

Vertical distribution of phosphorus species and iron in sediment at open sea stations in the middle Adriatic region

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Sedimentary phosphorus species concentrations were examined in cores (0-10 cm) from 5 locations in the open middle Adriatic in June 2002. Measurements included organic phosphorus (OP) and inorganic P species: 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). Total iron (Fe-TOT) and iron-oxyhydroxides (Fe(III)OOH) concentrations were also determined as well as granulometric composition, organic matter (OM), organic carbon (C-ORG) and carbonate content (CA). Sediment pore water measurements included redox-potential (E_H) and orthophosphate concentration. All relevant data were subjected to correlation, Cluster and Principal Component Analysis (PCA). Cluster analysis indicated that granulometric composition and carbonate content are the leading factors of distinction between the stations. PCA revealed that the fine fraction of sediments has a key role in the vertical distribution of Fe-TOT and P-ORG. Linkage among P-AUT, P-DET and C-ORG results from river input influence, while association between OM, P-Fe, E_H and OP arises from complex internal processes in the sedimentary P cycle.

Key words: phosphorus, sediment, iron, Adriatic Sea

INTRODUCTION

Phosphorus (P) is a key element used by all living organisms for energy transport and growth. In marine systems P availability controls primary production over long time-scales (KARL *et al.*, 1995; HOWARTH *et al.*, 1995; TYRELL 1999; BENITEZ-NELSON, 2000). In the open central Adriatic Sea orthophosphate concentrations in the water column are extremely low, therefore P is a limiting nutrient for primary production

(VUKADIN & STOJANOSKI, 1976; ZORE-ARMANDA *et al.*, 1991). Due to anthropogenic influence in coastal areas the P, as well as the nitrogen, concentration increases leading to the formation of a trophic gradient from the open sea towards the coastal area (LEGOVIĆ, 1994; BARIĆ *et al.*, 1996; KRSTULOVIĆ *et al.*, 1997).

Knowledge of P distribution in the water column and sediments is essential for understanding the availability and ecological effects of P on marine environments.

Dissolved P (HPO_4^{2-}) is utilized by organisms and transformed into particulate organic matter in the euphotic zone. Organic P is the major form in particulate organic matter which undergoes remineralization through the water column, while a negligible part (~1%) escapes regeneration and is passively buried in sediments (DELANEY, 1998). Minor forms in the water column are authigenic apatite P and exchangeable P (both resulting from organic P transformation), P adsorbed onto particles of metal oxides and hydroxides, and non-reactive detrital P (FAUL *et al.*, 2005).

P forms delivered to the sediment-water interface could be regenerated into orthophosphate, adsorbed as P associated with metal oxides and hydroxides, or precipitated as an authigenic apatite P (FAUL *et al.*, 2005). The distribution of P forms in sediment is greatly influenced by the biological environment (organic matter degradation by microbes, meiofaunal bioturbation and bioirrigation processes) (ALLER, 1994), and physico-chemical sediment properties such as pH and redox-potential which affect HPO_4^{2-} adsorption/desorption (SUNDBY *et al.*, 1992; CANFIELD, 1994; JENSEN *et al.*, 1995).

In sediments, P forms are operationally defined by using sequential extraction methods which are based on the reactivity of a particular phase in a given extractant. Numerous authors in different marine areas of the world investigated the distribution of sediment organic P, as well as of inorganic P forms such as P adsorbed on to iron-oxides and hydroxides, and P in authigenic, detrital and biogenic apatite (RUTTENBERG & BERNER, 1993; JENSEN *et al.*, 1995; SLOMP *et al.*, 1996; ANSHUTZ *et al.*, 1998; SCHENAU & DE LANGE, 2000; LOPEZ, 2004; PAYTAN *et al.*, 2003; FAUL *et al.*, 2005).

Investigations of P in the surface sediment layer (0-2 cm) in the central Adriatic Sea (MATIJEVIĆ, 2006; MATIJEVIĆ *et al.*, 2008a) showed that inorganic and organic P portions in total P greatly depend on granulometric composition, carbonate content and trophic status of the water column. The sequential extraction method of sediment P forms (SEDEX, according to RUTTENBERG (1992), modified by MATIJEVIĆ *et al.*, 2008a) indi-

cated that organic P concentrations reflected the trophic status of the area, while authigenic apatite P showed no significant differences among sites. Sediment from an anthropogenically influenced area had the highest values of iron-bound P, while P in biogenic apatite proved to be the most sensitive indicator of fish farming influence on the marine sediment (MATIJEVIĆ *et al.*, 2006, 2008a).

In this paper we present preliminary results of P forms, obtained using modified SEDEX analysis, in sediment at 5 open sea stations in the central Adriatic whose locations were chosen due to different water mass characteristics (BULJAN & ZORE-ARMANDA, 1976) and currents (ORLIĆ *et al.*, 1992) and potentially different conditions of organic matter input. We focused on the vertical distribution of P forms (0-10 cm sediment depth) and their interactions with other parameters determined in the sediment (total iron, CDB-extractable iron concentrations, granulometric parameters, organic matter, organic carbon content as well as HPO_4^{2-} concentrations and redox-potential in sediment pore water). Parameters in the bottom layer of the water column (orthophosphate concentration, temperature, salinity and oxygen saturation) were also investigated.

MATERIAL AND METHODS

Sampling and analytical determinations

Sampling of the seawater and sediments was performed in June 2002 at five stations in open waters of the central Adriatic (Fig. 1). Basic information such as coordinates, station depths and characteristics of the bottom layer of the water column are presented in Table 1.

Seawater for determination of oxygen saturation and orthophosphate (HPO_4^{2-}) concentration was sampled using Nansen bottles (Hydrobios-Kiel). Oxygen saturation was determined by classical Winkler titration, while HPO_4^{2-} concentration was determined colorimetrically on an AutoAnalyzer-3 according to GRASSHOFF (1976).

Salinity and temperature in the water column were measured using a SEABIRD-25 CTD probe. Sediment samples were collected in six

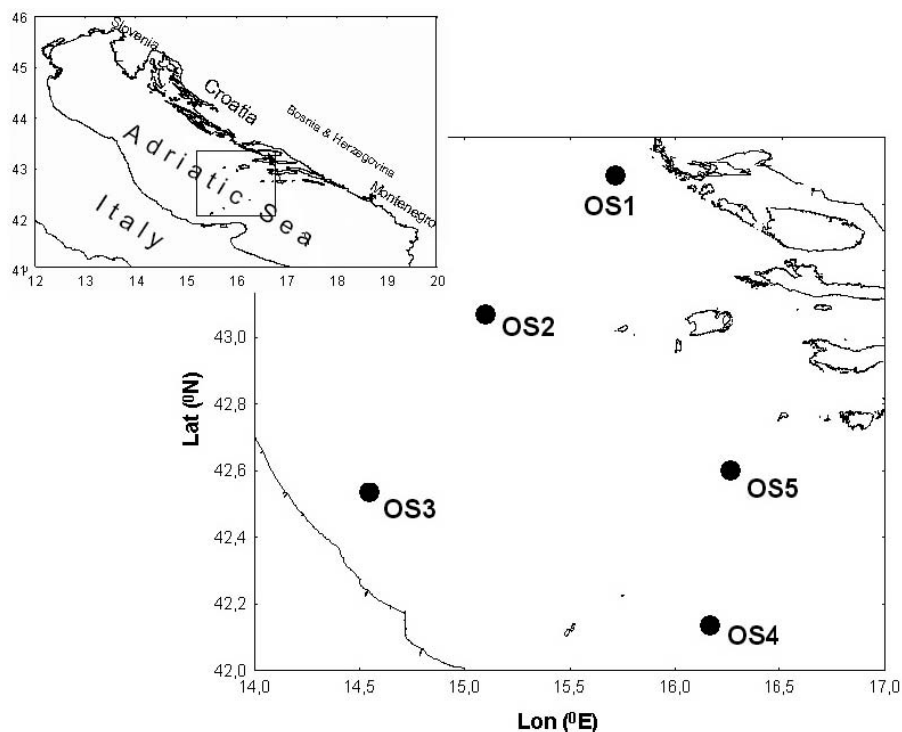


Fig. 1. Map of the investigated stations

replicates by gravity corer using transparent plastic liners (i.d.=6.5 cm). Two cores for sediment P analysis were divided into 10 slices (1 cm thick), frozen and stored in clean plastic bags until lab analysis. Freeze-dried sediment samples were grounded and sieved ($\phi < 250 \mu\text{m}$) and then extracted using the SEDEX method (RUTTENBERG, 1992), modified by MATIJEVIĆ *et al.* (2008a), for inorganic P species determination (P in biogenic apatite (P-FD), P adsorbed onto iron-oxy/hydroxides (P-Fe), P in authi-

genic apatite (P-AUT), and P in detrital apatite (P-DET). Details of the sequential extraction scheme are published elsewhere (MATIJEVIĆ *et al.*, 2008a). Total and organic phosphorus (TP and OP) were determined using the method of ASPILA *et al.*, (1976). Phosphorus concentrations in extractant 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.

Table 1. Station coordinates, depth, temperature (T), salinity (S), pH, oxygen saturation (O₂ %) and orthophosphate concentration in the bottom layer of the water column at investigated stations in June 2002

	OS1	OS2	OS3	OS4	OS5
Latitude N	43°29,00'	43°04,00'	42°32,00'	42°22,00'	42°36,00'
Longitude E	15°43,00'	15°06,00'	14°33,00'	16°13,00'	16°16,00'
Depth (m)	170	260	111	110	175
T (°C)	11.18	10.65	12.79	12.54	13.93
S	38.51	38.46	38.48	38.58	38.32
O ₂ (%)	86.13	88.13	89.85	89.14	88.34
pH	8.21	8.23	8.23	8.25	8.23
HPO ₄ ²⁻ ($\mu\text{mol L}^{-1}$)	0.065	0.065	0.090	0.123	0.080

In the third and fourth core (divided into the following subsamples: 0-4; 4-8; 8-12; 12-16 cm depending on the length of the core) granulometric composition of the sediment samples was determined either by sieving ($>63 \mu\text{m}$) or by the hydrometric method ($<63 \mu\text{m}$). Sediment type was classified according to SHEPARD (1954). In the same core organic matter content was determined gravimetrically (VDOVIĆ *et al.*, 1991), while carbonate content was determined as loss of weight after treatment with 4M HCl (LORING & RANTALLA, 1992). Sediment organic carbon (C-ORG) content was determined using a CHNS-O analyzer (EA 1110, CE instruments). Prior to analysis, samples were treated with HCl to remove carbonates (UJIÉ *et al.*, 2001). Concentrations of total iron (Fe-TOT) were measured by the F-AAS method using a Perkin-Elmer Analyst 800. About 0.1 g of dried sediment samples were digested with HNO_3 -HF- HClO_4 mixture according to the method developed previously in our laboratory (UJEVIĆ *et al.*, 2000). The accuracy of the analytical procedure was repeatedly checked by analyzing samples of certified reference material SRM-1646 (NIST, USA).

Total iron oxides in surface sediment were determined in citrate-dithionite-bicarbonate (CDB) buffer solution obtained after the extraction of sediment P-Fe species. CDB agent is specific for both amorphous and crystalline iron oxides (which are the most reactive iron forms in sediment) consisting mainly of Fe(III)OOH (CANFIELD *et al.*, 1992). Aliquots of solution (5 cm^3), after the extraction of sediment samples with CDB, were diluted to 25 cm^3 and analyzed for Fe also by F-AAS method on a Perkin-Elmer Analyst 800.

Two separate sediment cores were taken for immediate determination of redox-potential and HPO_4^{2-} concentrations in sediment pore water. The sediment cores for HPO_4^{2-} determination were divided into 10 slices (1 cm thick), and each subsample was centrifuged at 2400 rpm for 15 minutes. The supernatant of pore water (100 - $500 \mu\text{L}$) was diluted with artificial seawater to 10 or 25 cm^3 volumes, and HPO_4^{2-} concentration was determined colorimetrically on an AutoAnalyzer-3 according to GRASSHOFF (1976).

Measurement of redox-potential was performed in the undisturbed sediment core by

using Pt-electrode and Ag/AgCl (3M KCl) reference electrode connected to an Iskra MA 5730 voltmeter. For electrode standardization saturated quinhydrone solutions in pH=4 and pH=7 buffers were used. Redox potential adjustments were obtained for quinhydrone pH=4 buffer solution to +259 mV and for pH=7 solution to +85 mV (Metrohm Ag, Herisau, Switzerland). Details of the Eh measurements were published elsewhere (MATIJEVIĆ *et al.*, 2007).

Data analysis

Results are presented as box-whisker diagrams (as median, 25th percentile, 75th percentile, and range), and/or with vertical profiles. One-way ANOVA (analysis of variance) was conducted to test for significant differences in parameter concentrations (granulometric composition, organic matter and carbonate content, concentrations of different P- and Fe-forms) between stations. Spearman's rank correlation (r , p) was used to examine associations between each of the measured parameters. Cluster analysis and Principal Component Analysis (PCA) were used to investigate the differences/similarities between the stations considering all investigated parameters. It should be pointed out that due to the different thickness of sediment subsamples for different analyses (sediment for P species analysis was sliced in 1 cm subsamples from 0 to 10 cm depth, while cores for granulometric composition, OM and carbonate content were sliced in 0-4, 4-8, 8-12 etc. cm subsamples; see section 2.1.), for Cluster and PCA we used/calculated mean values of all parameters for 0-4, 4-8 and 8-10 cm subsamples.

RESULTS AND DISCUSSION

Granulometric composition, carbonates, organic matter and organic carbon content in sediments

Predominant grain size fractions in the sediment cores were clay ($59 \pm 15\%$) and silt ($35 \pm 14\%$), while sand and gravel were minor fractions ($6 \pm 11\%$ and $1 \pm 1\%$, respectively) (Fig. 2).

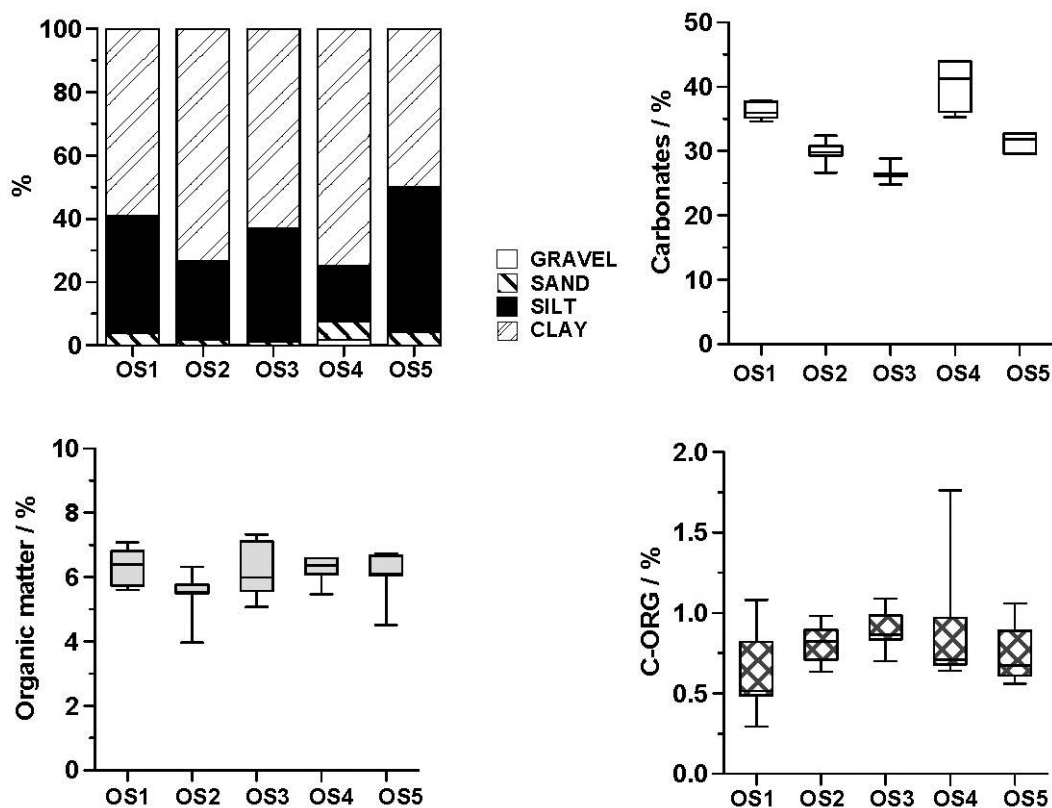


Fig. 2. Average grain size fractions in sediments (gravel, sand, silt and clay), box-whisker diagrams of organic matter (OM), carbonate (CA) and organic carbon (C-ORG) content in sediment cores (0-24 cm depth) at 5 stations (OS1, OS2, OS3, OS4, OS5) in June 2002

The fractions were found in proportions and patterns similar to those reported by other authors (DE LAZZARI *et al.*, 2004; VDOVIĆ & JURACIĆ, 1993). However, results of statistical analysis showed that gravel, sand and silt content at station OS4 is significantly different (gravel and sand higher, silt lower) in comparison to other stations. According to Shepard's classification (SHEPARD, 1954) the sediment type at all stations is silty clay, except for station OS4 which belongs to clay. Greater proportions of fine-sized particles in sediments at deeper offshore stations were also found for the eastern Adriatic area (MATIJEVIĆ *et al.*, 2008b). Sediment types determined in our samples are a result of the OS station positions near Jabuka Pit and Palagruža Sill which receive terrigenous clay particles controlled by the Padane flux (VAN STRAATEN, 1970; TOMALDIN, 2000) and by transversal transport of the Apennine sediment from the shelf edge.

Organic matter content (OM) ranged from 4.0 to 7.3%, while carbonates (CA) ranged from 26.1 to 42.7%, with small standard deviations as a result of similar vertical distributions of these parameters in sediments (Fig. 3). As would be expected, higher carbonate content was found in the coarse-sized fraction (gravel and sand) (Table 2). Our results correspond well to published data for the eastern Adriatic, where organic matter greater than 5% was found in fine-grained sediments, and was positively correlated with silt and negatively correlated with sand (MATIJEVIĆ *et al.*, 2008b). The highest CA content at station OS4 corresponds to the greater proportion of sand in sediments (Fig. 2), which is characteristic for middle Adriatic sediments where coarse-sized particles usually originate from carbonate shells of micro and macro faunal organisms (BOGNER *et al.*, 2005).

Table 2. Linear correlation coefficients between organic phosphorus (OP), total phosphorus (TP), inorganic P species concentrations (P-FE, P-AUT, P-DET, P-FD), total iron concentration (Fe-TOT), granulometric composition, organic matter (OM), carbonate (CA), organic carbon (C-ORG) and sediment redox potential (E_H) (n=15)

N=15	Gravel	Sand	Silt	Clay	OM	C-ORG	E_H	CA	Fe-TOT	P-Fe	P-AUT	P-FD	P-DET	OP-
Gravel	1.000													
Sand	0.737													
Silt	-0.705	-0.616												
Clay	0.415	0.161	-0.877											
OM	-0.126	0.003	0.073	-0.088										
C-ORG	0.316	-0.120	-0.028	0.089	-0.312									
E_H	0.022	0.011	-0.204	0.252	0.190	0.072								
CA	0.651	0.772	-0.457	0.097	-0.002	-0.304	0.184							
Fe-TOT	-0.823	-0.827	0.535	-0.155	-0.150	-0.040	-0.144	-0.669						
P-Fe	0.229	0.111	-0.290	0.293	-0.389	0.495	-0.390	-0.288	0.036					
P-AUT	0.407	0.268	-0.199	0.076	-0.159	0.493	-0.375	-0.195	-0.373	0.503				
P-FD	-0.392	-0.179	-0.098	0.250	-0.070	-0.647	0.274	0.169	0.411	-0.443	-0.667			
P-DET	0.690	0.255	-0.210	0.082	-0.194	0.577	-0.289	0.170	-0.515	0.399	0.408	-0.740		
OP	-0.306	-0.464	0.165	0.077	-0.315	0.313	-0.409	-0.694	0.562	0.556	0.212	-0.203	0.099	
TP	0.025	-0.359	0.040	0.158	-0.463	0.459	-0.140	-0.394	0.212	0.331	0.185	-0.333	0.446	0.729

Correlation coefficients in bold are significant to at least the level $p < 0.05$

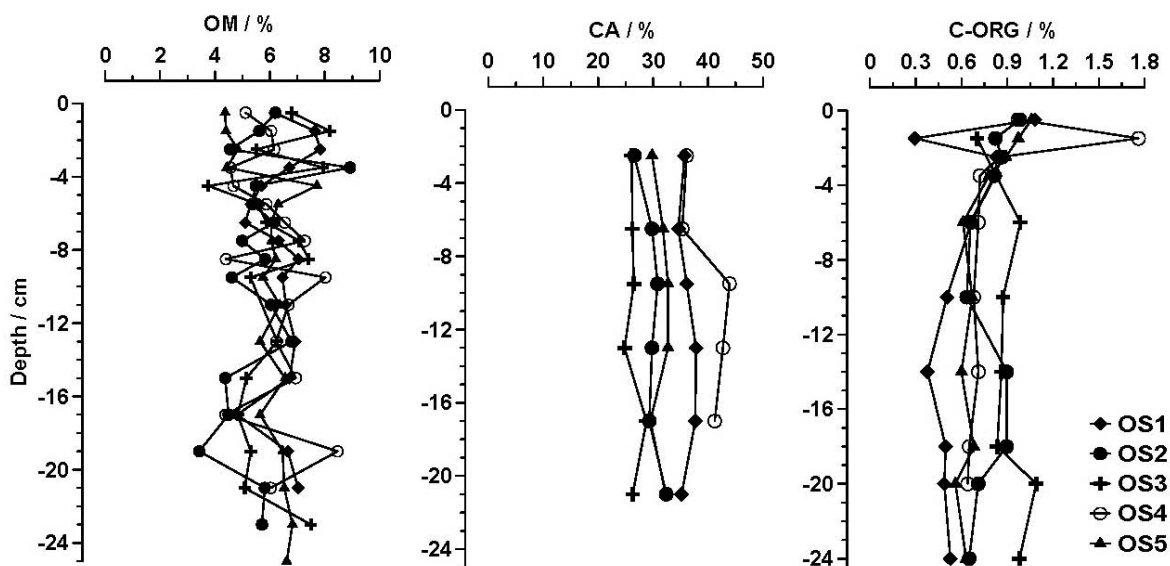


Fig. 3. Vertical profiles of organic matter (OM), carbonate (CA) and organic carbon (C-ORG) content in sediment cores (0-24 cm depth) at open sea stations (OS1, OS2, OS3, OS4, OS5) in June 2002

Organic carbon (C-ORG) content in sediments at OS stations ranged from 0.29 to 1.76%, with an average value of $0.77 \pm 0.24\%$ (Fig. 2), which is in the range of data published for Adriatic 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 some anthropogenically influenced coastal areas of the middle and north Adriatic (MATIJEVIĆ *et al.*, 2006; NAJDEK *et al.*, 2007). There is no obvious trend in the vertical distribution of C-ORG concentration at OS stations (Fig. 3). The highest C-ORG content was determined at station OS3 which can be explained due to the highest proportion of silt in sediment at this station (Fig. 2) and considering the positive correlation established between C-ORG content and silt in surface Adriatic sediments (MATIJEVIĆ *et al.*, 2008b). Such a correlation was not established for the 0-10 cm sediment layers at OS stations, although C-ORG was correlated with apatite P species (Table 2).

Redox-potential and orthophosphate concentrations in the sediment pore-water

Sediment redox-potential recorded in sediment cores at investigated OS stations ranged

from +25 to +85 mV (Fig. 4). The main characteristic is a uniform vertical E_H distribution in sediments at all stations without transitions to the zone of negative potential.

According to COLMAN & HOLLAND (2000), the redox transition between oxic and suboxic states takes place between +300 and +150 mV (O_2 and NO_3^- concentrations near the detection limits), while the transition from suboxic to anoxic conditions (presence of HS^- or S^{2-}) takes place at potentials from 0 to -150 mV. It should be pointed out that, since the Pt electrode used for our measurements showed the highest sensitivity to sulphide presence, the determined E_H describes S^{2-} concentrations in seawater or sediment pore water, rather than their oxic or anoxic status (MATIJEVIĆ *et al.*, 2007). Accordingly, positive E_H values determined in sediments at OS stations indicate the absence of sulphate reduction. Very low sulphide concentrations in sediment are probably caused by low to medium organic matter sedimentation rates in this part of the Adriatic (GIORDANI *et al.*, 2002; BOLDRIN *et al.*, 2002).

HPO_4^{2-} concentrations in sediment pore water ranged from 11.4 to 23.6 $\mu\text{mol dm}^{-3}$ (Fig. 4). The highest HPO_4^{2-} concentrations at stations

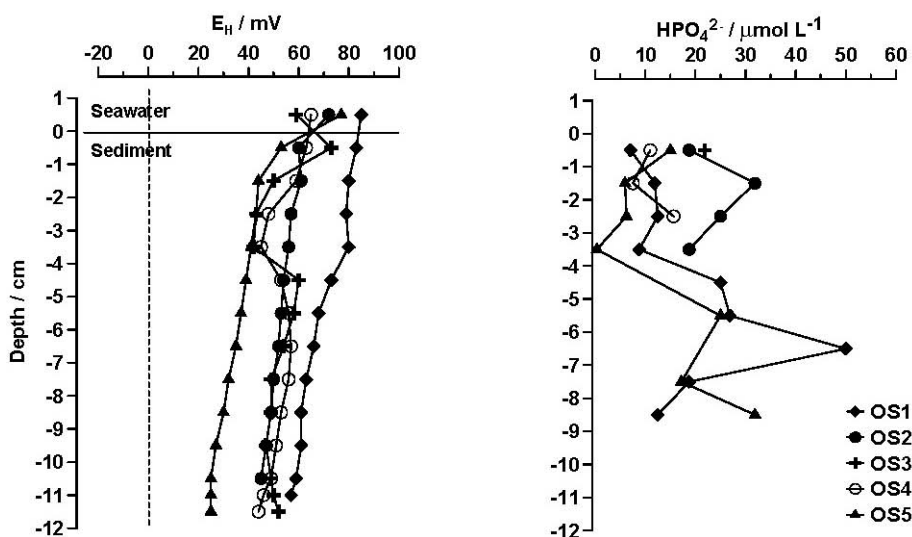


Fig. 4. Vertical profiles of sediment redox potential (E_H) and orthophosphate (HPO_4^{2-}) concentrations in sediment pore-water at investigated stations (OS1, OS2, OS3, OS4, OS5) in June 2002

OS1 and OS5 were found in deeper sediment layers (Fig. 4) which is in agreement with earlier reported pore-water data for marine sediments (BARIĆ *et al.*, 2002; JENSEN *et al.*, 1995; GRANDELL *et al.*, 2000). These HPO_4^{2-} values in the subsurface sediment pore water were related to different factors and processes, such as an increase in the pore-water alkalinity linked with the changing of electron acceptor in the process of organic matter degradation (WATANABE & TSUNOGAI, 1984), partial carbonate dissolution in the sediments, or microbe influences (FROELICH *et al.*, 1988; PASSIER *et al.*, 1997).

Considering the almost linear vertical profiles of E_H (Fig. 4) and its positive values, we can assume that HPO_4^{2-} concentrations reported here are probably not the result of an exchange of electron acceptors, but a consequence of other processes influencing the binding or releasing of HPO_4^{2-} .

Total and organic phosphorus concentrations in sediments

Total phosphorus concentrations (TP) at investigated stations ranged from 17.2 to 27.6 $\mu\text{mol g}^{-1}$ (Fig. 5). TP concentrations did not differ significantly between stations; the lowest

mean was recorded at OS1 ($20.7 \pm 0.9 \mu\text{mol g}^{-1}$) and the highest at station OS5 ($22.8 \pm 1.2 \mu\text{mol g}^{-1}$). These results are slightly higher than average TP concentrations in the different sediment types along the eastern Adriatic coastal area ($6.5\text{--}24.8 \mu\text{mol g}^{-1}$) (MATIJEVIĆ *et al.*, 2008b) and in the wider Adriatic area ($9.7\text{--}22.6 \mu\text{mol g}^{-1}$) (FAGANELI *et al.*, 1994; DOLENEC *et al.*, 1998). Considering the sediment type at all stations (silt), higher TP values at open sea stations in comparison to the wider Adriatic area could be expected due to higher P adsorption affinity to clay minerals (DOLENEC *et al.*, 1998) as well as a positive correlation found between TP and fine-grained sediments (MATIJEVIĆ *et al.*, 2008b).

Vertical profiles of TP concentrations in sediment (0-10 cm depth) are constant at most of the stations, except for OS4 where a decrease is observed with increasing depth. Similar TP vertical distributions in sediments at the OS stations were found during investigations in the middle Adriatic in 1997/1998 (MATIJEVIĆ, 2001). Rather constant TP concentrations in sediment profiles were found by RUTTENBERG & BERNER (1993) and SLOMP *et al.* (1996), while the proportion of P contained in the different solid-phase P forms was quite variable. According to the same authors, invariable TP sediment profiles indicat-

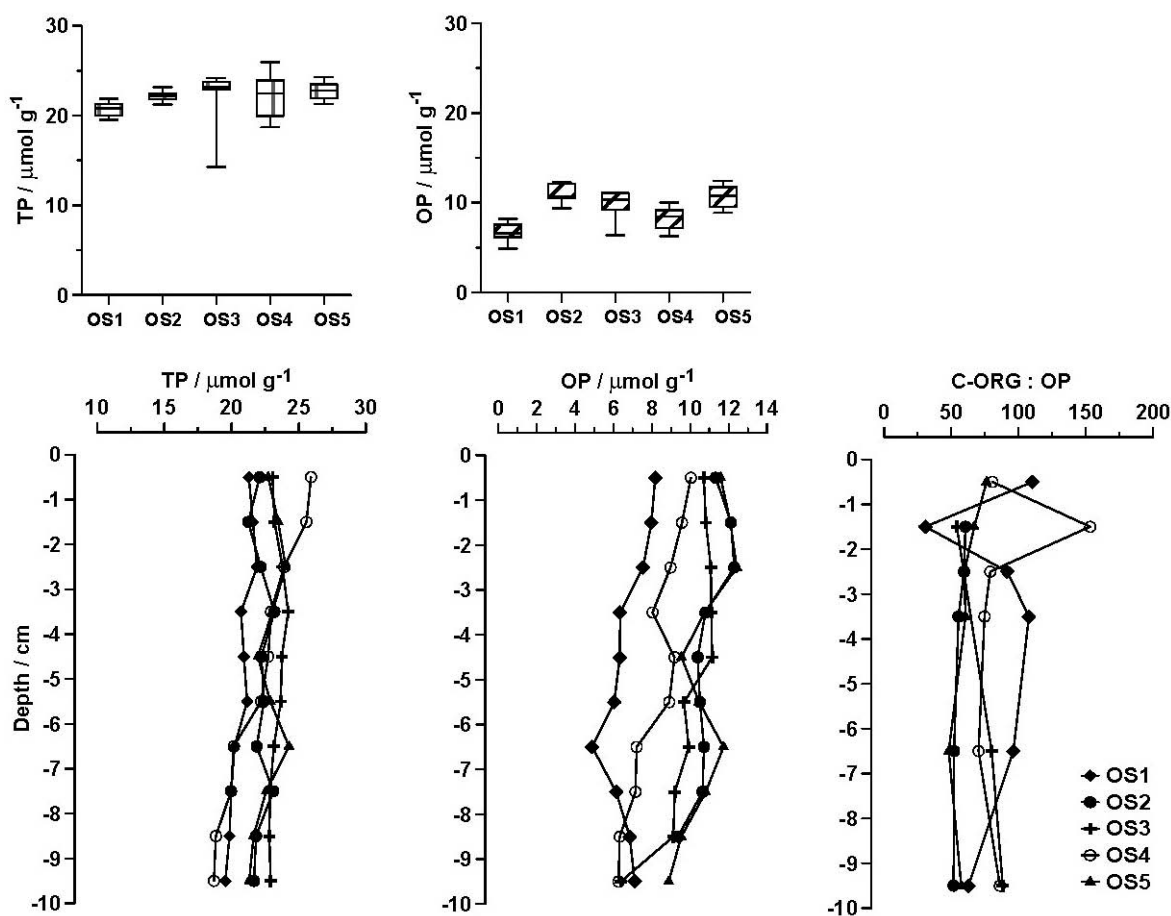


Fig. 5. Box-whisker diagrams and depth profiles of sedimentary total phosphorus and organic phosphorus (TP and OP), as well as C-ORG/OP atomic ratio at open sea stations (OS1, OS2, OS3, OS4 and OS5) in June 2002

ed the retention of remineralized P in sediments over the depth intervals as a consequence of transformation of P from one form to another.

Organic phosphorus (OP) concentrations determined at OS stations ranged between 4.7 and $13.4 \mu\text{mol g}^{-1}$ (Fig. 5). According to the results of statistical analyses, concentrations at OS1 and OS4 were significantly lower in comparison to stations OS2, OS3 and OS5. The lowest average value was found at OS1 and the highest at station OS5 ($6.7 \pm 1.2 \mu\text{mol g}^{-1}$ and $10.9 \pm 1.4 \mu\text{mol g}^{-1}$, respectively). These results are in the range of OP concentrations previously determined in silty sediments and greater (by up to three times) compared to sand-like sediments in the middle Adriatic (MATIJEVIĆ, 2006; MATIJEVIĆ *et al.*, 2008a,b). Correlation analysis

showed an inverse correlation of OP concentrations at OS stations with carbonate content in sediment ($r = -0.694$) (Table 2).

Similar to OP concentrations, its proportion in total phosphorus (OP/TP) was the lowest at OS1 and the highest at station OS5 (32% and 47%, respectively). These OP/TP levels were also found in silty and clay-like sediments in the eastern Adriatic (MATIJEVIĆ *et al.*, 2008a,b) as well as in Aarhus Bay and North Atlantic sediments (JENSEN *et al.*, 1995; SLOMP *et al.*, 1996).

Different vertical profiles of OP concentrations at OS stations (Fig. 5) are probably the result of different conditions of input and sedimentation of organic matter at certain stations. The calculated C-ORG/OP atomic ratio in the sediment profiles (0–10 cm) ranged from

31 to 154, with the highest values at station OS1 (Fig. 5). This is in accordance with previously published data for Adriatic sediments (FAGANELI, 1994; DOLENEC *et al.*, 1998), where C-ORG/OP atomic ratios <200 were also found along the western and southeastern Adriatic coast, which indicated a good preservation of organic P compounds. C-ORG/OP atomic ratios >200 are an indication of favored degradation of organic matter or the input of terrestrial organic matter with generally high C-ORG/OP ratios (800-2050) (LIKENS *et al.*, 1981). In the middle Adriatic coastal area C-ORG/OP ratios >200 (atomic) were established in coarse-sized sediments influenced by fish farming or terrestrial organic matter input (MATIJEVIĆ *et al.*, 2006).

Inorganic phosphorus species and iron concentrations in sediments

Phosphorus bound in biogenic apatite P-FD

The fish debris P fraction (P-FD) includes phosphorus bound in biogenic apatite originating from hard parts of fish material (fish bones

and teeth) and very small amounts of P loosely adsorbed onto mineral surfaces and carbonates (SCHENAU & DE LANGE, 2000).

P-FD concentrations ranged from 0.7 to 4.2 $\mu\text{mol g}^{-1}$ (Fig. 6). These results are in accordance with the previously estimated P-FD range for middle Adriatic sediments (0.8 to 10.5 $\mu\text{mol g}^{-1}$), where the highest concentrations were found under tuna farm cages as the direct consequence of fish farming (MATIJEVIĆ 2006., MATIJEVIĆ *et al.*, 2008a). Higher average values were recorded at stations located near Jabuka Pit (OS1, OS2>OS3, OS4, OS5).

The proportion of the P-FD fraction in the pool of inorganic P species (P-FD/IP) ranged from 7.6 at OS3 to 21.6% at station OS1 (Table 3). This agrees well with previously determined P-FD/IP values for middle Adriatic sediments (15-30%) (MATIJEVIĆ, 2006) where generally higher proportions were found at stations with coarse-sized sediments and higher CA content.

Depth profiles of sedimentary P-FD concentrations at OS stations were almost linear, except at Jabuka Pit station (OS2) characterized by

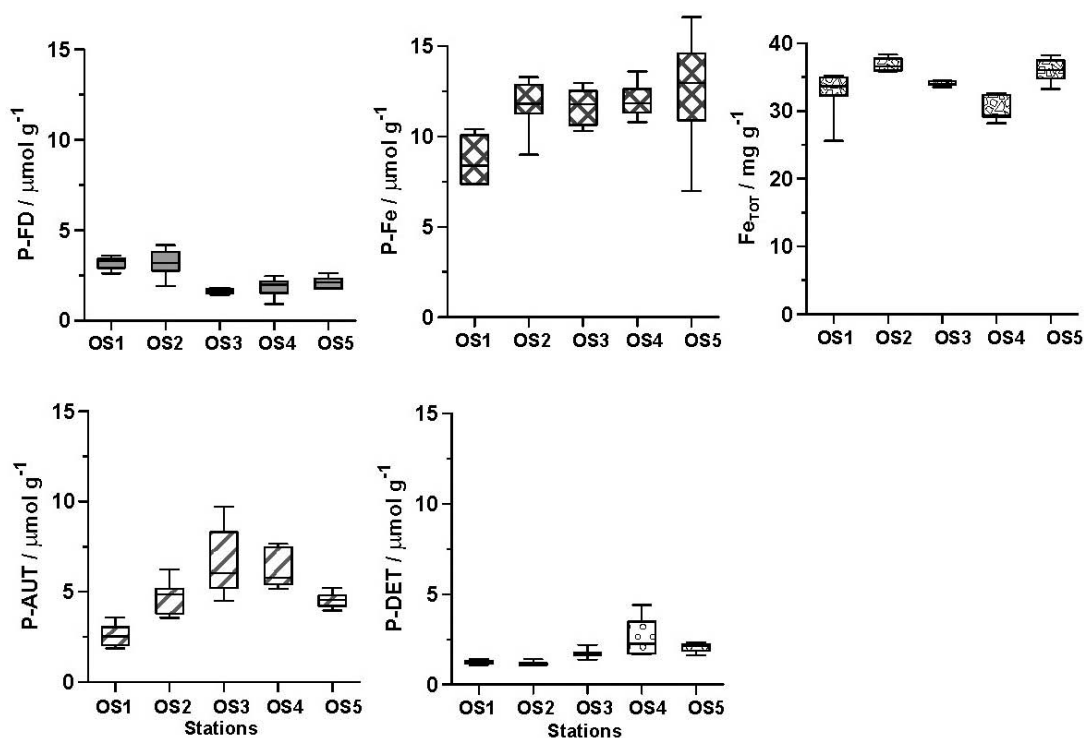


Fig. 6. Box-whisker diagrams of concentrations of inorganic phosphorus species (P-FD, P-Fe, P-AUT, and P-DET) and total iron (Fe-TOT) in sediment layers (0-10 cm) at investigated stations (OS1, OS2, OS3, OS4, OS5) in June 2002

Table 3. Comparison of proportions of different P fractions (P-FD, P-Fe, P-AUT and P-DET) in the inorganic phosphorus (IP) pool (presented as average \pm standard deviation) at investigated stations with values previously found in the wider area of the central Adriatic (Matijević, 2006) as well as in sediment at a central Adriatic tuna farm (Matijević *et al.*, 2008a)

Station	P-FD/IP (%)	P-Fe/IP (%)	P-AUT/IP (%)	P-DET/IP (%)
OS1	21.0 \pm 5.9	53.0 \pm 7.1	17.5 \pm 7.1	8.5 \pm 2.5
OS2	15.3 \pm 3.7	56.2 \pm 4.6	23.0 \pm 4.5	5.5 \pm 0.6
OS3	7.6 \pm 1.2	54.2 \pm 6.3	30.1 \pm 7.4	8.0 \pm 1.9
OS4	8.2 \pm 2.9	52.6 \pm 5.7	27.7 \pm 6.1	11.5 \pm 4.6
OS5	10.2 \pm 2.7	58.1 \pm 8.6	22.0 \pm 6.1	9.7 \pm 1.5
Central Adriatic (Matijević, 2006)	15-30	32-51	9-29	4-24
Tuna farm (Matijević <i>et al.</i> , 2008a)	40-51	41-47	6-17	0.5-11

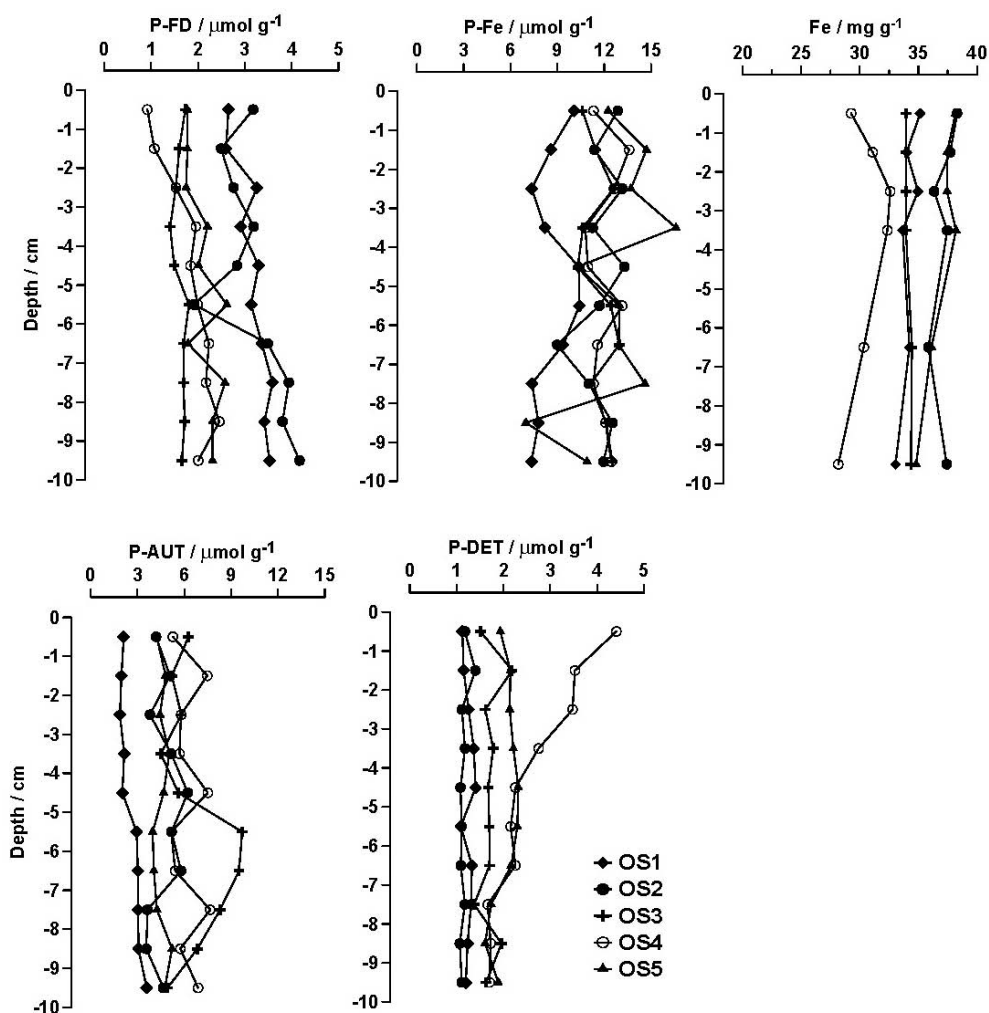


Fig. 7. Depth profiles of sedimentary inorganic phosphorus species (P-FD, P-AUT, P-FD and P-DET) and Fe-TOT in the sediment (0-10 cm) at investigated stations in June 2002

larger oscillations in the vertical P-FD distribution (Fig. 7). Almost twice higher concentrations at stations from the Jabuka Pit group than at stations from the Palagruža Sill group (OS3, OS4 and OS5) could be due to the higher degree of preservation of the fish debris in sediment as a consequence of the circulation of water masses at these locations in the Adriatic Sea (ORLIĆ *et al.*, 1992; ZAVATARELLI *et al.*, 2000).

Phosphorus bound to iron oxyhydroxides (P-Fe)

The phosphorus fraction bound to iron oxyhydroxides (P-Fe) was the predominant fraction of inorganic P at investigated stations, and ranged between 4.2 and 18.5 $\mu\text{mol g}^{-1}$ (Fig. 6, Table 3). The predominance of P-Fe in IP was also found in marine sediments from different areas of the world (JENSEN *et al.*, 1995; SLOMP *et al.*, 1996; ANSHUTZ *et al.*, 1998; LOPEZ *et al.*, 2004). Concentrations at station OS1 ($8.7 \pm 1.5 \mu\text{mol g}^{-1}$) were significantly lower in comparison to other stations (OS1 < OS2, OS3, OS4, OS5), with the highest value determined at station OS5 ($12.6 \pm 2.7 \mu\text{mol g}^{-1}$). The Fe-P/IP portion ranged between 53 and 58%, which is slightly higher than the range previously determined for middle Adriatic sediments (32-51%) (Table 3).

Vertical distributions of P-Fe concentrations in sediments at OS stations differed between stations; they were characterized by surface concentrations grouped in a small range, and larger oscillations in deeper sediment layers (Fig. 7). This could be the result of adsorption and desorption of HPO_4^{2-} from iron oxyhydroxides in sediment. According to the literature, that is the main factor controlling the HPO_4^{2-} flux at the sediment/water interface and depending on pH value and redox potential (JENSEN *et al.*, 1995; STUMM & MORGAN, 1996; GOMEZ *et al.*, 1999). Published data for the middle Adriatic tuna farm sediments (MATIJEVIĆ *et al.*, 2008a), showed a positive correlation between P-Fe and Fe(III)OOH concentrations as a consequence of adsorption/desorption processes. On the contrary, P-Fe concentrations in sediment profiles at OS stations were significantly positively correlated only

with the P-ORG fraction ($r=0.556$), and did not depend significantly on the granulometric composition of sediments (Table 2).

Total iron (Fe-TOT) and iron oxyhydroxides (Fe(III)OOH)

Considering the link between P and the redox dynamics of iron as a result of the scavenging capacity of the precipitating oxyhydroxides (GUNNARS & BLOMQUIST, 1997), we performed parallel measurements of total iron (Fe-TOT) in sediments at OS stations (0-24 cm depth). In addition, we also determined concentrations of dithionite extractable iron (Fe(III)OOH) in surface sediments. Fe-TOT content in sediments differed significantly between stations (OS2 > OS3, OS5, OS1 > OS4), ranging from 20.3 to 37.8 mg g^{-1} (Fig. 6). Obtained values are in good agreement with previously published values for the middle Adriatic (16.6-31.6 mg g^{-1}) and the entire Adriatic (12.7-41.8 mg g^{-1}) surface sediments (DOLENEC *et al.*, 1998). The vertical Fe-TOT distribution at station OS3 displayed no clear vertical trend ($p > 0.05$) (Fig. 7) while at OS1, OS2 and OS5 concentrations decreased with increasing depth. The vertical profile at station OS4 was characterized by a sub-surface maximum (2 cm depth), and a minimum at a depth of 10 cm. This minimum is probably a consequence of CA content increase since we established a strong negative correlation between Fe-TOT and carbonates (Table 2). As could be expected, the concentrations of Fe-TOT in sediments were strongly positively correlated with the content of fine-grained particles (silt and clay) ($r=0.844$) and inversely correlated with large particles (gravel and sand) content ($r > -0.820$) and CA content ($r = -0.669$) (Table 2).

Concentrations of dithionite extractable iron (total Fe-oxyhydroxides, amorphous+crystalline; Fe(III)OOH) were determined only in surface sediment layers (0-2 cm) which contain the reactive mobile P fraction (ANSCHUTZ *et al.*, 1998). Fe(III)OOH concentrations ranged from 126.2 (OS2) to 145.7 (OS1) $\mu\text{mol g}^{-1}$. These concentrations are in the range of data obtained for stations of silty-like sediments in the central

Adriatic area ($36.4\text{--}214.5 \mu\text{mol g}^{-1}$), and are significantly higher in relation to sand-like tuna farm sediments in Croatian coastal areas ($9.1\text{--}63.6 \mu\text{mol g}^{-1}$) (MATIJEVIĆ *et al.*, 2006).

The nature of associations of P with Fe is indicated by the Fe:P molar ratio in the sediment, which is considered to be a measure of free sorption sites for HPO_4^{2-} on iron oxyhydroxides surfaces (JENSEN *et al.*, 1995). Generally, the lower Fe:P ratio suggests saturation of sorption sites or less capability to adsorb HPO_4^{2-} resulting in orthophosphate efflux to the overlying water. The Fe:P molar ratios in the CDB extractable fraction in surface sediments (0-2 cm) of the OS stations (Fe:P=8.5-13.8) were somewhat lower than values established for modern oxic marine sediments (Fe:P=14-29) (DE LANGE, 1986; LUCOTTE *et al.*, 1994; ANSCHUTZ *et al.*, 1998) or estuarine sediments (Fe:P=13-24) (COELHO *et al.*, 2004) and similar to, or higher than, the values recorded in Danish coastal sediments (Fe:P=2-11) (JENSEN *et al.*, 1995). Furthermore, the obtained ratio for OS stations (Fe:P=8.5-13.8) is significantly higher in comparison to values previously found in coastal Croatian sediments below tuna cages (Fe:P=1.0-5.8) (MATIJEVIĆ *et al.*, 2007).

The low Fe:P ratio at tuna farms was a consequence of the reduction of Fe^{3+} to Fe^{2+} in sediment under the negative redox-potential, resulting in HPO_4^{2-} desorption. This process did not take place in well-oxidized OS sediments of the middle Adriatic considering positive E_H values at OS stations (Fig. 4) and the established higher Fe:P ratios. Further investigations including all presented parameters and orthophosphate flux measurements at the sediment-water interface could verify these results.

Phosphorus bound to authigenic apatite (P-AUT)

Concentrations of P bound in authigenic apatite (P-AUT) ranged between $1.1 \mu\text{mol g}^{-1}$ and $10.8 \mu\text{mol g}^{-1}$. According to analysis of variance, stations could be divided into 3 distinct groups (OS1<OS2, OS5<OS3, OS4) with the lowest value at station OS1 ($2.6\pm 0.7 \mu\text{mol g}^{-1}$) and the highest value at station OS3 (6.7 ± 2.2

$\mu\text{mol g}^{-1}$) (Fig. 6). The highest values were found at stations closest to the Italian coast. These values are up to twice higher than the previously determined range for the middle Adriatic surface sediment layer (0-2 cm depth) where the highest concentrations of P-AUT fraction were found in fine-sized sediments. On the contrary, the P-AUT portion in the IP pool obtained at OS stations (17.5-30.1%) agrees with established proportions for the middle Adriatic sediments (9-29%) (Table 3).

The presented P-AUT/IP ratios for the OS stations are in accordance with values obtained for sediment from the Arabian Sea (10-25%) (SCHENAU & DE LANGE, 2001) where the same method for isolation of the apatite P forms in sediments was used. Some authors have found higher portions of P-AUT in IP (20-50%) in different types of sediments (JENSEN *et al.*, 1998; EIJSINK *et al.*, 2000; SLOMP *et al.*, 1996). This was probably due to usage of different methods for extraction of P-AUT (i. e. acetic extraction step of apatite P form without prior distinction of the biogenic apatite fraction).

Greater oscillations of vertical P-AUT profiles were recorded in sediment at stations OS3 and OS4, while the vertical distributions of P-AUT at other stations were almost linear (Fig. 7). According to RUTTENBERG (1992), P-AUT (and P-DET) concentrations are not directly influenced by processes in the water column and, considering their seasonal variations or sediment vertical distributions, they are the most inert P species (RUTTENBERG, 1992; JENSEN *et al.*, 1995).

Phosphorus bound in the detrital apatite (P-DET)

Mean values of P bound in detrital apatite (P-DET) at stations OS1 and OS2 were significantly lower in comparison to other stations. Overall values ranged from 1.07 to $4.41 \mu\text{mol g}^{-1}$, with the highest average value at station OS4 ($2.59\pm 0.93 \mu\text{mol g}^{-1}$) (Fig. 7). These results correspond well with a previously determined range of P-DET for the middle Adriatic ($0.04\text{--}3.44 \mu\text{mol g}^{-1}$; MATIJEVIĆ *et al.*, 2008a) where

the highest P-DET concentration was recorded in sediment at a station under river influence. According to RUTTENBERG (1992), P-DET is a characteristic form in marine sediments under fluvial influence, containing P in detrital apatite spherical particles with smooth edges and a small specific area. P-DET concentrations obtained at OS stations were positively correlated with gravel ($r=0.690$) and C-ORG content ($r=0.577$), and negatively with P-FD ($r=-0.740$) (Table 2).

The P-DET proportion in the inorganic P pool (4.5-21.0%) presents the smallest IP fraction (Table 3). The obtained P-DET/IP ratios are similar to previous data for the middle Adriatic and higher than the values in tuna farm sediments overloaded due to settling of large amounts of biogenic material (fish particles) (Table 3). The established P-DET/IP range for open-sea stations also complies well with proportions reported in the literature for carbonate and silty sediments ($P\text{-DET}/IP \leq 20\%$) (EIJSSINK *et al.*, 2000; LOPEZ, 2004; SCHENAU & DE LANGE, 2001).

Vertical profiles of P-DET at station OS4 significantly differed from the almost linear profiles of P-DET at other stations (Fig. 7) due to elevated values in the upper sediment layer (0-4 cm) and which were 2-5 times higher in comparison to deeper layers. Considering the location of this station and circulation of water masses in this part of the Adriatic (ZORE-ARMANDA *et al.*, 1991; BULJAN & ZORE-ARMANDA, 1976), this can be explained by terrestrial input from Italian rivers. In the sandy sediments in the northwestern part of the Adriatic a P-DET increment was also found to be probably generated by the Po river circulation (MATIJEVIĆ *et al.*, 2008b).

Statistical data analysis

Additional statistical analyses of the data were carried out using cluster analysis (Euclidean distance method) and principal component analysis (GRANT & MIDDLETON, 1990). For both types of analysis we used all relevant data for the sediment (0-10 cm) (organic and inorganic P species concentrations, total iron concentration, organic matter content, carbonate content,

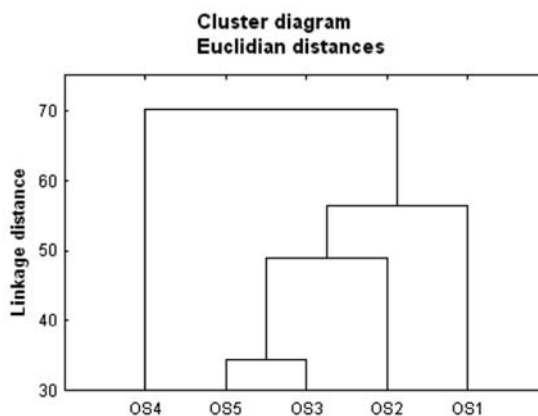


Fig. 8. Dendrogram for hierarchical clustering of the OS stations, using single linkage and Euclidean distance calculated from obtained data (inorganic and organic phosphorus concentration, granulometric composition, organic matter and carbonate content)

granulometric composition, organic carbon content and redox potential).

Cluster analysis distinguished two main clusters of stations (Fig. 8). Station OS4 was significantly different from the stations grouped in another cluster (OS1, OS2, OS3 and OS5) due to the highest content of coarse-sized particles and carbonates, P-TOT and P-DET concentrations, as well as the lowest Fe-TOT concentrations.

The PCA of data extracted three principal components (PC) which explained 75% of the total variance (Table 4), indicating that these axes are useful for examining the major differences between element distributions at investigated stations.

The first group (Factor 1), which explained 34% of the variance, includes Fe-TOT and granulometric composition of sediments indicating that Fe-TOT distribution is primarily associated with the fine sediment fraction. P-ORG is partially represented in Factor 1 and partially in Factor 3, indicating that P-ORG is associated with fine fractions of sediment, which is in accordance with previously reported data for middle Adriatic sediments (MATIJEVIĆ, 2006).

The second group (Factor 2; 25% of total variance) includes apatite P species (P-AUT, P-DET and P-FD) and C-ORG content demonstrating that neither granulometric composition, OM or CA content have a significant influ-

Table 4. PCA results: table of loadings of the principal components obtained in the analysis. Significant loadings (>0.7000) are bolded, while loadings >0.6000 are underlined

	Factor 1	Factor 2	Factor 3
Gravel	-0.8001	0.4664	0.0683
Sand	-0.9558	0.0548	0.0515
Silt+clay	0.9623	-0.0907	-0.0540
Organic matter (OM)	0.0263	-0.0111	-0.7584
Organic carbon (OC)	0.1683	0.8267	0.1074
Redox potential (E_H)	-0.0205	-0.0950	<u>-0.6487</u>
Carbonate content (CA)	-0.8850	-0.2435	-0.1338
Fe-TOT	0.8597	-0.3633	0.2390
P-Fe	0.0062	0.4707	<u>0.6660</u>
P-AUT	-0.1871	<u>0.6769</u>	0.2870
P-FD	0.0937	-0.9185	-0.0233
P-DET	-0.3126	0.7797	0.1977
Organic P	<u>0.6066</u>	0.2618	<u>0.6261</u>
Total P	0.3967	0.4676	0.4561
Variance explained	33.56%	25.22%	16.13%

ence on these compounds. Association between P-DET, P-AUT and C-ORG derives from similar vertical distributions in the surface sediment layer. Namely, their concentrations are higher in the surface layer as a direct consequence of riverine input, mainly at stations OS3 and OS4. The opposing effect of P-FD in this group is probably the consequence of a different source of this apatite P fraction, which mainly originates from remains of fish skeletons settled on the seafloor.

Factor 3 accounted for 16% of the total variance and is composed of OM, P-Fe, E_H and OP, indicating that OM is associated with sediment redox potential and has an opposing influence on the vertical distribution of marked P fractions. The adverse effect of OM on P-Fe and P-ORG vertical distributions probably results from organic matter degradation processes and a

complex sedimentary P cycle (JENSEN *et al.*, 1995; STUMM & MORGAN, 1996).

CONCLUSIONS

Total phosphorus concentrations investigated in June 2002 did not differ significantly between 5 open sea stations, and were within the range of concentrations previously determined in middle Adriatic fine-sized sediments.

Organic P concentrations were significantly lower at stations with higher carbonate content in sediments. The C-ORG/OP atomic ratio indicated good preservation of organic P compounds in sediments. Inorganic P concentrations (P-FD, P-AUT, P-DET and P-Fe) varied between the stations due to different conditions of sedimentation at investigated locations, or due to internal processes and transformations in sediments.

The proportions of certain IP species (P-FD, P-Fe, P-AUT and P-DET) in inorganic sediment P pool were within the range of values previously determined for the middle Adriatic, with P-Fe as the predominant fraction. Relatively high Fe:P molar ratios and a positive redox-potential (E_H) in surface sediment indicated HPO_4^{2-} adsorption on the Fe oxides/hydroxides. Sedimentary depth profiles (0-10 cm) of P-Fe, P-AUT and P-ORG concentrations varied depending on location, probably due to different sources of organic matter, as well as due to conversion from one P species to another. The concentration of P-DET was enhanced in the surface sediment layer at stations under the influence of terrestrial input from Italian rivers.

Cluster analysis indicated that granulometric composition and carbonate content is the leading factor of distinction between the stations.

Results of PCA of data showed that the fine fraction of sediments plays a key role in the vertical distribution of Fe-TOT and P-ORG. The second factor pointed to an association among

apatite P species and C-ORG concentrations. The link between authigenic and detrital apatite P and C-ORG (second factor) is a result of the influence of the riverine input of organic matter, and not of the sediment characteristics. The opposing effect of P-FD in this group is a consequence of a different source of biogenic apatite P which mainly originates from the remains of fish skeletons. Association between OM, P-Fe, E_H and OP included in the third PCA factor derives from internal complex processes in the sedimentary P cycle.

Further investigations in the middle Adriatic could verify the relationship between the OM in the water column and its degradation in the sediment, taking into account the sequential analysis of P species in the particulate matter and their vertical distribution in the sediment. Additional examinations including Fe(III)OOH concentrations and HPO_4^{2-} in sediment pore water, as well as flux measurements at the sediment-water interface, are also needed to validate preliminary results obtained in this paper.

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Vertikalna raspodjela kemijskih oblika fosfora i željeza u sedimentu postaja otvorenog mora na području srednjeg Jadrana

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SAŽETAK

U sedimentu sa 5 postaja otvorenog mora srednjeg Jadrana ispitane su koncentracije različitih oblika fosfora (P) u jezgrama debljine 0-10 cm. Mjerenja su uključivala organski fosfor (OP) i anorganske vrste P: P u biogenom apatitu, (P-FD), P adsorbiran na okside i hidrokside željeza (P-Fe), P u autigenom apatitu (P-AUT), i P u detritusnom apatitu (P-DET). Koncentracije ukupnog željeza i željeznih oksid-hidroksida (Fe(III)OOH) su također određene kao i granulometrijski sastav, sadržaj organske tvari (OM), organskog ugljika (C-ORG) i karbonata (CA) u sedimentu. U pornoj vodi sedimenta su izmjereni redoks potencijal (E_H) i koncentracija ortofosfata. Svi su podaci bili predmet korelacijske, Cluster i PC analize. Cluster analiza je ukazala na granulometrijski sastav i sadržaj karbonata kao vodeće čimbenike razlikovanja između postaja. PC analiza je pokazala da sitno-zrnata frakcija sedimenta ima ključnu ulogu u vertikalnoj raspodjeli Fe-TOT i P-ORG u sedimentu. Povezanost između P-AUT, P-DET i C-ORG je rezultat utjecaja riječnog donosa, dok veza između OM, P-Fe, E_H and OP proizlazi iz kompleksnih procesa ciklusa P u sedimentu.

Ključne riječi: fosfor, sediment, željezo, Jadransko more