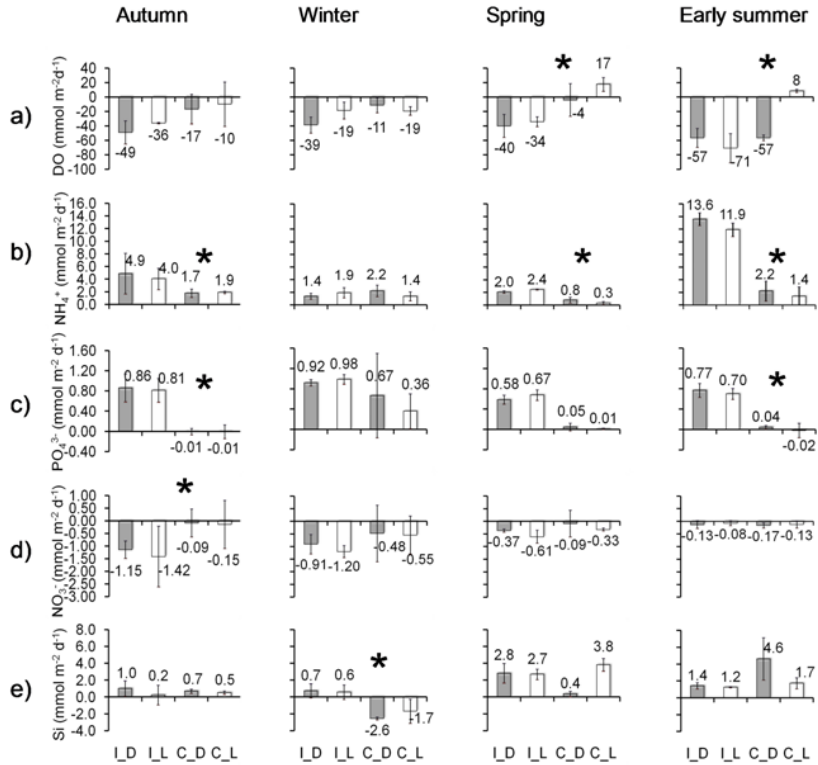


Fig. 2 Benthic fluxes of dissolved oxygen (DO), ammonium (NH₄⁺), soluble reactive phosphorus (PO₄³⁻), nitrate (NO₃⁻) and silicate (Si) in dark (D) and light (L) chambers under the fish farm cage (I) and at the control station (C) in the four sampling campaigns. Asterisk: significant differences (ANOVA, $p < 0.05$) between fish farm and control station.

4. Discussion

4.1. Bottom water and sediment

Water temperature varied according to season. The lower concentrations of DO observed at the fish farm compared to those at the

control station may be attributable to the consumption of oxygen by fish respiration and the aerobic decomposition of OM. The higher concentrations of NH_4^+ observed at the fish farm in autumn may have been caused by fish excretion (Dosdat 2001; Aksu and Kocatas 2007) and possible decomposition of OM. The differences in NO_3^- , which were found to be greater at the fish farm, were most likely due to oxidation of NH_4^+ to form NO_3^- (Dosdat 2001). The higher concentrations of NO_3^- in the Mediterranean in winter were also found by Maldonado et al. (2005). As P is a limiting nutrient in the Mediterranean (Siokou-Frangou et al. 2010), this may be the reason why we found lower concentrations of P; these values are similar to those observed by Kaymakci et al. (2010). The highest concentration of Si at the sea bottom in summer was also observed by Kaymakci et al. (2010) and may be due to mineralization of biogenic Si accumulated at the sea bottom.

OM content was consistently higher under the cages than at the control station, a finding which is known to occur under fish farm cages located in open seawater (Mantzavarakos et al. 2007; Borja et al. 2009). OM in sediment mostly originates from non-ingested fish feed, either due to over-feeding or poorly managed diet or feeding regime. Accumulation of fish faeces, farmed fish mortality and cage cleaning may also increase OM in the sediment (Molina and Vergara 2005). The highest OM content was found in early summer under the cages owing to the higher temperatures, which increased the metabolism of the fish and, consequently, their rate of feeding. This led to greater losses in fish feed and greater rates of excretion. OM values observed in this study were similar to those seen at other fish farms (Sakamaki et al. 2006; Nizzoli et al. 2007) although Mantzavarakos et al. (2007) observed higher values in OM in the Mediterranean Sea.

In this study, TP in the sediment below the cages was consistently higher than at the control station, which is in line with the findings of

Karakassis et al. (1998). The highest concentrations were found in summer, as was also observed by Mantzavarakos et al. (2007). All of the above values, along with those observed for OM, were due to the increase in solid waste originating from increased production, typical of the season. TP concentrations in sediments under Mediterranean Sea fish farms observed in other studies (e.g. Karakassis et al. 1998) were of a similar order of magnitude to our results; however, Mantzavarakos et al. (2007) found TP concentrations to be lower.

On the basis of the Eh measurements, we found sediments under the cages to be consistently more negative, with the greatest negative value observed in early summer possibly due to the higher OM content, as this measurement is highly correlated to OM content ($r=-0.70$, $p<0.01$) and TP ($r=-0.79$, $p<0.01$; Table 2). Reducing conditions in fish farm sediments were found in other studies (e.g. Karakassis et al. 1998; Ferrón et al. 2009).

The study illustrates the effects that aquaculture activity has on the sediment in the proximity of fish farms. The sediment experiences an increase in OM and TP content, which at the same time become more reductive. It is important for companies and the competent environmental authorities to take into account the changes in aquaculture activity throughout the year resulting from changes in the prevailing water temperature. In addition to the general effect on the sediments and hence the environment, there are also seasonal changes which cause an increase in aquaculture activity and thus have a greater impact. The amount of activity also affects the parameters measured in the bottom water, but since the farm facility is close to the open sea, the water is constantly being refreshed, and thus, the differences are not as pronounced as the parameters measured in the sediments.

4.2. Benthic fluxes

No significant differences were found between dark and light benthic chambers for any of the fluxes measured, which can be explained by the fact that I_z values were close to zero for nearly all the samples taken, except for an early summer sample at the control station which was 12.3 W m^{-2} . The low rate of primary production seen at a depth of 19 m, therefore, did not significantly influence flux estimation. The negative fluxes of DO indicate that the sediments consumed oxygen from the water column in the case of the dark benthic chambers. This can be explained by the aerobic mineralization of OM in which heterotrophic microorganisms use oxygen as the terminal electron acceptor. In the light benthic chambers, the majority of fluxes were found to be negative, which indicates that the consumption of oxygen by mineralization was higher than that which could have been released as a result of primary production.

Positive values for DO fluxes were measured only in spring and at the beginning of summer at the control station. Microphytobenthic assemblages were observed in the spring in this area as well as in the early summer, and I_z was greater (see Table 1). DO consumed by the sediments was generally more negative under the fish farm cages than at the control station due to the higher OM content of the fish farm ($r=0.60$, $p<0.01$) (see Table 2). The oxygen consumption of the sediment below the cages showed an increase over the control station of between $13 \text{ mmol m}^{-2} \text{ day}^{-1}$ in the winter and approximately $42 \text{ mmol m}^{-2} \text{ day}^{-1}$ in both the spring and early summer. The maximum value for sediment consumption of DO was observed in the early summer under the cages, co-occurring with higher bottom water temperatures ($20 \text{ }^\circ\text{C}$), higher rates of feeding and higher OM content found in the sediment. These conditions were similar to those observed by Nizzoli et al. (2007) and Ferrón et al. (2009). Other studies that examined DO fluxes on

aquaculture facilities obtained results similar to those seen in this study (e.g. Ferrón et al. 2009) or lower fluxes (e.g. Nizzoli et al. 2007; Freitas et al. 2008). We consider that sediment oxygen demand is an index which can be used to estimate the benthic regeneration rate, as well as being a good parameter for assessing how well this industrial activity is being managed. DO fluxes were also found to be inversely proportional to NH_4^+ fluxes ($r=-0.83$, $p<0.01$), which indicates that the greater the consumption of oxygen during mineralization of OM, the greater the release of NH_4^+ to the water column (Berelson et al. 2003).

Table 2 Pearson's correlation coefficients for relationships between variables measured in bottom water and sediment. Values in bold are significant at $p<0.05$; values in italics are significant at $p<0.01$. The number of observations ranged from 8 to 16. *Temp* temperature, *bot* bottom, *sed* sediment.

| | DO flux | PO_4^{3-} flux | Si flux | NH_4^+ flux | NO_3^- flux | Temp bot | OM sed | Eh sed | TP sed | NO_3^- bot |
|-------------------------|--------------|-------------------------|-------------|----------------------|----------------------|--------------|-------------|-------------|--------|---------------------|
| DO flux | 1.00 | | | | | | | | | |
| PO_4^{3-} flux | -0.56 | 1.00 | | | | | | | | |
| Si flux | -0.17 | -0.27 | 1.00 | | | | | | | |
| NH_4^+ flux | -0.83 | 0.56 | - | 1.00 | | | | | | |
| NO_3^- flux | 0.13 | -0.71 | 0.24 | -0.08 | 1.00 | | | | | |
| Temp bottom | -0.32 | -0.25 | 0.59 | 0.39 | 0.51 | 1.00 | | | | |
| OM sediment | -0.60 | 0.24 | 0.34 | 0.70 | 0.10 | 0.71 | 1.00 | | | |
| Eh sediment | 0.67 | -0.59 | - | -0.61 | 0.30 | -0.53 | 0.70 | 1.00 | | |
| TP sediment | -0.72 | 0.83 | 0.00 | 0.77 | -0.49 | 0.21 | 0.69 | 0.79 | 1.00 | |
| NO_3^- bottom | -0.13 | 0.67 | - | 0.10 | -0.92 | -0.63 | - | - | 0.46 | 1.00 |

Below the cages, the flux of ammonium from the sediment to the water column was greater than at the control station, increasing by 11 mmol m⁻² day⁻¹ at the start of summer. NH₄⁺ fluxes at the fish farm were greater in early summer (12.7±1.0 mmol m⁻² day⁻¹), followed by autumn and then spring (see Fig. 2b). This correlated with the OM content in the sediment ($r=0.70, p<0.01$). Ferrón et al. (2009) observed NH₄⁺ fluxes of 5 to 20 mmol m⁻² day⁻¹, and Nizzoli et al. (2007) found values ranging from 10 to 57 mmol m⁻² day⁻¹. Both studies also found that the greatest fluxes occurred in the summer, when temperatures and aquaculture activity were higher. Especially noteworthy was the fact that for three of the four sampling campaigns, significant differences in NH₄⁺ fluxes were observed between the fish farm and control station.

PO₄³⁻ fluxes were higher under the cages than at the control station, rising from 0.44 mmol m⁻² day⁻¹ in winter to 0.84 mmol m⁻² day⁻¹ in autumn, due to the higher content of TP in the sediment ($r=0.83, p<0.01$). PO₄³⁻ fluxes were correlated (see Table 2) to NH₄⁺ ($r=0.57, p<0.05$) and DO fluxes ($r=-0.56, p<0.05$). This can be explained by the decomposition of OM, which involves an uptake of DO to produce NH₄⁺ and PO₄³⁻. Nevertheless, there was no direct relationship between this and OM content, probably due to the fact that the uppermost layer of the sediment, which was probably well oxygenated, retained PO₄³⁻. We also obtained an interesting correlation between PO₄³⁻ flux and Eh ($r=-0.59, p<0.05$), which was attributable to the fact that P may be released under anaerobic conditions (Rodríguez 1999), such as those observed in below the superficial sediment layer. Ferrón et al. (2009) observed flux data for PO₄³⁻ similar to those seen in this study.

Nitrate fluxes were consistently negative; NO₃⁻ in the water column was consumed by the sediment due to benthic denitrification occurring in the suboxic and anoxic sediment layers, where NO₃⁻ acts as a terminal acceptor

of electrons (Herbert 1999). In samples taken in the autumn, winter and spring, NO_3^- fluxes were found to be more negative at the fish farm than at the control station; NO_3^- consumption is as much as $1.2 \text{ mmol m}^{-2} \text{ day}^{-1}$ higher on the fish farm compared to the control, despite the fact that significant differences were found in autumn only. These differences may be explained by the higher concentrations of OM under the cages where suboxic/anoxic zones of the sediments are closer to the surface, favouring increased benthic denitrification. Greater negative fluxes were observed in autumn and winter under the cages, co-occurring with the higher concentrations of NO_3^- in the bottom water (see Table 1). The correlation between NO_3^- fluxes and initial concentrations of NO_3^- in the bottom waters was $r=-0.92$ ($p<0.01$). Previous studies have shown a clear negative relationship between NO_3^- flux and NO_3^- concentration in bottom water (Sakamaki et al. 2006). The high concentrations of NO_3^- in the bottom waters increase its flux into sediments, increasing NO_3^- concentrations in interstitial water, which in turn favours bacterial nitrate respiration. As the concentration of NO_3^- increases, NO_3^- is reduced to $\text{N}_2/\text{N}_2\text{O}$ and N is lost from the system due to denitrification (Herbert 1999).

The highest and most positive Si fluxes were observed in spring and early summer due to the increase in Si dissolution rates caused by the higher temperatures (Cermelj et al. 2001). The correlation between Si fluxes and temperature (see Table 2) was 0.59 ($p<0.05$). Fish farm activity does not seem to affect Si fluxes as OM from the fish farm had a low Si content. Other studies (e.g. Freitas et al. 2008) also indicate that Si fluxes are not significantly influenced by aquaculture activities and they also find positive flows, similar to those seen in Ferrón et al. (2009).

To determine the implications that these fluxes might have for the water column, it is first necessary to quantify their importance to primary

production. Morán and Estrada (2005) studied the north-western basin of the Mediterranean Sea and observed that total phytoplankton biomass was closely correlated with primary production and proposed a linear regression model which integrated daily rates of primary production (PP_{int}) with integrated values of chl-*a* ($\text{chl-}a_{\text{int}}$). Since we had data from all our sampling campaigns for chl-*a* taken every 2 m depth in the water column, we were able to calculate the average chl- a_{int} for both the control and fish farm. In both areas, the average chl- a_{int} was similar, at around 7.2 mg m^{-2} . Subsequently, we used the relation postulated by Morán and Estrada (2005) to estimate the integrated daily production, which was $139 \text{ mg C m}^{-2} \text{ day}^{-1}$ (ca. $12 \text{ mmol C m}^{-2} \text{ day}^{-1}$). Assuming nutrient utilization ratios approaching Redfield and no nitrogen fixation (Redfield et al. 1963; Niencheski and Jahnke 2002), phytoplankton would require ca. $2 \text{ mmol N m}^{-2} \text{ day}^{-1}$, $0.1 \text{ mmol P m}^{-2} \text{ day}^{-1}$ and $2 \text{ mmol Si m}^{-2} \text{ day}^{-1}$. We calculated average N benthic flux from the sum of the fluxes of NH_4^+ , NO_3^- and NO_2^- (data not shown) for both the control and fish farm, giving 1.3 and $4.4 \text{ mmol N m}^{-2} \text{ day}^{-1}$, respectively. At the control station, nearly three quarters of phytoplankton N requirements can be met by benthic N fluxes, whereas at the fish farm, the benthic fluxes are 2.5 times higher than these requirements. Average P benthic fluxes were $0.1 \text{ mmol P m}^{-2} \text{ day}^{-1}$ for the control and $0.8 \text{ mmol P m}^{-2} \text{ day}^{-1}$ for the fish farm, which indicates that phytoplankton P requirements are met by benthic fluxes in both cases, even though on the fish farm, they are eight times higher. The average benthic Si fluxes at the control and fish farm were similar at approximately $1 \text{ mmol Si m}^{-2} \text{ day}^{-1}$, which is half of the diatom Si requirements. The above results show that the fish farm has a far higher availability of P and N than the control, while the contribution of Si by the sediment is the same in both locations. On the fish farm, these differences might lead to a modification in the structure of the phytoplankton community and promote the growth of species which do not use Si as a nutrient.

However, the greater availability of N and P on the fish farm was not reflected in differences in PP_{int} , which was similar in both zones, at around 7.2 mg m^{-2} . This indicates that there is a high amount of dilution in the zone as a consequence of the high hydrodynamic behaviour of open seawater, making it impossible to detect differences in the phytoplankton biomass. This corroborates the observations made for similar fish farms in the Mediterranean by Pitta et al. (1999) and Sarà et al. (2006).

5. Conclusions

Floating cage aquaculture in the marine environment generates an accumulation of OM in sediments, which reaches peak values in summer. The variations in the accumulation of OM occurring on fish farms are very closely linked to the metabolic activity of the fish bred on farms, and this depends on the water temperature. As a result, sediments undergo biochemical changes which primarily affect oxygen consumption, release of NH_4^+ and PO_4^{3-} and NO_3^- consumption by the sediment. However, Si fluxes seem unaffected by fish farm activity since the contribution of Si by fish farms is currently negligible. In the future, if the use of fish feed of vegetable origin instead of fish meal becomes more widespread, it will become necessary to reassess the Si contributed by fish farm activity.

Our results for benthic flux in situ are the first obtained for caged fish farms in the Mediterranean and they show that sediments can play an important role in nutrient cycling. Furthermore, benthic fluxes can have an important influence the concentrations of oxygen and nutrients in the water column; oxygen consumption is as much as $42 \text{ mmol m}^{-2} \text{ day}^{-1}$ higher on the fish farm compared to the control site. Although no important consequences are detected in the water column, the accumulation of organic waste and oxygen concentrations in the water near the bottom will need constant monitoring owing to the hydrodynamic features of such locations. The flux

which has the greatest importance relative to the requirements of the primary producers is PO_4^{3-} . However, the system does not seem to be affected by the presence of such high fluxes, possibly because of the dilution due to the hydrodynamic behaviour of open seawater. In the future, it will be necessary to consider the broader (in time and space) repercussions that the input of nutrients has on the ecosystem as a whole.

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