

## Physical and chemical properties of the water column and sediments at sea bass/sea bream farm in the middle Adriatic (Maslinova Bay)

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*Physical and chemical characteristics of the water column and sediments at sea bass/sea bream farm located on the middle Adriatic island of Brač were investigated during the 2001-2006 period. Measurements and samplings were performed at stations inside the farm area and at reference station, approximately 1 km distant from the farm. Investigated parameters in the water column were temperature, salinity, transparency, suspended matter concentration, oxygen saturation and nutrient concentrations. Parameters measured in the sediments were granulometric composition, redox-potential, organic matter, organic carbon and total nitrogen content, phosphorus (P) species concentration (biogenic apatite P, authigenic apatite P, detrital apatite P, P bound to iron oxides and hydroxides and organic P).*

*Transparency in the water column at all stations followed the natural seasonal course, although constantly lower values at the farm stations relative to the reference site indicate a certain impact of fish farming on this parameter. Impact on chemical parameters was moderately expressed in the surface and middle layer of the water column through the deficiency of oxygen and increased concentrations of dissolved inorganic nitrogen, orthophosphate and urea due to fish excretion and degradation of their metabolic products.*

*Sediment inorganic P concentrations were enhanced under the cages compared to the reference site, while organic P was mainly within the range of "natural" middle Adriatic concentrations. Sequential analysis of inorganic P species showed an increased portion of biogenic apatite P and decreased detrital apatite P at the farm stations with respect to the inorganic P pool at the reference station as a direct consequence of fish farming. Sediment redox-potential, granulometric composition, organic matter content, carbonates as well as organic carbon and total nitrogen content reflected natural sediment characteristics rather than fish farm influence.*

**Key words:** fish farming, water column, sediment, nutrients, redox-potential, phosphorus, organic matter, Adriatic Sea

### INTRODUCTION

Mariculture activities in Croatia have expanded significantly during the last decade, as in other

Mediterranean countries. Fish farming (sea bream and sea bass, as well as bluefin tuna) production growth exhibited a significant increment from <1500 t/year in 1997 to >7000 t/year in 2006.

This expansion has led to enhanced concern for the environmental integrity of the Croatian coastal areas from both the scientific community and the public, particularly regarding the ecological influences of fish farming. Fish farming releases a variety of waste into the marine environment including nutrients, organic matter as well as pharmaceutical products, which can have undesirable impacts (FERNANDES, 2001). According to KARAKASSIS *et al.* (2005), there is a small risk of hypereutrophication at large spatial scales in the Mediterranean, while potential changes in the water column occur at short spatial scales. The effects of fish farming, monitored in the immediate vicinity of the fish cages (small spatial scales), on the nutrients and Chl *a* concentrations in the water column in most cases were not significant (PITA *et al.* 1999, 2006; LA ROSSA *et al.*, 2001; SOTO & NORAMBUENA, 2004). On the contrary, degradation of the seabed beneath and around the fish cages is the most widely documented effect of fish farming. These changes were demonstrated through disturbances of different parameters such as a negative sediment redox-potential (HARGRAVE *et al.* 1993; PAWAR *et al.* 2001), accumulation of organic carbon, phosphorus and nitrogen compounds (HALL *et al.*, 1990; HOLBY & HALL 1991, 1994; HARGRAVE *et al.*, 1997; PORELLO *et al.*, 2005a, MATIJEVIĆ *et al.*, 2006) and accordingly changed or reduced benthic communities (MAZZOLA *et al.*, 1999; KOVAČ *et al.*, 2001, 2004; KARAKASSIS *et al.*, 1999, 2000, 2002; LA ROSSA *et al.*, 2001; MIRTO *et al.*, 2002).

To reduce the negative ecological impact of fish farming activities on the marine environment in Croatia, adequate legislation has been introduced including necessary periodic monitoring of physical, chemical and biological parameters in the water column and sediments as well as the state of benthic communities at farms.

In this paper, we present results of measurements performed in the frame of the Croatian monitoring program at one sea bream and sea bass farm (SB&SB) in the middle Adriatic to evaluate the influence of fish farming. Investigated parameters of the water column were temperature, salinity, suspended matter concen-

trations, transparency, oxygen saturation and nutrient concentrations. Parameters explored in the sediment were redox-potential, organic carbon and total nitrogen content as well as concentrations of different phosphorus species.

## MATERIAL AND METHODS

The investigated sea bass (*Dicentrarchus labrax*) and sea bream (*Sparus aurata*) farm is located on the island of Brač (middle Adriatic) in the semi-enclosed Maslinova Bay. This farm was established in 1993, and has an annual production of 200 tonnes for both species with average breeding cycles of 24 months. The measurements/samplings were performed in December 2001, May 2002 and February 2003 at three locations inside the breeding area (M1, M2 and M3) and at a reference station (REF) (Fig. 1; Table 1). During the September 2005-August 2006 period, the measurements were performed only at the M2 and REF stations.

Temperature and salinity were measured in December 2001, May 2002 and February 2003 with an IDRONAUT 316 CTD probe. During the September 2005 - August 2006 period the T-S measurements were performed with a SEABIRD-25 CTD probe. The data obtained

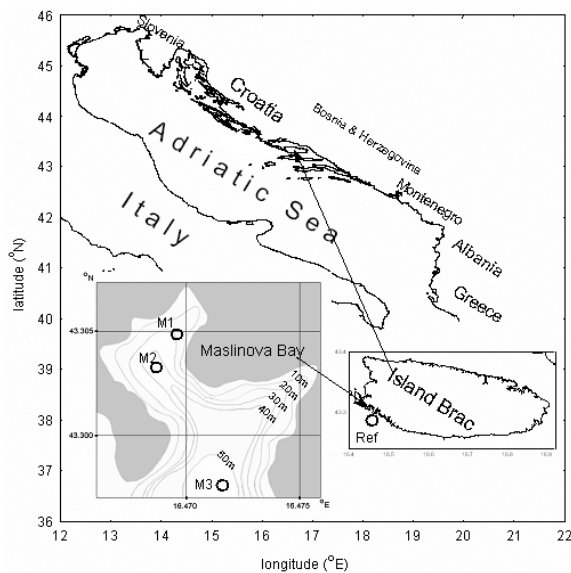


Fig. 1. Location of the Island of Brač in the Adriatic Sea with investigated stations in close proximity to the fish farm cages in Maslinova Bay (M1, M2 and M3) and reference station (REF)

Table 1. Station depths, sampling dates, temperature (T), salinity (S), total suspended matter (TSM), sediment types (FOLK, 1954), organic matter (OM), carbonate (CA), organic carbon (C-ORG) and total nitrogen (N-TOT) content in Maslinova Bay (M1, M2 and M3) and at the REF station

Station	Depth (m)	Sampling date	T (°C)	S	TSM (mg dm <sup>-3</sup> )	Sediment type	OM (%)	CA (%)	C-ORG (%)	N-TOT (%)
<b>M1</b>	12	Dec 2001	15.5-15.6	38.5-38.8	n. d.	sG	2.80	71	1.291	0.184
		May 2002	18.0-18.8	38.3-38.4	3-4	n. d.	2.64	92	0.539	0.027
	17*	Mar 2003	12.8-13.1	38.1-38.2	2-13	gS	2.51±0.40	88	0.603	0.057
<b>M2</b>	37	Dec 2001	15.5-15.6	38.2-38.8	4-26	mS	2.42	89	1.131	0.261
		May 2002	14.6-18.8	38.3-38.6	3-5	n. d.	2.27±0.38	75	0.711	0.038
		Mar 2003	12.8-13.0	38.1-38.3	3-20	(g)sM	2.19±0.03	n. d.	0.556	0.071
		Sep 2005-Aug 2006	12.2-24.2	36.6-38.7	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.
<b>M3</b>	55	Dec 2001	15.5-15.6	38.4-38.5	1-28	gM	3.18±0.27	80	0.92	0.114
		May 2002	14.2-19.2	38.2-38.7	2-3	n. d.	2.82±0.17	50	0.406	0.010
		Mar 2003	12.9-13.6	38.2-38.3	2-6	(g)sM	2.6	n. d.	0.339	0.036
<b>REF</b>	78	Dec 2001	15.6-15.9	38.4-38.8	8-21	sM	4.33±0.21	65	1.259	0.166
		May 2002	13.6-19.4	38.1-38.7	1-2	n. d.	2.57±0.06	65	0.388	0.010
		Mar 2003	13.1-13.1	38.3-38.3	2-8	sM	4.16±0.30	n. d.	0.375	0.046
		Sep 2005-Aug 2006	12.5-23.0	37.9-38.8	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.

\*M1 station was relocated in 2003 to 17 m depth

during all cruises were averaged for every meter of depth following the manufacturer's recommended procedure (Seabird Manual).

Transparency was measured with the white Secchi disk (30 cm diameter) during the same periods as for T-S measurements. The water samples were taken with Nansen bottles at the surface, middle and the bottom layer (2 m above the bottom) during 2001-2003, while in the 2005-2006 period water samples were taken at standard oceanographic depths. Dissolved oxygen was determined by the standard Winkler titration method (GRASSHOFF, 1976). Dissolved inorganic nutrient concentrations (nitrates, nitrites, ammonia, orthophosphates and silicates) and total nitrogen and phosphorus concentrations (after UV oxidation) were determined colorimetrically

with an AutoAnalyzer-3 (BRAN & LUEBBE, 2006), according to GRASSHOFF (1976). Urea concentrations were determined on a Shimadzu UV-VIS Spectrophotometer according to MULVENNA & SAVIDGE (1992).

Total suspended matter (TSM) concentrations (mg dm<sup>-3</sup>) were determined gravimetrically after filtration of 1 L of a water sample on a pre-weighed and pre-combusted Whatman GF/F filter (0.45 µm) after desiccation at 105°C for 24 h.

Sediment samples were collected in December 2001, May 2002 and February 2003 in duplicates by SCUBA-divers (depth <50 m) or gravity corer (depth >50 m) using transparent plastic liners (i. d. = 6.5 cm).

Redox-potential was measured in sediment cores, "in situ" by vertical penetration of a Pt

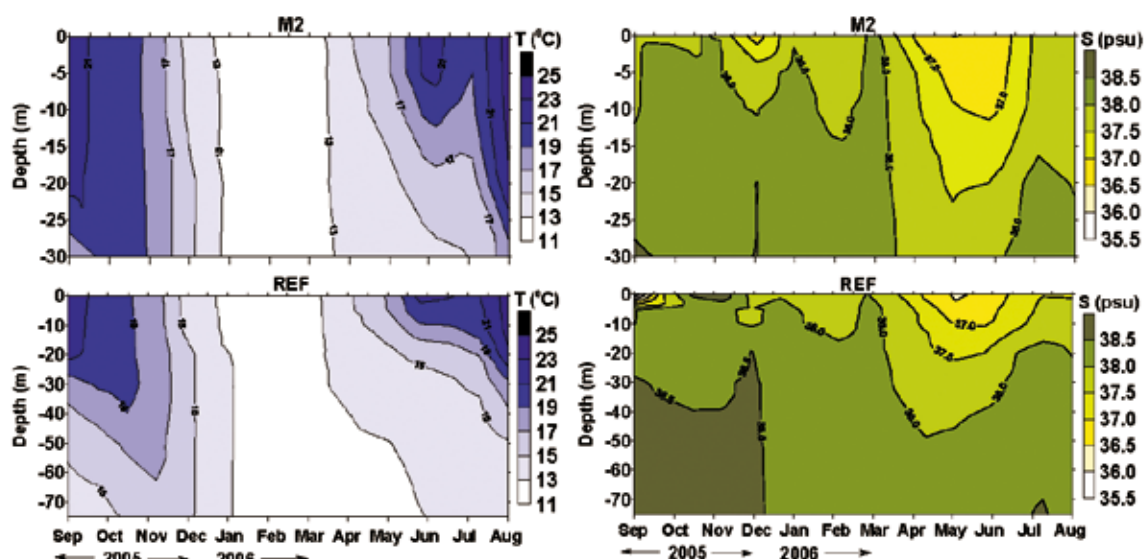


Fig. 2. Course of vertical temperature (left) and salinity (right) distributions at the M2 and REF stations in the period September 2005–August 2006

electrode connected to a Metrohm E-605 voltmeter, with a Ag/AgCl reference electrode in 3M KCl electrolyte. Calibration was performed in quinhydrone buffer solutions (pH 4 and pH 7) prepared according to Metrohm (Ag Herissau, Switzerland).

Granulometric composition of the sediment samples was determined by sieving ( $>63 \mu\text{m}$ ) and the hydrometric method ( $<63 \mu\text{m}$ ), while sediment type was classified according to FOLK (1954).

Carbonate content was determined according to LORING & RANTALA (1992), and organic matter content was determined gravimetrically after oxidation with  $\text{H}_2\text{O}_2$  and ignition at  $450^\circ\text{C}$  for 6 hours (VDOVIĆ *et al.*, 1991).

Organic carbon and total nitrogen content in sediments were determined using a CHNS-O analyzer (EA 1110, CE instruments). Before analysis, freeze-dried sediment samples were prepared according to UJIÉ *et al.* (2001) by acidification of the sediments with HCl to remove carbonates.

Sediment cores for P analysis were divided into slices (1 cm thick), frozen and stored in clean plastic bags until lab analysis. Freeze-dried sediment samples were ground and sieved ( $\phi < 250 \mu\text{m}$ ). 0.175 g (d. wt.) of sediment sample was extracted using the SEDEX method

(RUTTENBERG, 1992) modified by MATIJEVIĆ *et al.* (2008) for inorganic P species determination (P in biogenic apatite (P-FD), P adsorbed onto iron-oxy/hydroxides (P-Fe), P in authigenic apatite (P-AUT), and P in detrital apatite (P-DET). Details of the sequential extraction scheme are published elsewhere (MATIJEVIĆ *et al.*, 2008). Total and organic phosphorus (TP and OP) were determined using the method by ASPILA *et al.* (1976). Phosphorus concentrations in extracted solutions were measured with a Shimadzu UV-VIS Spectrophotometer according to STRICKLAND & PARSONS (1972). Standard sediment material PACS-2 (NRC-CNRC) was used for method evaluation.

## RESULTS AND DISCUSSION

### Thermohaline conditions in the water column

Temperature (T) and salinity (S) ranges at Maslinova Bay stations (M1, M2, M3) and the reference station (REF) measured in December 2001, May 2002 and February 2003 are shown in Table 1, while the vertical distributions of T and S on a monthly scale measured in the September 2005–August 2006 period (at the M2 and REF stations) are presented in Fig. 2.

During 2005-2006 both stations showed similar annual course of temperature. The warming had already started in April and the thermocline was developed to 10 m in June. Deepening of the thermocline continued until October, while it disappeared in November. A vertically homogenous temperature distribution was present throughout the December-March period in the entire water column and minimal values (10.6°C) were measured. The temperature maximum at the investigated area occurred in August (23.5°C) in the surface layer. Salinity showed an increase, especially in the lower layers from September to December 2005. Relatively low salinities were present at the surface in 2006, especially in June 2006. These conditions were caused by high precipitation in the spring-summer period of 2006.

### Transparency

Transparency measured during 2001 and 2003 at stations in Maslinova Bay, as well as data obtained from monthly measurements during the September 2005-August 2006 period at M2 and REF, are shown in Fig. 3.

Transparency measured during 2001 and 2003 ranged between 13 and 20 m with lower values at shallow farm stations (M1, M2) in relation to the deeper stations (M3 and REF). These results are in accordance with transpar-

ency ranges for the shallow coastal areas of the middle Adriatic (MOROVIĆ *et al.*, 2006).

The seasonal course of transparency at M2 and REF during the September 2005-August 2006 period have shown constantly lower values at the farm than at the REF station, although with a similar monthly distribution (Fig. 3). The highest values were observed during the summer thermocline (July-October), and the lowest during the period of well-mixed homogenous water column in the winter period (December-February). The exception was low transparency in June 2006 at station M2 (7 m) probably indicating that due to stratification particulate matter remained above the thermocline. Considering the similar seasonal transparency course at the farm and REF stations, this parameter reflects the natural course of transparency, although somewhat lower transparencies in Maslinova Bay may indicate the influence of fish farming. This is in agreement with BEVERIDGE *et al.* (1994) and WU *et al.* (1995) who reported a localised environmental impact with no significant changes in transparency and TSM near the fish farms.

Total suspended matter (TSM) concentrations measured during 2001, 2002 and 2003 at the farm stations (M1, M2 and M3) ranged between 1.3 and 28 mg dm<sup>-3</sup>, while at the REF station TSM ranged from 1.7 to 21 mg dm<sup>-3</sup> (Table 1). Common characteristics for all the stations were higher TSM in the Bay than at

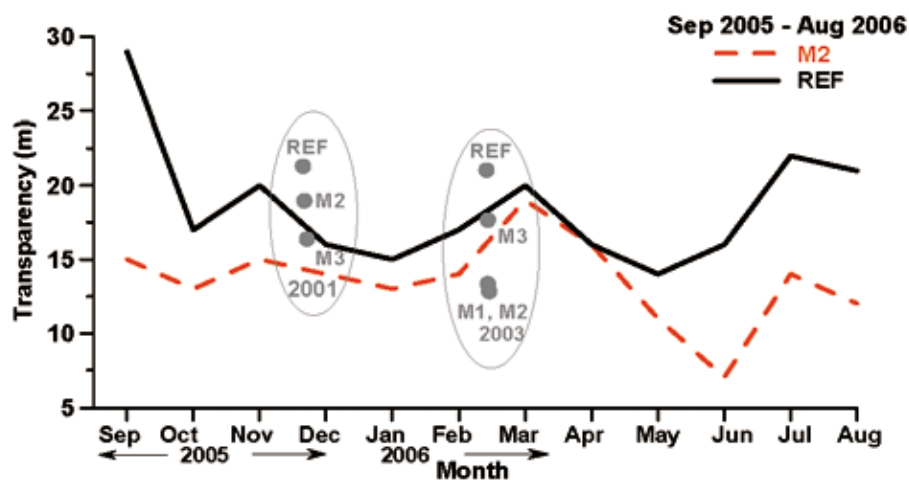


Fig. 3. Transparency measured during 2001 and 2003 at stations in Maslinova Bay and monthly transparency course obtained at M2 and REF stations from September 2005 to August 2006

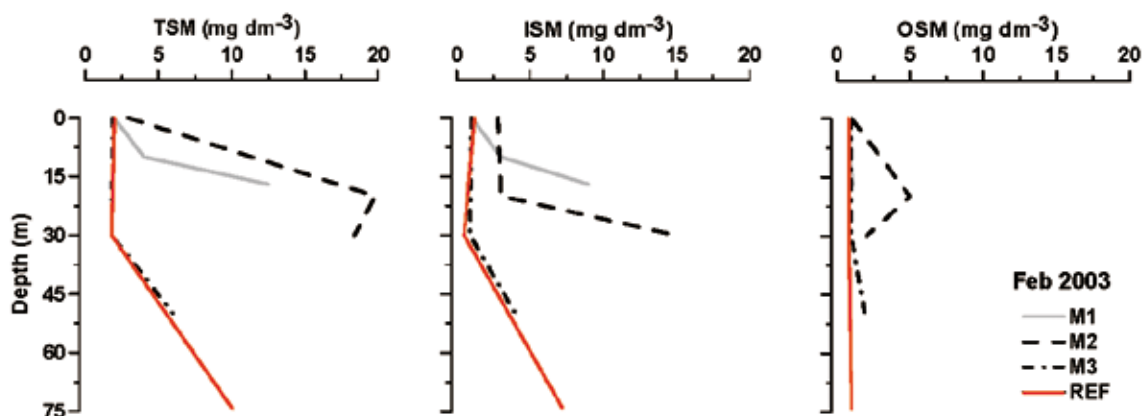


Fig. 4. Concentrations of total, inorganic and organic suspended matter (TSM, ISM and OSM) in the water column in Maslinova Bay (M1, M2 and M3) and reference (REF) stations in February 2003

the REF station and a similar vertical distribution with increased concentrations in the bottom layers. The highest concentrations in December 2001 are probably a consequence of strong Bora wind, of five days duration prior to the measurements, which could have mixed the bottom material and forced sediment resuspension causing high TSM concentrations in the Bay and at the REF station. Prevailing inorganic portions of suspended matter (ISM) in the bottom layer at all stations determined in Feb 2003 also indicate resuspension of inorganic material from the bottom, rather than organic material (OSM) originating from the farm activities (Fig. 4). The highest TSM concentrations agreed well with the lowest transparency during the same measurements (see Fig. 3).

Relative to European fish farms, the TSM concentrations in Maslinova Bay correspond to data ranges ( $0.4$  to  $21 \text{ mg dm}^{-3}$ ) reported for some Turkish and Italian SB&SB farms (YUCEL-GIER *et al.*, 2007; 2008; MODICA *et al.*, 2006; PORELLO *et al.*, 2005b) and are even lower than at one Greek farm (MANTZAVRAKOS *et al.*, 2007) where TSM concentration exceeded  $60 \text{ mg dm}^{-3}$  and were about three times higher than at the control site.

### Water column

Oxygen saturation in the water column during the 2001-2003 period ranged from 81.8 to 107.4% at M1, M2 and M3 stations while at the reference site the saturation range was slightly smaller (86.3 to 107.9%) (Fig. 5).

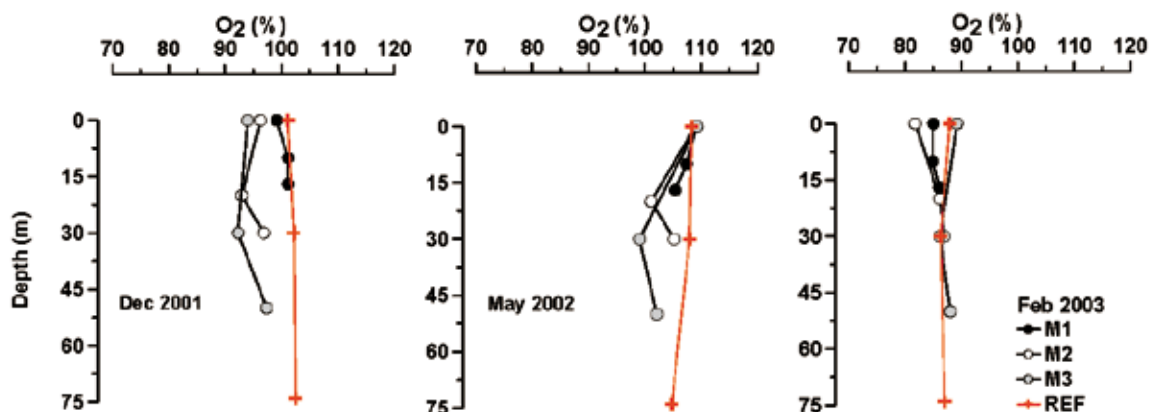


Fig. 5. Vertical distribution of oxygen saturation in the water column at farm and REF stations in Maslinova Bay in Dec 2001, May 2002 and Feb 2003

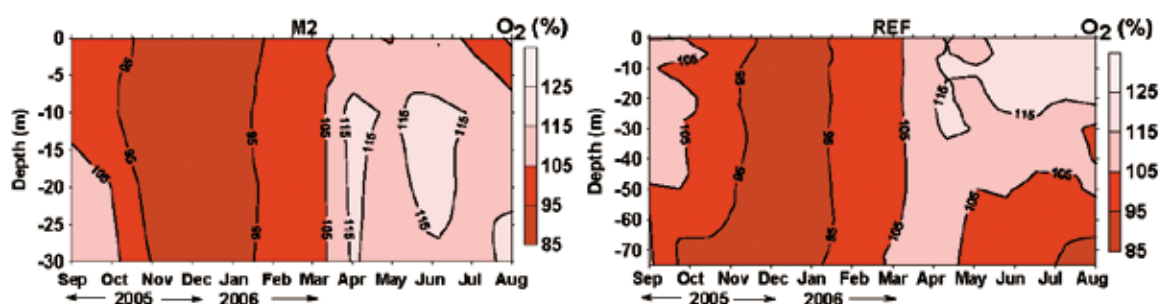


Fig. 6. Seasonal course of vertical oxygen saturation ( $O_2$  %) distribution in the water column at M2 and REF stations measured during September 2005-August 2006

At the farm stations oxygen saturation was generally lower (up to 9.9% in December 2001 at station M3,  $z=30\text{m}$ ) relative to the REF station, with a calculated overall (seasonal and depth) oxygen deficiency of  $0.16 \text{ mg dm}^{-3}$ . The lowest oxygen saturations were determined at the farm stations in the middle, and not in the bottom layer (Fig. 5).

This could be an indication of higher oxygen consumption directly by fish and oxidation of their metabolic products, rather than by decomposition of settled particulate matter. Monthly investigations of oxygen saturation performed at M2 and REF stations during 2005-2006 (Fig. 6) showed higher ranges at M2 (84.8 to 122.5%) and at the REF station (88.2 to 123.9%) than in the former period (see Fig. 5).

Similar to the results obtained during 2001/2003, the lowest oxygen saturations at

both stations were recorded during the cold period of year. Under-saturation of oxygen at the REF station was especially pronounced in the bottom layer from the end of September to mid January, while at farm stations it was observed in the 0-10 m layer from October to mid January. This discrepancy was probably caused partly by greater depth of the REF station (75 m) and higher respiration rates in the 0-10 m layer at the farm site. Temporal changes of oxygen concentrations in the 0-10 m layer of the water column (Fig. 7) indicate reduced oxygen at station M2, relative to the reference station during the entire year, with an average oxygen deficiency of  $0.38 \text{ mg L}^{-1}$ .

These results differ from reported undisturbed oxygen conditions found under the cages of SB&SB farms in the Tyrrhenian Sea (LA ROSSA *et al.*, 2002) and salmon farms in Chile

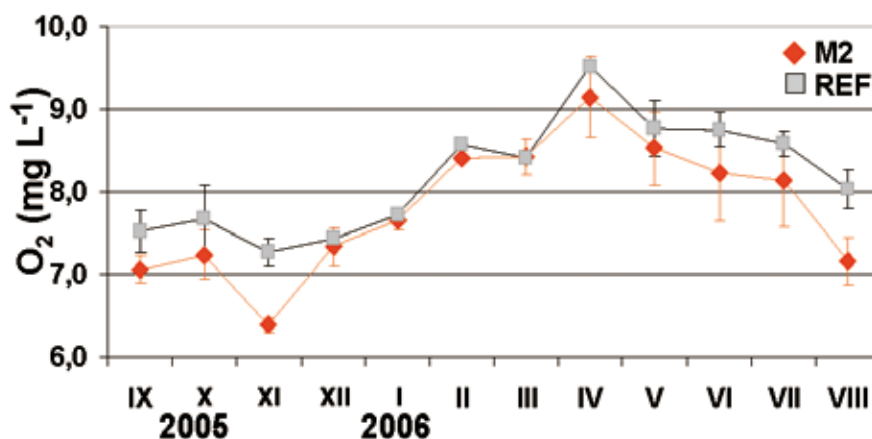


Fig. 7. Temporal changes of oxygen concentrations ( $\text{mg L}^{-1}$ ) in the 0-10 m layer of the water column at M2 and REF stations during the September 2005-August 2006 period

Table 2. Concentration ranges ( $\mu\text{mol L}^{-1}$ ) of dissolved inorganic (DIN) and organic nitrogen (N-org), orthophosphate ( $\text{HPO}_4^{2-}$ ), organic phosphorus (P-org) and orthosilicate ( $\text{SiO}_4^{4-}$ ) at Maslinova Bay stations (M1, M2, M3) and at the reference station (REF) during the 2001-2003 period

Station	Nutrients concentration ranges ( $\mu\text{mol L}^{-1}$ )				
	DIN	$\text{HPO}_4^{2-}$	$\text{SiO}_4^{4-}$	N-org	P-org*
M1, M2, M3	0.39-5.21	0.022-0.221	0.38-2.64	0.41-4.92	0.184-0.313
REF	0.48-4.96	0.040-0.210	0.36-2.35	0.23-4.18	0.202-0.256

\*Data available only for February 2003

(SOTO & NORAMBUENA, 2004), although are in agreement with the results of BERGHEIM *et al.*, 1982; BEVERIDGE & MUIR, 1982; PENCZAK *et al.*, 1982; PHILLIPS & BEVERIDGE, 1986 and MOLVER *et al.*, 1988 who have observed a cultured fish-induced oxygen demand. The oxygen consumption depends on the cultured fish mass and the species (80 to > 400 mg  $\text{O}_2 \text{ t}^{-1} \text{ h}^{-1}$ ) (WU, 1990; MCLEAN *et al.*, 1993) as well as on the water exchange rates (BEVERIDGE *et al.*, 1994; TERVET, 1981). The oxygen deficiency at the Maslinova Bay farm is only moderately expressed, suggesting that relatively good circulation is established between the bay and surrounding sea. The estimated water renewal period for the bay was from 2–10 days (IOF, 2004), indicate an exchange rate between 6.7 and 33.7  $\text{m}^3 \text{ s}^{-1}$ , which exceeds the critical minimum of water exchange rate

per annual fish production according to TERVET (1981).

During the 2001-2003 period, ranges of dissolved nutrient concentrations (sum of inorganic nitrogen species (DIN), orthophosphate ( $\text{HPO}_4^{2-}$ ), silicate ( $\text{SiO}_4^{4-}$ ), organic nitrogen (N-org) and organic phosphorus (P-org)) in the water column at Maslinova Bay stations (M1, M2, M3) were only slightly enhanced relative to the reference station (REF) (Table 2).

Spatial and temporal distribution of particular nutrients and their ratios (DIN /  $\text{HPO}_4^{2-}$ , DIN / N-org;  $(\text{NO}_3^- + \text{NO}_2^-) / \text{NH}_4^+$  and DIN /  $\text{SiO}_4^{4-}$ ) indicated to relatively weak influence of the fish farming on the dissolved nutrient pool. The exceptions were orthophosphate and organic nitrogen concentrations, which were enhanced at certain farm stations in comparison to the ref-

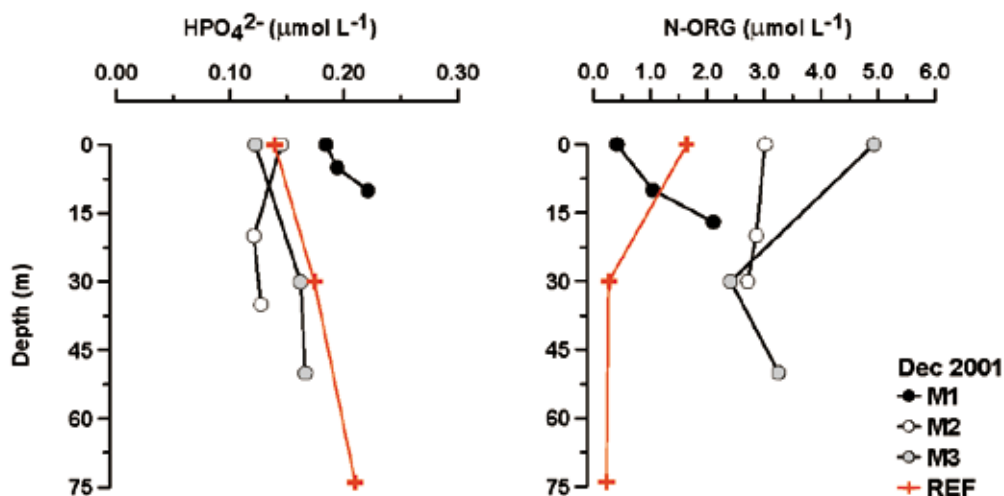


Fig. 8. Vertical distribution of orthophosphate and organic nitrogen concentrations at Maslinova Bay farm (M1, M2, M3) and at the REF station in December 2001



erence site in December 2001 (Fig. 8).

More frequent investigations of nutrient concentrations during the 2005-2006 period confirmed a certain influence of the fish farming on nutrient distribution. Namely, during the October-November and March-April periods the DIN,  $\text{HPO}_4^{2-}$  and urea concentrations were enhanced in the upper part of the water column (0-20m) compared to the REF station (Fig. 9). This can be attributed to fish excretions, degradation of their metabolic products as well as to the oxygen uptake considering the position of cages at these depths. Increase of nutrient concentrations due to fish farming has been reported by MATIJEVIĆ *et al.* (2006) for a middle Adriatic tuna farm, as well as by numerous authors including DAVENPORT *et al.* (1990); RUIZ *et al.* (2001); PITTA *et al.* (2006) and MERINO *et al.* (2007) for other regional seas. It should be emphasised that there are also reports indicating either no

impact or a minor effect on the nutrient pool (MALDONADO *et al.*, 2005; KARAKASSIS *et al.*, 2001). Our investigations have shown that nutrient enrichment occurs only in the upper part of the water column, while concentrations in deeper layers were even more elevated at the REF station (Fig. 9).

Nutrient maxima in the bottom layer of the REF station are probably a result of the periodic influence of the Neretva River on the sedimentation rate of particulate organic material in this area. Enhanced settling of organic matter results in increased nutrient regeneration and consequently higher fluxes of dissolved nutrients. Increased benthic fluxes of DIN and  $\text{HPO}_4^{2-}$  in the areas under the river's influence in the middle Adriatic area were already observed by BARIĆ *et al.* (2001). The importance of urea in the sediments was shown by LOMSTEIN *et al.* (1989), who emphasized its role as an intermedi-

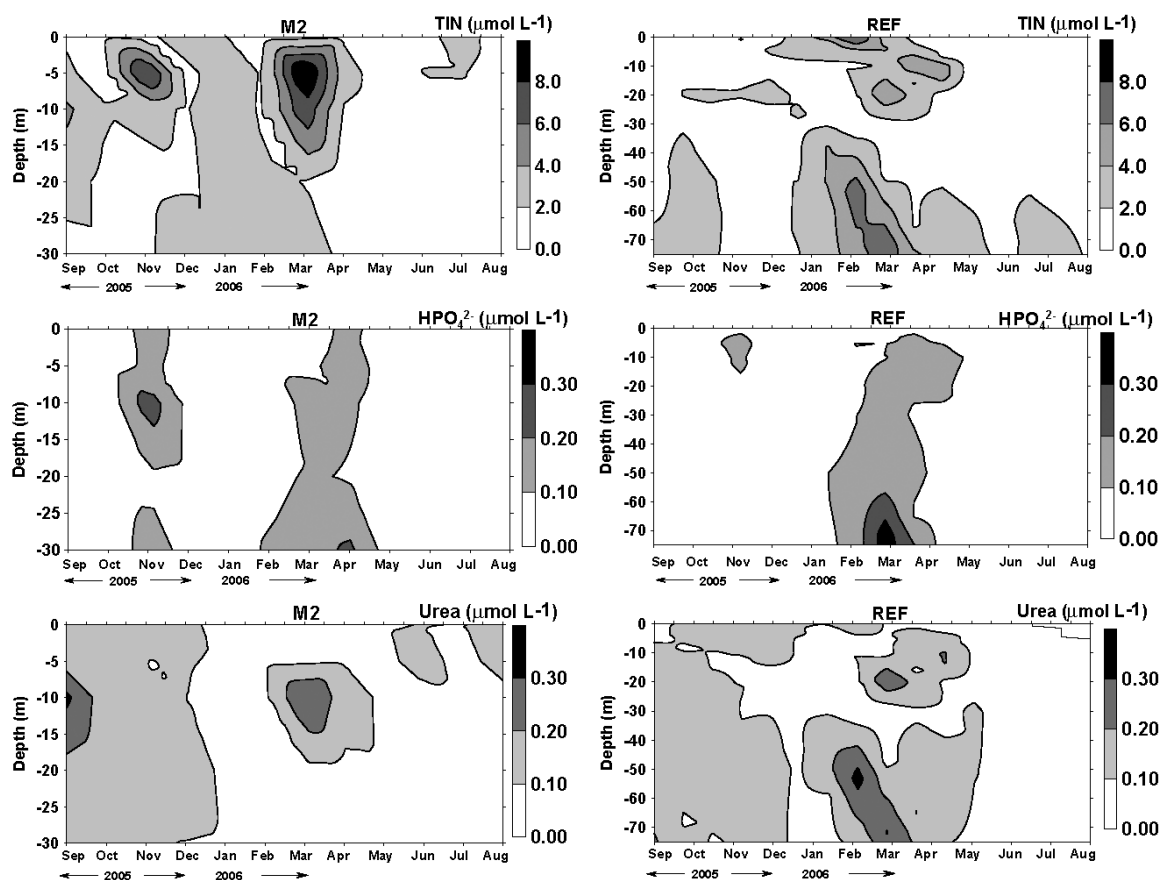


Fig. 9. Vertical distribution of dissolved inorganic nitrogen (DIN), orthophosphate ( $\text{HPO}_4^{2-}$ ) and urea in the water column of M2 and REF stations during the September 2005–August 2006 period

ate species in the oxidation of compounds from organic nitrogen to ammonia. According to the same authors, 80% of the urea pool is converted to ammonia, while 20% is exported through benthic fluxes to the water column.

### Sediment

The sediment types, organic matter and carbonate content at the investigated farm (M1, M2 and M3) and the REF station are presented in Table 1. Mean sediment grain size ranged from fine silt (15.3  $\mu\text{m}$ ) to very coarse sand (1231.1  $\mu\text{m}$ ) and sorting of particles was very poor. Fine-sized particles (silt and clay) prevailed at the deepest REF station, while at the shallower stations sand particles predominated.

Sediment carbonate content ranged from 50% to 92% with minor differences throughout the sampling period (Table 1). The highest carbonate content was found at the farm station M1, where coarse grains prevailed, while the lowest carbonates were found in the muddy sediments at the M3 and REF stations. According to previous investigations of middle Adriatic sediments, carbonates are most abundant in the coarse-grained sediment fraction, primarily as skeletal parts of organisms, although they could also be allochthonous due to weathering of the surrounding limestone rocks (MATIJEVIĆ *et al.*, in press).

Organic matter content (OM) ranged from 2.2 to 4.3% (Table 1) with lower values in coarse-grained carbonate sediments at the farm stations, while the highest organic matter was found at the REF station with fine-sized sediment. These results agree well with the already published data for middle Adriatic coastal sediments, where a positive correlation exists between organic matter and portion of fine-sized particles in sediments (BOGNER *et al.*, 2005). Considering this association, OM content in Maslinova Bay probably reflects natural sediment characteristics. MANTZAVRAKOS *et al.* (2007), reported no significant differences in OM distribution between the cage and reference stations at a Greek SB&SB farm, while KARAKASSIS *et al.* (1998) measured 5 times higher OM under the cages in relation to a reference station.

The organic carbon (C-ORG) contents ranged from 0.34 to 1.29% at the fish farm area (M1, M2 and M3), which were similar to values obtained for the REF station sediment (0.38 to 1.26%) (Table 1).

The C-ORG content found were within the range of published data for Adriatic Sea sediments (0.5-1.4%) (FAGANELI *et al.*, 1994; DOLENEC *et al.*, 1998; MATIJEVIĆ *et al.*, 2004) and lower (up to 5 times) in relation to fish farm sediments located in the north and the middle Adriatic Sea (NAJDEK *et al.*, 2007; MATIJEVIĆ *et al.*, 2006).

Total nitrogen content (N-TOT) ranged from 0.01 to 0.26% in the sediments at the farm area (M1, M2 and M3) and from 0.01 to 0.17% at the REF station (Table 1). These values are somewhat wider than the range obtained for middle Adriatic sediments (0.02-0.15%) (MATIJEVIĆ *et al.*, 2004). N-TOT at Maslinova Bay farm stations was in the range of data obtained for SB&SB farm stations in the Limski Channel (NAJDEK *et al.*, 2007) and lower than in tuna farm sediments, where N-TOT ranged from 0.07 to 0.95 % (MATIJEVIĆ *et al.*, 2006).

Due to relatively similar C-ORG and N-TOT content at farm and REF stations, the results presented herein indicate a minor influence and reveal a rather natural state of the sediment. This is not in accordance with the reported enhancement (1.5-5 times) of C-ORG and N-TOT content in sediments under the cages of other Mediterranean SB&SB farms (KARAKASSIS *et al.*, 2000; KOVAČ *et al.*, 2004), as well as for Canadian salmon farms (HALL *et al.*, 1990; HARGRAVE *et al.*, 1997).

### Sediment redox-potential

Sediment redox-potential ( $E_H$ ) measured during the 2001-2003 period at investigated stations in Maslinova Bay and at the REF station ranged between -103 mV and +118 mV (Fig. 10). According to MATIJEVIĆ *et al.* (2007), the negative  $E_H$  (from 0 mV to -185 mV) corresponds to enhanced sulphide concentrations. This agrees with a redox transition from suboxic to anoxic conditions, which takes place at potentials from 0 to -150 mV (COLMAN & HOLLAND, 2000). More

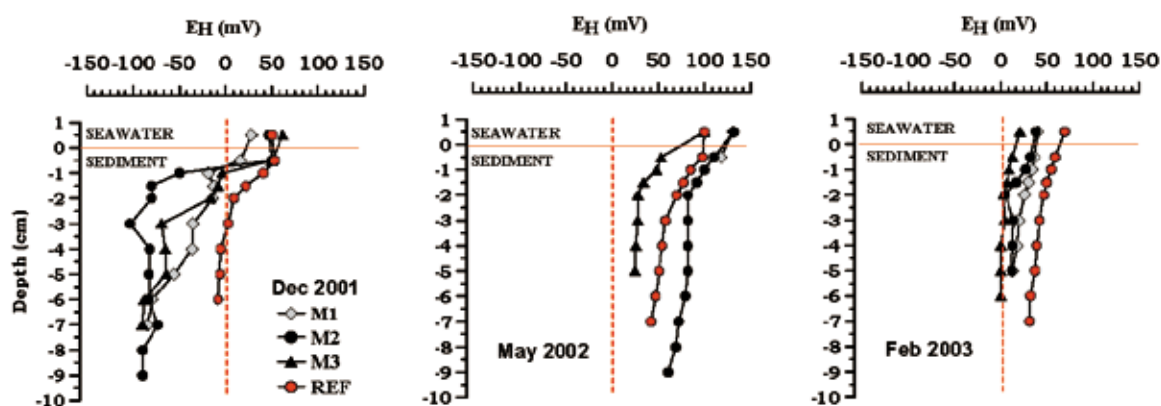


Fig. 10. Vertical profiles of sediment redox-potential at stations M1, M2, M3 and REF during December 2001, May 2002 and February 2003

negative  $E_H$  and shallower redox transition depths at farm stations (M1, M2 and M3) than at the REF station determined in December 2001 indicate higher organic matter input into the sediment. However,  $E_H$  measurements during 2002 and 2003 did not show significant differences between the farm and the REF stations.

According to previous investigations of middle Adriatic sediments, the negative  $E_H$  during the cold period of the year occurs as part of the seasonal oscillations of this parameter, while the phenomenon of shallower redox transition depths at farm stations have already been determined at tuna farms in this area (MATIJEVIĆ *et al.*,

2007; MATIJEVIĆ, 2006). Considering the above-mentioned occurrence of negative  $E_H$  in the middle Adriatic area and at tuna farm stations, the results of  $E_H$  measurements at Maslinova Bay stations indicate a minor SB&SB farm influence on this parameter.

#### Sediment phosphorus concentrations

Sediment phosphorus concentrations at the investigated stations, determined according to ASPILA *et al.* (1976), ranged from 3.9 to 38.2  $\mu\text{mol g}^{-1}$  for inorganic phosphorus (IP) and from 0 to 6.7  $\mu\text{mol g}^{-1}$  for organic phosphorus (OP) (Fig. 11).

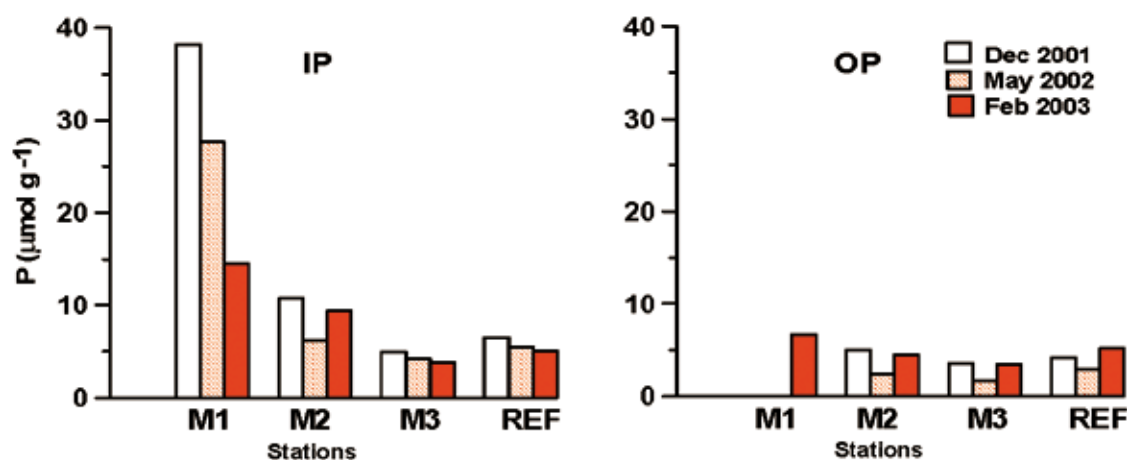


Fig. 11. Inorganic and organic phosphorus concentrations in sediments at stations M1, M2, M3 and REF determined during December 2001, May 2002 and February 2003

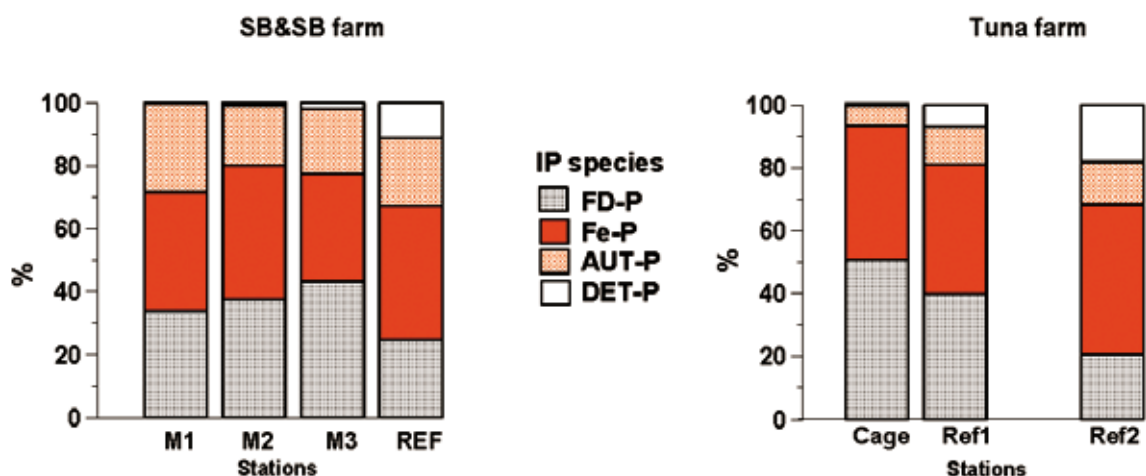


Fig. 12. Comparison of the portion of inorganic phosphorus species (*P* bound in fish debris FD-P, *P* adsorbed in iron oxides/hydroxides Fe-P, detrital apatite phosphorus DET-P, authigenic apatite phosphorus AUT-P) in the sediments sampled at Maslinova Bay stations in May 2002 with the data for the previously investigated middle Adriatic tuna farm (MATIJEVIĆ *et al.*, 2006)

IP concentration in the sediments at station M1, located under the cage for juvenile fish, was constantly higher than in the sediments at stations M2 and M3 as well as relative to the REF station. However, a strong IP decrease at station M1 determined in February 2003 can be explained with a slight displacement of the cages during 2003 (the station was relocated as the cages were displaced and station depth was changed from 10 to 17 m). IP concentrations at farm station M1 exceeded concentration ranges found in middle Adriatic sediments ( $3\text{--}37 \mu\text{mol g}^{-1}$ ), and were more similar to data obtained for tuna farm sediments ( $5\text{--}135 \mu\text{mol g}^{-1}$ ) (MATIJEVIĆ *et al.*, 2008). OP concentrations at the farm and the REF stations varied within the natural middle Adriatic range of  $0\text{--}21 \mu\text{mol g}^{-1}$  (MATIJEVIĆ *et al.*, 2008).

Increase of sediment P concentrations under the fish cages relative to the reference sites was reported also for salmon farms (SOTO & NORAMBUENA, 2004) and SB&SB farms (CANCEMI *et al.*, 2003; KARAKASSIS *et al.*, 1999; PORELLO *et al.*, 2005a). Most of the P results obtained for these fish farms are based on the Aspila method (ASPILA *et al.*, 1976), which provides results only for total IP and OP, and does not distinguish between the different inorganic P species. To determine the P species responsible for the increase in inorganic P concentration at the cage station (see Fig. 11), a modified SEDEX analy-

sis of IP species was performed (MATIJEVIĆ *et al.*, 2008). Investigated inorganic phosphorus species in sediments were P bound in the fish debris (FD-P), P adsorbed in iron oxides/hydroxides (Fe-P), detrital apatite phosphorus (DET-P) and authigenic apatite phosphorus (AUT-P).

The FD-P/IP portion of the P bound in biogenic apatite ("fish debris P") at the farm area (M1, M2 and M3 stations) ranged from 34 to 43% in comparison to 25% at the REF station (Fig. 12). Higher FD-P portions (51%) were also found in the sediments under tuna farm cages. These are supposed to be directly influenced by the settling of uneaten fish food (fish bones and skeletons, which are sources of biogenic apatite) (MATIJEVIĆ *et al.*, 2006, 2008). In previous investigations in the middle Adriatic Sea (Table 3) FD-P/IP portions ranged from 15-30%, with the highest values recorded at stations with the higher carbonate content in the sediments (MATIJEVIĆ, 2006).

The Fe-P/IP portion varied in a relatively narrow range (from 34 to 42%) in the sediments at all stations in Maslinova Bay, with the highest portion determined for the REF station. A similar portion was found for tuna farm sediments (MATIJEVIĆ *et al.*, 2006) (Fig. 12), so this fraction is probably not influenced by the fish farming.

Table 3. Portions (%) of inorganic P fractions (FD-P, Fe-P, AUT-P and DET-P) in total inorganic P (IP) in the surface sediment layer (0-2 cm depth) at Maslinova Bay stations (M1, M2, M3) in comparison to data for middle Adriatic tuna farm stations (MATIJEVIĆ *et al.*, 2006), as well as for the middle Adriatic area (MATIJEVIĆ, 2006)

IP species	SB&SB farm Maslinova Bay	Tuna farm (Grška Bay; MATIJEVIĆ <i>et al.</i> , 2006)	Middle Adriatic (MATIJEVIĆ, 2006)
FD-P/IP	34-43	40-51	15-30
Fe-P/IP	34-42	41-47	32-51
AUT-P/IP	19-28	6-17	9-29
DET-P/IP	0.3-12	0.5-18	4-24

For middle Adriatic sediments, the Fe-P portion ranged from 32 to 51% and was the most important IP fraction, responsible for orthophosphate flux at the sediment–seawater interface (MATIJEVIĆ, 2006). The predominance of the Fe-P in the IP was also found in the sediments of different world seas (SLOMP *et al.*, 1996; JENSEN *et al.*, 1995; ANSHUTZ *et al.*, 1998; LOPEZ *et al.*, 2004).

Authigenic apatite phosphorus portion in total IP (AUT-P/IP), ranged from 19% at station M2 to 28% at station M1 and it was similar to the portion found at the REF station. This was not the case with the sediments under the tuna cages (MATIJEVIĆ *et al.*, 2006), where the portions were lower than at the undisturbed REF station (Fig. 12). Considering the wide range (9-29%) of this portion at stations of different sediment types in the middle Adriatic, our results for the SB&SB farm stations in Maslinova Bay indicate that there is no significant impact of fish farming on AUT-P forms in sediment.

Detrital apatite phosphorus (DET-P) portion in IP was lower at farm stations (0.3% at M1) than at the REF station (12%), which is similar to the portions found for the location under tuna cages and related REF stations (Fig. 12). These portions are also lower in comparison to previously determined DET-P/IP portions for the middle Adriatic sediments (4-24%), where the highest portion was found in the sediments under strong river influence (MATIJEVIĆ *et al.*, 2008). The lowest DET-P portions determined at the fish farm stations (SB&SB or tuna farms) are probably a consequence of settled biogenic

material (pellets of fish food), which altered “natural” proportions between the IP species in the sediment.

## CONCLUSIONS

Monitoring of physical and chemical properties of the water column and sediments at a sea bass/sea bream farm in Maslinova Bay (island of Brač) revealed certain changes regarding the natural state of the environment.

Transparency in the water column at all stations followed the natural seasonal course of thermohaline conditions, although with constantly lower values at the farm stations relative to the reference site indicate the impact of fish farming. No significant influence on the total suspended matter distribution in the water column was observed.

Decreased oxygen saturations at the farm stations in the middle layer of the water column indicate higher oxygen consumption directly by fish and oxidation processes of their metabolic products rather than by decomposition of settled particulate matter. Temporal changes of oxygen concentrations revealed a state of oxygen deficiency at farm stations relative to the reference station.

Enhanced concentrations of dissolved inorganic nitrogen, orthophosphate and urea in the 0-20m layer of the water column at farm stations can also be attributed to fish excretions and degradation of their metabolic products.

Sediment inorganic P concentrations were enhanced under the cages compared to the refer-

ence site, while organic P was mainly within the range of "natural" middle Adriatic concentrations. Sequential analysis of inorganic P species showed an increased portion of biogenic apatite P and decreased detrital apatite P at the farm stations relative to the inorganic P pool at the reference sta-

tion as a direct consequence of fish farming.

Redox-potential, granulometric composition, organic matter content, carbonates as well as organic carbon and total nitrogen content reflected natural sediment characteristics rather than that under fish farm influence.

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## Fizička i kemijska svojstva vodenog stupca i sedimenta na uzgajalištu lubina i komarči u srednjem Jadranu (uvala Maslinova)

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### SAŽETAK

Na uzgajalištu lubina i komarči u srednjem Jadranu, uvala Maslinova (otok Brač), su tijekom 2001-2006 istraživane fizikalne i kemijske osobine vodenog stupca i sedimenta. Mjerenja i uzorkovanja su provedena na postajama unutar uzgajališta kao i na referentnoj postaji udaljenoj približno 1 km od uzgajališta. U vodenom stupcu su ispitivani: temperatura, salinitet, prozirnost, koncentracija suspendirane tvari, zasićenje kisikom i koncentracija hranjivih soli. U sedimentu su istraživani: granulometrijski sastav, redoks potencijal, sadržaj organskog ugljika i ukupnog dušika, koncentracija organskog i anorganskog fosfora, kao i koncentracija različitih oblika anorganskog fosfora (fosfor vezan u biogenom, autigenom i detritusnom apatitu, i fosfor vezan na okside i hidrokside željeza).

Prozirnost u vodenom stupcu je na svim postajama bila u skladu sa sezonskim oscilacijama, iako stalna niža prozirnost na postajama u uzgajalištu u odnosu na referentnu postaju upućuje na izvjesni utjecaj rada uzgajališta na ovaj parametar. Utjecaj na kemijske parametre je bio blago izražen u površinskom i srednjem sloju vodenog stupca kroz manjak kisika i povišene koncentracije otopljenog anorganskog dušika, ortofosfata i uree koje su rezultat ekskrecije riba i razgradnje njihovih metaboličkih produkata.

Koncentracija anorganskog fosfora u sedimentu je bila povišena ispod kaveza u usporedbi sa referentnom postajom, dok je organski fosfor bio u rasponu koncentracija uobičajenih za sediment srednjega Jadrana. Sekvencijalna analiza anorganskih vrsta fosfora pokazala je povišeni udio fosfora vezanog u biogenom apatitu i smanjeni udio fosfora u detritusnom apatitu na postajama uzgajališta u odnosu na referentnu postaju kao izravni utjecaj rada uzgajališta. Redoks potencijal sedimenta, granulometrijski sastav, udio organske tvari i karbonata, te organskog ugljika i ukupnog dušika su bili u rasponima vrijednosti za "prirodni" sediment srednjeg Jadrana.

**Ključne riječi:** uzgajalište riba, vodeni stupac, sediment, redoks potencijal, fosfor, organska tvar, Jadransko more