

The redox potential of sediment from the Middle Adriatic region

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Sediment redox potentials (E_H) at stations of different trophic status in the central Adriatic from 2001-2007 were investigated in this paper. For most part of the year at open sea and channel stations E_H values were mainly positive (+150 to 0 mV), even to 10 cm sediment depth. Positive E_H (absence of sulphate reduction with very low sulphide concentrations) at these stations is probably caused by low to medium organic matter sedimentation rates. Negative E_H values (presence of sulphide and appearance of anoxic conditions in sediment) and shallow redox transition depths in sediment were found in areas with higher productivity and organic matter sedimentation such as eutrophicated Kaštela Bay after a winter plankton bloom, a near shore station exposed to a city wastewater outlet and stations located under fish farm cages. Vertical profiles of sediment E_H , iron-bound phosphorus fraction and Fe(III)OOH investigated at a middle Adriatic tuna farm indicated a relationship between redox potential and phosphate adsorption/desorption processes.

Key words: sediment, redox potential, organic matter, Middle Adriatic

INTRODUCTION

The maintenance of life resulting from solar energy, nutrient supply and carbon dioxide is the main cause for non-equilibrium conditions in natural waters where photosynthetic reservoirs of oxygen and localised centres of highly negative p_e (i.e. electron activity) are produced. Non-photosynthetic organisms tend to restore equilibrium in the aquatic environment by catalytic decomposition of organic matter through energy-yielding redox reactions (STUMM, 1978).

These redox reactions are important in the carbon and nutrient cycle of the oceans and involve numerous electron acceptors with the most energetically favourable sequence of reactions (O_2 , NO_3^- , IO_3^- , Mn^{4+} , Fe^{3+} , SO_4^{2-} , CO_2) (FROELICH *et al.*, 1982; DE LANGE, 1986 a, b; COLMAN & HOLLAND, 2000). The electron activity of oxydo-reduction couples given in Table 1 is related via the Nernst equation (STUMM, 1978; STUMM & MORGAN, 1996; SIGG & STUMM, 1989) to the redox potential (E_H) as a measure of the oxidation potential.

Table 1. Sequence of organic matter oxidation reactions in marine environments (DE LANGE, 1986 a, b; COLMAN & HOLLAND, 2000)

OXIDATION REACTIONS	
Oxygen reduction	$(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4) + 138 \text{ O}_2 \rightarrow 106 \text{ CO}_2 + 16 \text{ HNO}_3 + \text{H}_3\text{PO}_4 + 122 \text{ H}_2\text{O}$
Nitrate reduction (denitrification)	$5(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4) + 472 \text{ HNO}_3 \rightarrow 530 \text{ CO}_2 + 276 \text{ N}_2 + 5\text{H}_3\text{PO}_4 + 886 \text{ H}_2\text{O}$
Iodate reduction	$(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4) + 236 \text{ IO}_3^- \rightarrow 236 \text{ I}^- + 318 \text{ CO}_2 + 24 \text{ N}_2 + 3\text{H}_3\text{PO}_4 + 390 \text{ H}_2\text{O}$
MnO ₂ reduction	$(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4) + 236 \text{ MnO}_2 + 472 \text{ H}^+ \rightarrow 236 \text{ Mn}^{2+} + 106 \text{ CO}_2 + 8 \text{ N}_2 + \text{H}_3\text{PO}_4 + 366 \text{ H}_2\text{O}$
Fe ₂ O ₃ reduction	$(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4) + 212 \text{ Fe}_2\text{O}_3 + 848 \text{ H}^+ \rightarrow 424 \text{ Fe}^{2+} + 106 \text{ CO}_2 + 16 \text{ NH}_3 + \text{H}_3\text{PO}_4 + 530 \text{ H}_2\text{O}$
Sulphate reduction	$(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4) + 53 \text{ SO}_4^{2-} \rightarrow 106 \text{ CO}_2 + 16 \text{ NH}_3 + 53 \text{ S}^{2-} + \text{H}_3\text{PO}_4 + 106 \text{ H}_2\text{O}$

Practical measurements of the redox potential in the marine environment are commonly performed with inert electrodes, mostly Pt electrodes (COOPER, 1937; HARTMANN HANSEN *et al.*, 1978; SHOW *et al.*, 1994; MORSE & MORIN, 2005) but also with other electrode materials such as gold, iridium, carbon, graphite and glassy carbon (RIOS-MENDOZA *et al.*, 2003). Apart from direct measurements, redox potential can also be specified indirectly through the I/IO₃⁻, as well as the As³⁺/As⁵⁺, systems (LISS, *et al.*, 1973; KÖLLING, 2000).

Due to formation of PtO or PtO₂ films on the Pt-electrode surface in aerobic solutions (WHITFIELD, 1974), as well as due to the fact that many redox reactions in seawater do not readily couple with another (STUMM, 1978), the meaning of measured E_H values in seawater is debatable (WOLLAST, pers. com.; BERNER, 1981; KÖLING, 1986; GRENTHE *et al.*, 1992; STUMM & MORGAN, 1996). A detailed theoretical background on the interactions between electrode, aqueous electron activities and redox potential in natural waters is given by HOSTETTLER (1984).

Due to the uncertain reliability of redox measurements in oxic seawater, E_H is usually determined in marine sediments, where it can be used as a detector of the transition depths from oxic to suboxic and suboxic to anoxic conditions. According to COLMAN & HOLLAND (2000) redox transition from oxic to suboxic conditions

in marine sediment is marked by O₂ and NO₃⁻ depletion, as well as Mn²⁺ and Fe²⁺ occurrence, which corresponds to redox potential values between +300 and +150 mV. Redox transition from suboxic to anoxic conditions is marked by reduction of SO₄²⁻ to S²⁻ which, after hydrolysis or precipitation, forms HS⁻(aq) or mono/disulphide minerals such as FeS and pyrite (FeS₂). This redox transition takes place between 0 mV and -150 mV (COLMAN & HOLLAND, 2000).

Considering the importance of sediment redox potential as an essential feature of the physical-chemical state of marine sediment, systematically taken measurements can provide information about temporal and spatial changes of redox transition depths in marine sediments (COLMAN & HOLLAND, 2000) and consequently organic matter sedimentation rates, sediment depths of prevailing nitrification, denitrification and ammonia generation processes (RISGAARD-PETERSEN *et al.*, 2003), phosphate adsorption/desorption (FROELICH *et al.*, 1988; BENITEZ-NELSON, 2000; PAYTAN *et al.*, 2003) as well as hydrogen sulphide and sulphide mineral formation zones.

Among numerous papers reporting the redox potential in sediment in different areas of the world, E_H in the Mediterranean area was used rather as an ancillary indicator of natural and anthropogenic organic matter input to the sediment (AZZONI *et al.*, 2005; CALACE *et al.*, 2006; TERRADOS *et al.*, 1999; MARBA & DUARTE, 2001;

CANCEMI *et al.*, 2003; KARAKASSIS *et al.*, 1998, 1999, 2000; PORELLO *et al.*, 2005; KALANTZI & KARAKASSIS, 2006) than as the main investigated parameter. Due to the lack of systematically taken redox measurements in the middle Adriatic area, and except for some occasional studies (KUŠPILIĆ & BARIĆ, 1996; KUŠPILIĆ, 2001; KUŠPILIĆ *et al.*, 2002; BOGNER *et al.*, 2003; MATIJEVIĆ *et al.*, 2003, 2004, 2006; MATIJEVIĆ, 2006), we present in this paper for the first time data for an annual cycle of redox conditions in marine areas of different trophic states.

MATERIAL AND METHODS

Laboratory E_H measurements

Laboratory measurements of redox potential in model solutions of sulphide and ammonium ions in seawater were performed at room temperature in a closed Metrohm 100 mL polarographic vessel. Stock solutions of sodium sulphide (0.5 mol L^{-1}) and ammonium chloride (0.04 mol L^{-1}) were prepared from $\text{Na}_2\text{S} \times 9\text{H}_2\text{O}$ (Kemika p.a.) and NH_4Cl (Merck p.a.) dissolved in de-ionised MiliQ water. Due to the highly hygroscopic nature of $\text{Na}_2\text{S} \times 9\text{H}_2\text{O}$ the crystals were gently dried with filter paper prior to weighing. Model solutions were prepared in deaerated seawater spiked with stock solutions of sulphide and ammonium ions to final concentrations of 5 mmol L^{-1} and 0.4 mmol L^{-1} , respectively. Deaeration was achieved by bubbling argon for 30 min through seawater, and afterwards over the seawater model solutions. Final concentrations of S^{2-} and NH_4^+ were chosen on the basis of constant sulphate/chlorinity ratio in seawater (CULKIN, 1965) as well as on earlier investigations of ammonium concentrations in middle Adriatic sediment pore water (KUŠPILIĆ, 2001).

Measurements were performed with a Pt-electrode and Ag/AgCl (3 M KCl) reference electrode both connected to a voltmeter. For the purpose of laboratory and field measurements Metrohm E-605 or Iskra MA 5730 voltmeters were used. Prior to measurement the Pt electrode was mechanically cleaned with

fine-grained abrasive paper and rinsed with 10% hydrochloric acid and distilled water. For electrode standardization saturated quinhydrone solutions in pH 4 and pH 7 buffers were used (KÖLLING, 2000). 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). After the standardization both electrodes were rinsed in distilled water.

Field measurements

Field investigations were carried out in the central Adriatic with RV "Bios" and "Navicula" monthly from December 2001 to December 2002 at stations of different trophic status: station S1 in eutrophicated Kaštela Bay, a mezotrophic coastal channel station (S2) and an oligotrophic open sea station (S3), while investigations at a near shore station influenced by urban wastewater discharge (S4) were carried out during 2002-2007 (Fig. 1). Investigations at tuna farms (A, C) and sea bream/sea bass farm (B) were performed during the 2001-2005 period. Sampling periods, station coordinates, sediment types (FOLK, 1954) and organic matter contents (VDOVIĆ *et al.*, 1991) for investigated stations are given in Table 2.

Sediment samples were collected in triplicate by SCUBA-divers ($z < 50 \text{ m}$) or gravity corer ($z > 50 \text{ m}$) with transparent plastic liners (i. d. = 6.5 cm). Measurement of redox potential was obtained immediately in the undisturbed sediment core after sample collection in the onboard laboratory. After standardization both electrodes were rinsed in distilled water and immersed into the overlying seawater of the sediment samples. When the equilibrium potential was set, the Pt electrode was pushed in 0.5 cm steps into the sediment to a depth of 6-10 cm and the potential was recorded.

Additionally collected sediment samples were divided into slices each 1 cm thick, frozen, freeze-dried, and stored in clean plastic bags until lab analysis of sediment phosphorus species bounded to iron oxides and oxyhydroxides (P-Fe). Measurements of sediment P-Fe concentrations were obtained on a Shimadzu UV-VIS Spectrophotometer according to

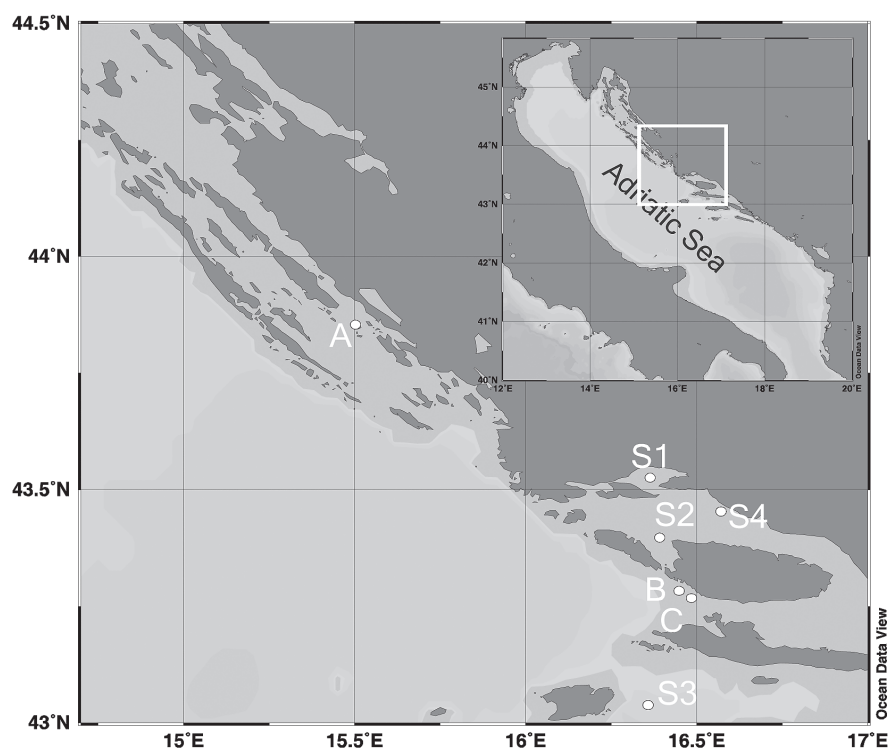


Fig. 1. Map of investigated stations in the central Adriatic area

Table 2. Station coordinates, sampling periods, sediment types according to FOLK (1954) (gM=gravelly mud; (g)mS=slightly gravelly muddy sand; gM=gravelly mud; gS=gravelly sand; mS=muddy sand; M=mud; gmS=gravelly muddy sand) and organic matter content in sediment

Station	Lat.	Lon.	Depth (m)	Sampling period	Sediment type	Organic matter (%)
S1	43°31,0'	16°22,0'	37	2001-2002	M	6.4±1.1
S2	43°25,6'	16°23,9'	52	2001-2002	M	7.9±0.8
S3	43°00,0'	16°20,0'	102	2001-2002	gmS	3.0±0.4
S4	43°29,7'	16°31,5'	24	2002-2007	mS	n. d.
A	43°50,7'	15°29,9'	26	Jun 2001	mS	n. d.
A-REF	43°49,3'	15°30,1'	70	Jun 2001	gM	n. d.
B	43°18,4'	16°28,2'	12	Dec 2001 May 2002 Mar 2003	sG	2.6±0.2
B-REF	43°17,5'	16°27,9'	78	Dec 2001 May 2002 Mar 2003	sM	4.1±0.2
C	43°17,4'	16°28,9'	45	Jun 2003 Apr 2004 Jan 2005	gS	2.5±0.4
C1	43°17,5'	16°28,7'	48	Jun 2003 Apr 2004 Jan 2005	gmS	2.0±0.2
C-REF	43°16,7'	16°28,7'	81	Jun 2003 Apr 2004 Jan 2005	(g)sM	3.8±0.5

n.d. = not determined

a modified SEDEX procedure (RUTTENBERG, 1992; ANSHUTZ *et al.*, 1998 and SCHENAU & DE LANGE, 2000). Citrate-dithionite-bicarbonate (CDB) buffer solution used for P-Fe extraction was analysed for iron oxides also extracted during the SEDEX procedure (ANSHUTZ *et al.*, 1998). CDB agent is specific for both amorphous and crystalline iron oxides, which are the most reactive iron forms in sediment, and consisting mainly of Fe(III)OOH (CANFIELD *et al.*, 1992). Fe in CDB solution was analysed by flame atomic absorption spectrophotometry (F-AAS). Granulometric composition (FOLK, 1954) and organic matter content (VDOVIĆ *et al.*, 1991) were determined from the same sediment cores (Table 2).

Water samples collected by Nansen bottles were analysed on nutrient concentrations using modified automated methods according to GRASSHOFF (1976) on a Technicon Auto-Analyzer III (Bran & Luebbe, Germany), while chlorophyll *a* concentrations were determined fluorometrically from 90% acetone extracts (STRICKLAND & PARSONS, 1972) with a Turner TD 700 laboratory fluorometer.

RESULTS AND DISCUSSION

Laboratory E_H measurements

Prior to field measurements of redox potential in marine sediments, the Pt electrode was tested in the laboratory to sensitivity towards dissolved atmospheric oxygen, ammonium and sulphide concentrations. Experiments carried out in deaerated seawater showed no change of redox potential with respect to potential recorded in seawater saturated with atmospheric oxygen. E_H measurements in deaerated seawater spiked with NH_4Cl stock solution up to 0.4 mmol L^{-1} also showed no significant changes, while spiking with Na_2S stock solution up to 5 mmol L^{-1} strongly affected the measured redox potential (Fig 2a, 2b). Figure 2b shows that redox potentials from $+170$ to 0 mV correspond to low sulphide concentration ranges from $1 \text{ } \mu\text{mol L}^{-1}$ to 0.3 mmol L^{-1} , while potentials from 0 mV to -185 mV correspond to enhanced concentrations from 0.3 mmol L^{-1} to 5 mmol L^{-1} . This is in accordance with COLMAN & HOLLAND (2000), who showed that the redox transition between oxic and suboxic states takes place between potentials from $+300$ to 150 mV (O_2 and NO_3^- concentrations near the detection limits), while

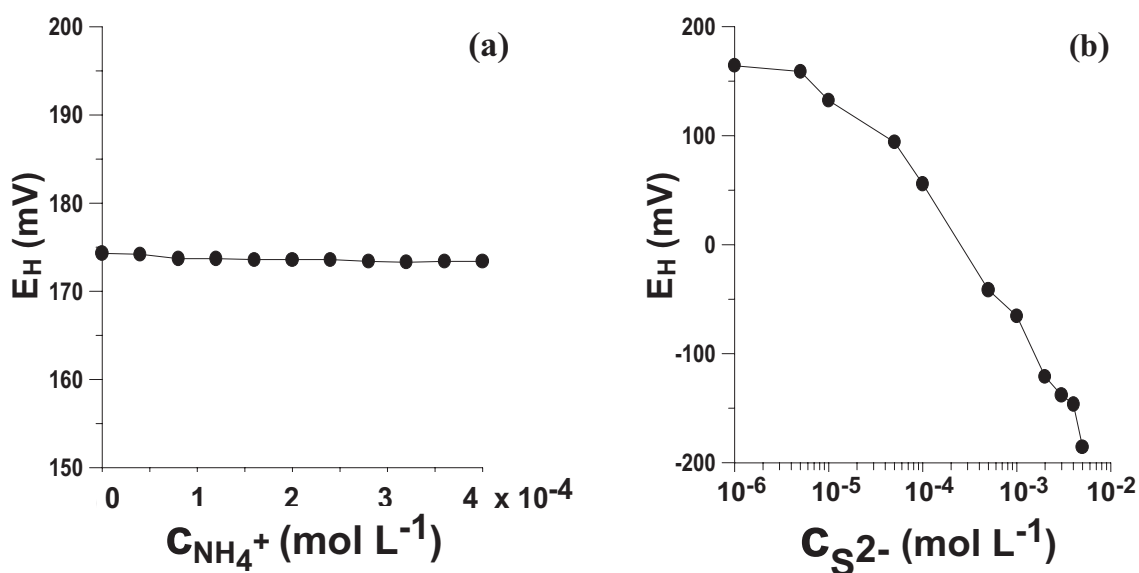


Fig. 2. Redox potential measured by Pt electrode in deaerated seawater with increasing ammonium (NH_4^+) and sulphide (S^{2-}) concentration

transition from suboxic to anoxic conditions (presence of HS^- or S^{2-}) takes place at potentials from 0 to -150 mV.

Accordingly from our experiments, as well as from the earlier investigations of BERNER (1963), the Pt electrode used in our measurements was found to be most sensitive to sulphide presence. This implies that the redox potential, measured in seawater or sediment pore water, describes sulphide concentrations in these environments rather than their oxic or anoxic status. The possible influence of other redox pairs ($\text{Mn}^{4+}/\text{Mn}^{2+}$ or $\text{Fe}^{3+}/\text{Fe}^{2+}$) onto the redox potential was not examined.

Field measurements

Redox potentials determined during 2001/2002 at stations of different trophic status in the middle Adriatic area (S1, S2 and S3) are presented in figure 3. The main characteristic for all stations are positive (+150 to 0 mV) redox potentials for most part of the year, while in the shallower near-shore stations (S1 and S2) even more positive (>150 mV) sediment surface layers were found. These positive potentials indicate the absence of sulphate reduction with very low sulphide concentrations, even to 10 cm sediment depths.

Established E_H sediment profiles are probably a consequence of low to medium organic matter sedimentation rates in this generally oligotrophic part of the Adriatic (GIORDANI *et al.*, 2002; BOLDRIN *et al.*, 2002). In more productive near shore and continental shelf sediments high surface productivity and relatively shallow water column depth result in high organic carbon fluxes to the sediment, which promotes higher respiration rates. These high rates are typically evidenced by shallow oxygen penetration depths (< 1cm) (ARCHER & DEVOL, 1992; CANFIELD *et al.*, 1993; BRANDES & DEVOL, 1995).

Negative potentials (presence of sulphide) and appearance of anoxic conditions in sediment at stations S1, S2 and S3 were found during the winter months of 2001, 2002 and in August 2002. Basic differences between stations were in redox transition depths. In sediment at station S1 the redox transition depth in the winter period

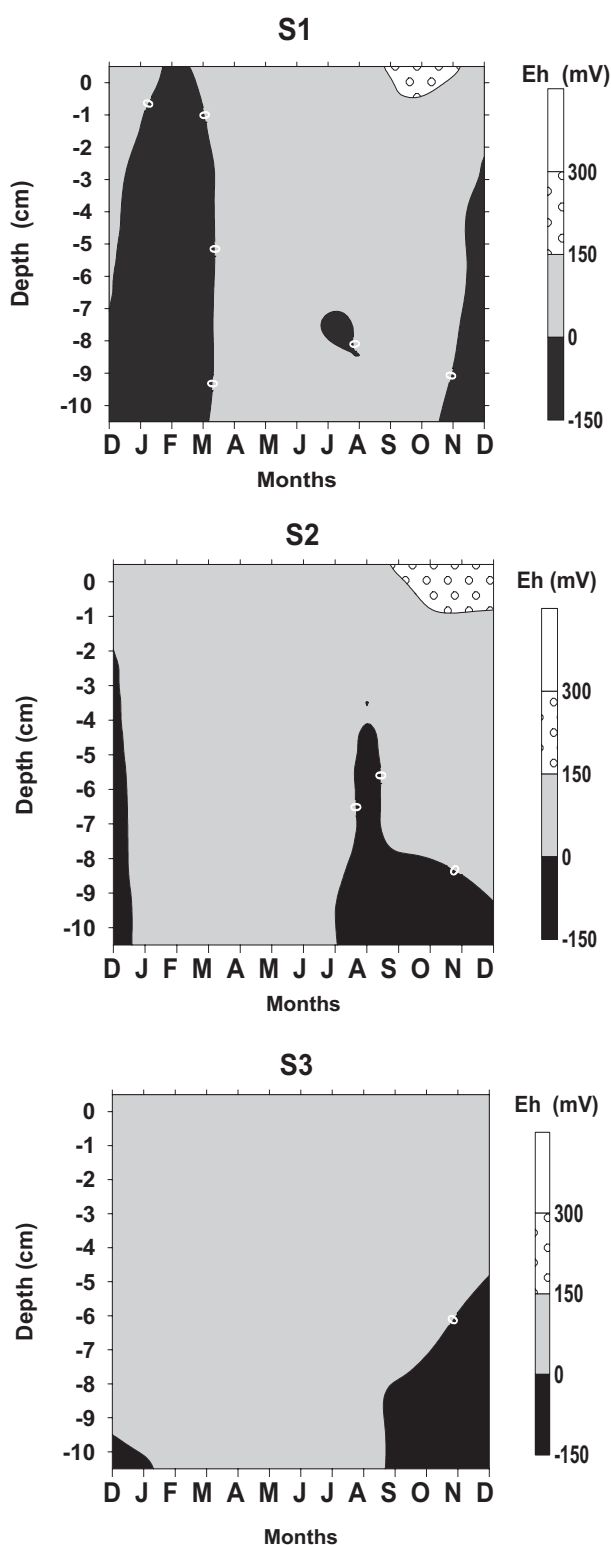


Fig. 3. Sediment redox potential (E_H /mV) at eutrophicated bay (S1), channel station (S2) and open sea station (S3)

was near the surface (0 - 2.5 cm depth), while in sediment at stations S2 and S3 the redox transition depths were deeper (from 4.5 - 9.5 cm). On the contrary, in the summer period the redox transition depth in sediment at station S1 (August 2001) was between 7 and 8 cm depth, deeper than at stations S2 and S3 (Fig. 3). These results are not in accordance with literature data (ALLER, 1980, 1994; KLUMP & MARTENS, 1981; JENSEN *et al.*, 1995) where redox transitions take place at different sediment depths depending on season, i.e. redox transition depths are generally closer to the sediment-water interface in summer than in the winter period.

Due to numerous factors which influence the seasonal variation of sediment redox potential (temperature, phytoplankton blooms followed by organic matter sedimentation, currents, bioturbation/bioirrigation) (ALLER, 1980, 1994; KLUMP & MARTENS, 1981; JENSEN *et al.*, 1995) we suppose that negative E_H and shallow redox transition depths at station S1 in the winter period are a consequence of intensive plankton blooms. According to long term investigations of primary production and chl *a* concentration, winter blooms at the Kaštela Bay station are usual (NINČEVIĆ, pers. com.) and probably cause enhanced organic matter input to the sediment.

The influence of organic matter sedimentation on the redox potential of middle Adriatic sediment has been well documented for the Brač Channel area, where a new sewage outlet for the town of Split was constructed and activated in September 2004. Redox potentials in sediment were monitored at station S4 (located approximately 100 meters from the wastewater outlet) during the period from 2002 to 2007. E_H values for the surface sediment layer (0.5 - 1 cm depth) at station S4 are shown in Fig. 4.

Prior to the outlet's activation, E_H was mostly positive with one short period of slightly negative values in June 2003, which is probably part of the natural E_H oscillation. However, after the wastewater system's activation, from 2005 to 2007 the redox potential of the surface sediment layer constantly decreased from positive to negative values. We suppose that the observed negative trend is a direct consequence of wastewater discharge at this station. Considering the mechanical filtration of the wastewater effluent prior to discharge, the main impact to the marine environment occurs through dissolved inorganic and organic matter which can explain the observed delay in sediment response to anthropogenic input.

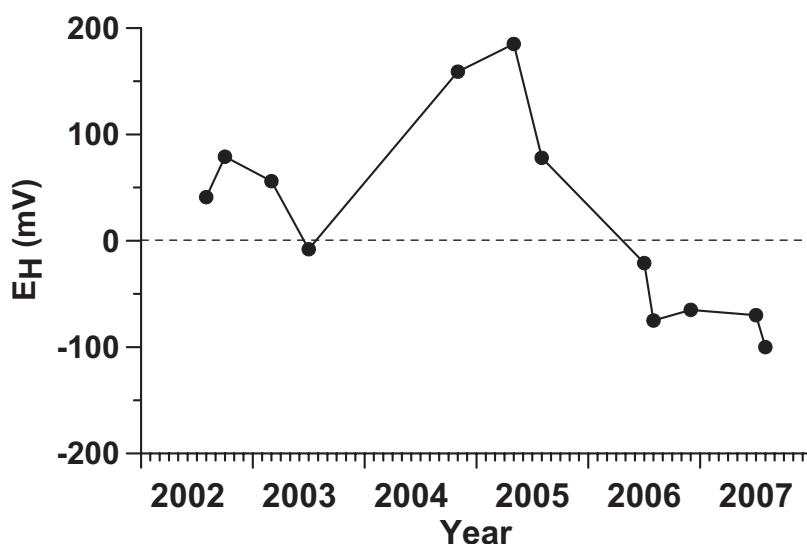


Fig. 4. Sediment redox potential in surface sediment layer (0.5-1 cm) at station S4 located near wastewater outlet in the central Adriatic area during monitoring periods (2002-2007)

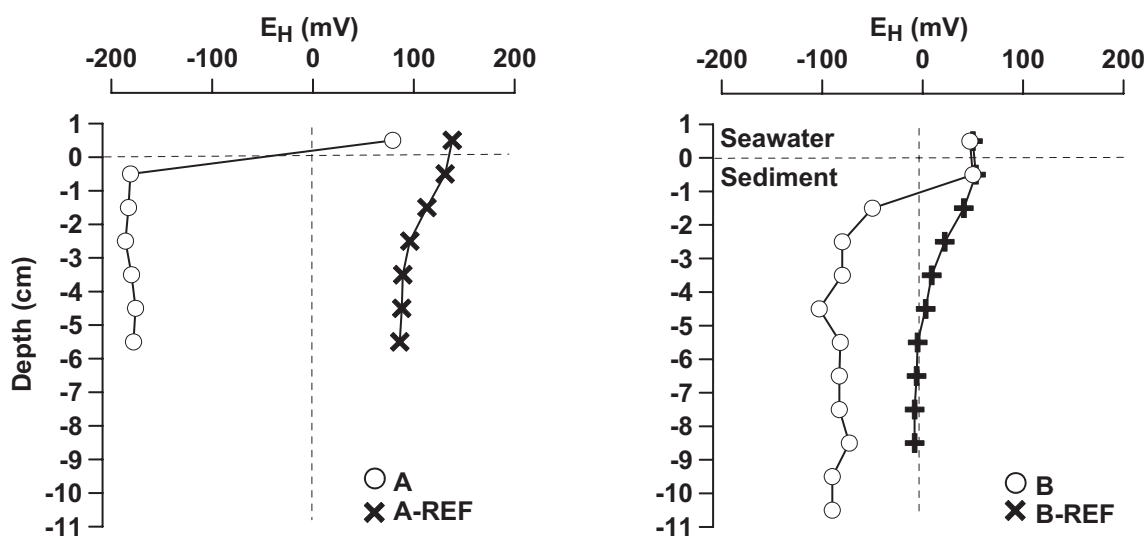


Fig. 5. Sediment redox potential measured at tuna farm station A (under the cage), A-REF (station 500 m distant from the cage) versus sediment E_H at sea bass and sea bream farm station B (under the cage) and at B-REF (station 500 m distant from the cage)

Another example of enhanced productivity and sedimentation are fish farms in the middle Adriatic area. E_H measurements in sediments at most of the fish farms showed more negative values in sediment under the cages than at unaffected reference stations. Shallow redox transition depths (0.5 - 1 cm) indicate higher organic matter input into sediment originating from settled fish food remains and excretory metabolic products.

The lowest redox potential was measured in sediment under the cage at tuna farm A (from -180 to -186 mV) while sediments beneath sea bass and sea bream farm B showed less negative values (from -50 to -103 mV) (Fig. 5). These extremes are in accordance with increased values for other parameters measured in sediment and the water column such as the increase of sediment total nitrogen and organic carbon content, inorganic sediment phosphorus concentration and orthophosphate concentration in the bottom layer of the water column (MATIJEVIĆ *et al.*, 2006).

Although the findings presented herein indicate a strong relationship between organic matter sedimentation and sediment redox potential state, basic statistical analysis of

biotic parameters in the water column (chl *a* concentration, primary production) and E_H for stations S1, S2 and S3 showed no significant correlations (MATIJEVIĆ, 2006). The influence of abiotic parameters (bottom layer temperature, oxygen and nutrient concentrations) on E_H in the sediment surface layer (0.5 - 1 cm depth) was also examined at the investigated stations through basic statistical analysis and significant correlations were found only at station S1 for the bottom layer temperature ($R=0.67$, $p<0.05$) and oxygen concentration ($R=-0.77$, $p<0.05$). The correlations established here do not agree with literature data finding the redox potential state more positive at lower temperatures and higher oxygen supply for organic matter degradation (ALLER, 1980, 1994; KLUMP & MARTENS, 1981; JENSEN *et al.*, 1995). Temporal changes of biotic and abiotic parameters used for correlation analysis for station S1 are presented in Fig. 6.

Excluding the lack of statistically significant correlations between E_H and nutrient concentrations (inorganic and organic nitrogen and phosphorus species) at stations S1, S2 and S3, the occurrence of enhanced concentrations of orthophosphate in the bottom water layer

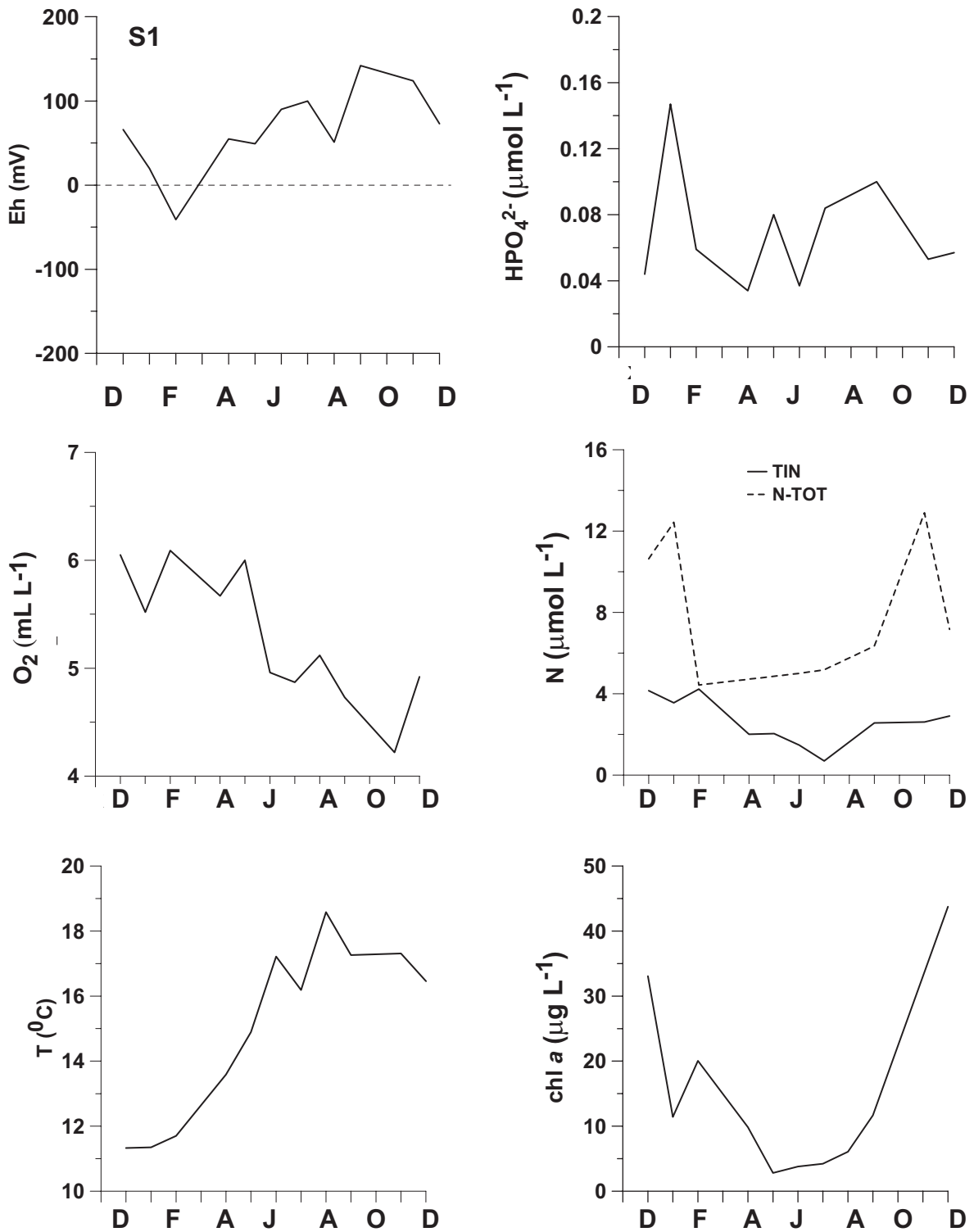


Fig. 6. Temporal changes of sediment redox potential in surface sediment layer (0.5-1 cm) at S1 station during the 2001/2002 period and parameters measured in the bottom layer of the water column (oxygen concentration, temperature, orthophosphate, total and inorganic nitrogen concentrations) and chl a concentrations

above anoxic tuna farm sediment (MATIJEVIĆ *et al.*, 2006) points to an impact of the sediment redox conditions on the phosphorus sediment flux at the sediment-water interface.

Investigations of sediment vertical profiles of phosphorus species bound to iron oxides and hydroxides (P-Fe) and E_H at station C under the tuna cage showed that the P-Fe abrupt decrease (2-3 cm) exactly matched the redox potential transition depth (Fig. 7). That is probably a consequence of orthophosphate desorption from P-Fe species into sediment pore water. Confirmation of this may be seen in the vertical profiles of the Fe(III)OOH / P-Fe ratio for the same station which is the inverse of the P-Fe profile as a result of a decrease of the Fe^{3+} form (Fig. 7).

According to the literature, adsorption and desorption of orthophosphate from iron oxyhydroxides in sediment is the main factor controlling the orthophosphate flux at the sediment/water interface (JENSEN *et al.*, 1995). Releasing or binding of orthophosphate at the surfaces of iron oxyhydroxides depends on the pH value and redox potential state (STUMM & MORGAN, 1996; GOMEZ *et al.*, 1999). According to experiments obtained under anoxic conditions in the sediment of Méjean Lagoon (GOMEZ, 1999), reduction of Fe^{3+} to Fe^{2+} with orthophos-

phate being released occurred at redox potential values between +100 and -50 mV at pH = 7, at -100 mV at pH = 8 and at $E_H = -150$ mV at pH = 9.

CONCLUSIONS

Laboratory E_H measurements in a seawater model solution showed that redox potential, determined by Pt electrode, is strongly affected by sulphide ions while the influence of ammonium salts and dissolved atmospheric oxygen was not established. This implies that redox potential measured using a Pt electrode in seawater or sediment pore water describes sulphide concentrations in these environments rather than their oxic or anoxic status.

Field measurements in sediments at open sea and channel stations in the middle Adriatic showed positive redox values (+150 to 0 mV) for most part of the year, probably as a consequence of low to medium organic matter sedimentation rates in this generally oligotrophic part of the Adriatic.

At stations with occasionally or permanently higher sedimentation rates (the Kaštela Bay station after a winter plankton bloom, the near shore station exposed to a sewage outlet and the fish farming stations) negative E_H val-

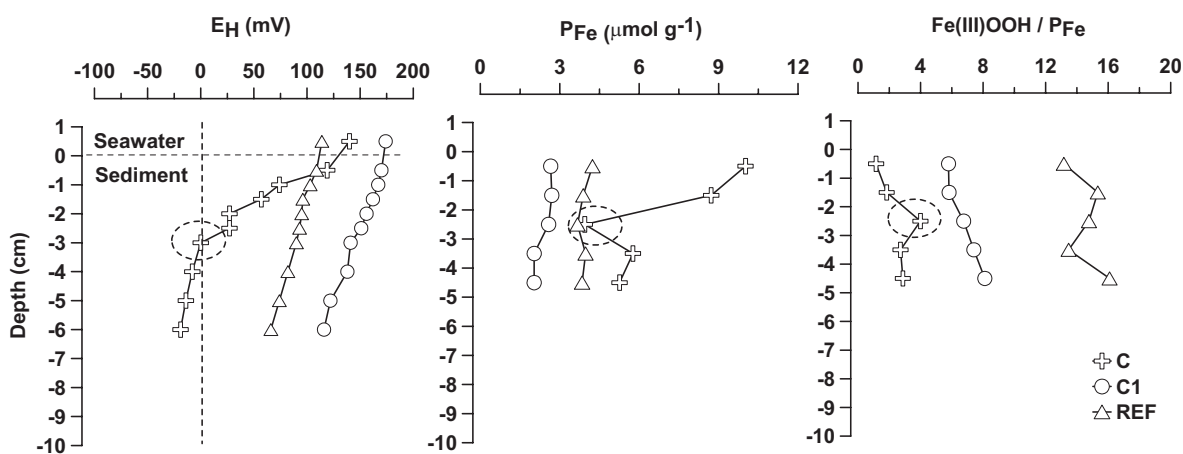


Fig. 7. Sediment vertical profiles of redox potential, sediment P-Fe concentration and Fe(III)OOH / P-Fe ratio at tuna farm station C (under the cage), C1 (station 200 m distant from the cage) and REF (station 500 m distant from the cage) in January 2005

ues (presence of sulphide and appearance of anoxic conditions in sediment) and shallower redox transition depths were found.

Statistical analysis of redox potential and various biotic (chl *a* concentration and primary production in the water column) and abiotic (temperature, oxygen and nutrient concentration) parameters showed a significant correlation only between E_H and bottom layer temperature and oxygen at the Kaštela Bay station. This indicates the possible additional influence

of other parameters on the redox potential such as sediment organic matter molecular structure, bioturbation or bioirrigation processes and sea currents influence which were not examined for this area.

Investigation of vertical profiles of sediment E_H , iron-bound phosphorus concentration and Fe(III)OOH concentration at the middle Adriatic tuna farm indicated a relationship between redox potential and phosphate adsorption/desorption processes.

REFERENCES

- ALLER, R.C. 1980. Quantifying solute distributions in the bioturbated zone of marine sediments by defining an average microenvironment. *Geochim. Cosmochim. Acta*, 44: 1955-1965.
- ALLER, R.C. 1994. Bioturbation and remineralization of sedimentary organic matter: effects of redox oscillation. *Chem. Geol.*, 114: 331-345.
- ANSHUTZ, P., S. ZHONG & B. SUNDBY. 1998. Burial efficiency of phosphorus and the geochemistry of iron in continental margin sediments. *Limnol. Oceanogr.*, 43: 53-64.
- ARCHER, D.E. & A.H. DEVOL. 1992. Benthic oxygen fluxes on the Washington shelf and slope. A comparison of *in situ* microelectrode and chamber flux measurements. *Limnol. Oceanogr.*, 37: 614-629.
- AZZONI, R. G., GIORDANI & P. VIAROLI. 2005. Iron-sulphur-phosphorus interactions: implications for sediment buffering capacity in a Mediterranean eutrophic lagoon (Sacca di Goro, Italy). *Hydrobiologia*, 550: 131-148.
- BENITEZ-NELSON, C. 2000. The biogeochemical cycling of phosphorus in marine systems. *Earth Sci. Rev.*, 51: 109-135.
- BERNER, R.A. 1963. Electrode studies of hydrogen sulfide in marine sediments. *Geochim. Cosmochim. Acta*, 27: 563-575.
- BERNER, R.A. 1981. A new geochemical classification of sedimentary environments. *J. Sediment. Petrol.*, 51: 359-365.
- BERNER, R.A. & S.D.E. CANFIELD. 1989. A new model for atmospheric oxygen over Phanerozoic time. *Am. J. Sci.*, 289: 333-361.
- BOGNER, D., S. MATIJEVIĆ, G. KUŠPILIĆ & A. BARIĆ. 2003. Utjecaj uzgajališta riba na sadržaj udjela organskog ugljika, ukupnog dušika i fosfora u morskom sedimentu (Impact of fish cage farming on presence of organic carbon, nitrogen and phosphorus in the sediment). 18th Congress of Croatian chemists and chemistry engineers, Proceedings, In: S. Zrnčević (Editor). Zagreb, Croatian Association of chemistry engineers and technologists, 272 pp.
- BOLDRIN, A., S. MISEROCCHI, S. RABITTI, M.M. TURCHETTO, V. BALBONI & G. SOCAL, 2002. Particulate matter in the southern Adriatic and Ionian Sea: characterisation and downward fluxes. *J. Mar. Syst.*, 33-34: 389-410.
- BRANDES, J.A. & A.H. DEVOL. 1995. Simultaneous nitrate and oxygen respiration in coastal sediments: Evidence for discrete diagenesis. *J. Mar. Res.*, 53: 771-797.
- CALACE, N., N. CARDELLICCHIO, B.M. PETRONIO, M. PIETRANTONIO & M. PIETROLETTI. 2006. Sedimentary humic substances in the northern Adriatic Sea (Mediterranean Sea). *Mar. Environ. Res.* 61: 40-58.
- CANCEMI, G., G. DE FALCO & G. PERGENT. 2003. Effects of organic matter input on a *Posidonia oceanica* meadow. *Est. Coast. Shelf Sci.*, 56: 961-968.
- CANFIELD, D.E., R. RAISWELL & S. BOTTRELL. 1992. The reactivity of sedimentary iron minerals toward sulphide. *Am. J. Sci.*, 292: 659-683.
- CANFIELD, D.E., B.B. JØRGENSEN, H. FOSSING, R. GLUD, J. GUNDERSEN, N.B. RAMSING, H. THAMDRUP, J.W. HANSEN, L.P. NIELSEN & P.O.J. HALL. 1993. Pathways of organic carbon oxi-

- dition in three continental margin sediments. *Mar. Geol.*, 113: 27-40.
- COLMAN, A.S. & H.D. HOLLAND. 2000. The global diagenetic flux of phosphorus from marine sediments to the oceans, redox sensitivity and the control of atmospheric oxygen levels. *Marine Authigenesis: From Global to Microbial*, SEPM Special Publ. 66, pp. 53-75.
- COOPER, L.H.N. 1937. Oxidation-reduction potential in sea water. *J. Mar. Biol. Ass. U. K.* 22(1): 167-176.
- CULKIN, F. 1965. The major constituents of sea water. In: J.P. Riley & G. Skirrow (Editors). *Chemical Oceanography*. Acad. Press, London, Vol. 1, pp. 121-158.
- DE LANGE, G.J. 1986.a Early diagenetic reactions in interbedded pelagic and turbidic sediments in the Nares Abyssal Plain (western North Atlantic): consequences for the composition of sediment and interstitial water. *Geochim. Cosmochim. Acta*, 50: 2543-2561.
- DE LANGE, G. J. 1986.b Chemical composition of interstitial water in cores from the Nares Abyssal Plain (Western North Atlantic). *Oceanol. Acta*, 9: 159-168.
- FOLK, R. L. 1954. The distinction between grain size and mineral composition in sedimentary rock nomenclature. *J. Geol.* 62: 344-356.
- FROELICH, P. N., M.L. BENDER, N.A. LUEDTKE, G.R. HEATH & T. DE VRIES. 1982. The marine phosphorus cycle. *Am. J. Sci.*, 282: 474-511.
- FROELICH, P.N., M.A. ARTHUR, W.C. BURNETT, M. DEAKIN, V. HENSLEY, R. JAHNKE, L. KAUL, , K.H. KIM, K. ROE, A. SOUTAR & C. VATHAKANON. 1988. Early diagenesis of organic matter in Peru continental margin sediments: phosphorite precipitation. *Mar. Geol.*, 80: 309-343.
- GIORDANI, P. W. HELDER, E. KONING, S. MISEROCCHI, R. DANOWARO & A. MALAGUTI, 2002. Gradients of benthic-pelagic coupling and carbon budgets in the Adriatic and Northern Ionian Sea. *J. Mar. Syst.*, 33-34: 365-387.
- GOMEZ, E., C. DURILLON, G. ROFES & B. PICOT. 1999. Phosphate adsorption and release from sediments of brackish lagoons: pH, O₂ and loading influence. *Water Res.*, 33: 2437-2447.
- GRASSHOF, K. 1976. *Methods of seawater analysis*. Verlag Chemie, Weinheim, 307 pp.
- GRENTHE, I., W. STUMM, M. LAAKSUHARJU, A.-C. NILSSON & P. WIKBERG. 1992. Redox potentials and redox reactions in deep groundwater systems. *Chem. Geol.*, 98: 131-150.
- HARTMANN HANSEN, M., K. INGVOSEN & B.B. JORGENSEN. 1978. Mechanisms of hydrogen sulphate release from coastal marine sediments to the atmosphere, *Limnol. Oceanogr.*, 23: 68-76.
- HOSTETTLER, J. D. 1984. Electrode electrons, aqueous electrons and redox potentials in natural waters. *Am. J. Sci.*, 284: 734-759.
- JENSEN, H.S., P.B. MORTENSEN, F.Ø. ANDERSEN, E.K. RASMUSSEN, & A. JENSEN. 1995. Phosphorus cycling in coastal marine sediment. *Limnol. Oceanogr.*, 40: 908-917.
- KALANTZI, I. & I. KARAKASSIS. 2006. Benthic impacts of fish farming: Meta-analysis of community and geochemical data. *Mar. Pollut. Bull.*, 52: 484-493.
- KARAKASSIS I., M.TSAPAKIS & E.HATZIYANNI. 1998. Seasonal variability in sediment profiles beneath fish farm cages in the Mediterranean. *Mar. Ecol. Prog. Ser.* 162: 243-252.
- KARAKASSIS I., E.HATZIYANNI, M.TSAPAKIS & W. PLAITI. 1999. Benthic recovery following cessation of fish farming: a series of successes and catastrophes. *Mar. Ecol. Prog. Ser.*, 184: 205-218.
- KARAKASSIS I., M.TSAPAKIS, E.HATZIYANNI, K. N. PAPADOPOULOU. & W. PLAITI. 2000. Impact of cage farming of fish on the seabed in three Mediterranean coastal areas. *ICES J. Mar. Sci.*, 57: 1462-1471.
- KLUMP, J. V. & MARTENS, C. S. 1981. Biogeochemical cycling in an organic rich coastal marine basin-II. Nutrient sediment-water exchange processes. *Geochim. Cosmochim. Acta*, 45: 101-121.
- KÖLLING, M. 1986. Vergleich verschiedener Methoden zur Bestimmung des Redoxpotentials natürlicher Wässer (Comparison of different methods for determination of redox potentials in natural waters). *Meyniana*, 38: 1-19.
- KÖLLING, M. 2000. Comparison of different Methods for Redox Potential Determination in Natural Waters. In: J. Schüring, H.D. Schulz,

- W.R. Fischer, J. Böttcher, W.H.M. Duijnsveld (Editors). Redox - Fundamentals, Processes and Applications. Springer, Berlin/Heidelberg, pp. 42-54.
- KUŠPILIĆ G. & A. BARIĆ. 1996. Polarographic determining of sulphureous compounds in interstitial water of sea sediment. *Hrv. Vode*, 16: 181-187.
- KUŠPILIĆ, G. 2001. Flux of nitrogen, phosphorus and silicate between the sea water / sediment boundary in the onshore and offshore waters of the middle and south Adriatic. Ph. D. Thesis, University of Zagreb, 91 pp.
- KUŠPILIĆ, G. S. MATIJEVIĆ & B. ANTOLIĆ. 2002. Ekološke posljedice kaveznog uzgoja tuna u srednjem Jadranu (Ecological effects of the cage reared tuna in the middle Adriatic Sea). The 1st Croatian conference on ecological engineering. In: N. Koprivanac (Editor). Zagreb, Hrvatsko društvo kemijskih inženjera i tehnologa i Hrvatski inženjerski savez (Croatian Association of chemistry engineers and technologists and Croatian engineer association), p. 109.
- LISS, P.S., J.R. HERRING, & E.D. GOLDBERG. 1973. The iodide/iodate system in seawater as a possible measure of redox potential. *Nature*, 242: 108-109
- MARBÁ, N. & C.M. DUARTE. 2001. Growth and sediment occupation by seagrass *Cymodocea nodosa* roots. *Mar. Ecol. Prog. Ser.*, 224: 291-298.
- MATIJEVIĆ, S., D. BOGNER, G. KUŠPILIĆ & A. BARIĆ. 2003. Utjecaj rada uzgajališta tuna na fizikalno-kemijske karakteristike sedimenta i pridnenog sloja vodenog stupca (Impact of tuna fish farms on physical and chemical sediment characteristics and bottom water column). Proceedings of the 18th Meeting of Croatian chemists and chemistry engineers. In: S. Zrnčević (Editor). Zagreb, Hrvatsko društvo kemijskih inženjera i tehnologa, p. 271.
- MATIJEVIĆ, S., G. KUŠPILIĆ, D. BOGNER & A. BARIĆ. 2004. Fish farming influence on physical and chemical properties of sediment and water column in the middle Adriatic. *Rapport du 37e Congres de la CIESM (0373-434X)* 37: p. 222.
- MATIJEVIĆ, S., G. KUŠPILIĆ & A. BARIĆ. 2006. Impact of a fish farm on physical and chemical properties of sediment and water column in the middle Adriatic Sea. *Fresenius Environ. Bull.*, 15(9): 1058-1063.
- MATIJEVIĆ, S. 2006. Distribution of chemical phosphorus species in the middle Adriatic sediment. Ph. D. Thesis, University of Zagreb, 123 pp.
- MORSE, J.W. & J. MORIN. 2005. Ammonium interaction with coastal marine sediments: influence of redox conditions on K^* . *Mar. Chem.*, 95: 107-112.
- PAYTAN, A., B.J. CADE-MEHUN, K. MCLAUGHLIN, & K.L. FAUL. 2003. Selective phosphorus regeneration of sinking marine particles: evidence from ^{31}P -NMR. *Mar. Chem.*, 82: 55-70.
- PORELLO, S., P. TOMASSETTI, L. MANZUETO, M. G. FINOIA, E. PERSIA, I. MERCATALI & P. STIPA. 2005. The influence of marine cages on the sediment chemistry in the Western Mediterranean Sea. *Aquaculture* 249: 145-158.
- RIOS-MENDOZA, L.M., J.V. MACIAS-ZAMORA & A.R. ZIRINO-WEISS. 2003. Iridium: an option for measurement of the redox potential. *Sci. Mar.*, 29(4): 509-520.
- RISGAARD-PETERSEN, N., L.P. NIELSEN, L.P. RYSGAARD, T. GALSGAARD & R.L. MEYER. 2003. Application of the isotope pairing technique in sediments where anammox and denitrification coexist. *Limnol. Oceanogr., Methods* 1: 63-73.
- RUTTENBERG, K.C. 1992. Development of a sequential extraction technique for different forms of phosphorus in marine sediments. *Limnol. Oceanogr.*, 37: 1460-1482.
- SCHENAU, S.J. & G.J. DE LANGE. 2000. A novel chemical method to quantify fish-debris in marine sediments. *Limnol. Oceanogr.*, 45: 963-971.
- SHAW, T.J., E.R. SHOLKOVITZ & G. KLINKHAMMER. 1994. Redox dynamics in the Chesapeake Bay: The effect on sediment/water uranium exchange. *Geochim. Cosmochim. Acta*, 58(14): 2985-2995.

- STRICKLAND, J.D.H. & T.R. PARSONS. 1972. A practical handbook of seawater analysis. Bull. Fish. Res. Board Can. 167: 1-310.
- STUMM, W. 1978. What is the pE of the sea, *Thalassia Jugosl.*, 14(1/2): 197-208.
- STUMM, W. & J. J. MORGAN. 1996. Aquatic Chemistry. In: John Wiley & Sons (Editors). New York, 583 pp.
- SIGG, L. & W. STUMM. 1989. Aquatische Chemie, Verlag de Fachvereine, Zürich, 388 pp.
- TERRADOS, J., C.M. DUARTE, L. KAMP-NIELSEN, N.S. R. AGAWIN, E. GACIA, D. LACAP, M.D. FORTES, J. BORUM, M. LUBANSKI & T. GREVE. 1999. Are seagrass growth constrained by the reducing conditions of the sediment? *Aquat. Bot.*, 65: 175-197.
- WHITFIELD, M. 1974. Thermodynamic limitations on the use of the platinum electrode in Eh measurements, *Limnol. Oceanogr.* 19: 857-865.
- VDOVIĆ, N., J. BIŠČAN & M. JURAČIĆ. 1991. Relationship between specific surface area and some chemical and physical properties of particulates: study in the Northern Adriatic. *Mar. Chem.*, 36: 317-328.

Received: 7 September 2007

Accepted: 12 November 2007

Redox potencijal sedimenta na području srednjeg Jadrana

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SAŽETAK

U ovom su radu prikazani rezultati istraživanja redoks potencijala (E_H) u sedimentu postaja različitog trofičkog stupnja u području srednjeg Jadrana. U većem su dijelu godine E_H vrijednosti za postaju u kanalu i postaju otvorenog mora bile pozitivne (od +150 do 0 mV) i do 10 cm dubine sedimenta. Pozitivni E_H (odsutnost redukcije sulfata sa vrlo malim koncentracijama sulfida) u sedimentu ovih postaja je vjerojatno uzrokovan niskom do srednjom brzinom sedimentacije organske tvari. Negativni E_H (prisutnost sulfida i pojave anoksičnih uvjeta u sedimentu) i plitke dubine redoks prijelaza u sedimentu su nađene u područjima visoke produktivnosti i sedimentacije organske tvari kao što su: eutrofizirani Kaštelanski zaljev nakon zimskog cvata planktona, priobalna postaja u blizini podmorskog kanalizacijskog ispusta, te postaje smještene ispod kaveza za uzgoj ribe. Vertikalni profili E_H , koncentracije fosfora vezanog na željezo u sedimentu (P-Fe), kao i koncentracije Fe(III)OOH u sedimentu ispitivani na uzgajalištu tuna u srednjem Jadranu upućuju na povezanost redoks potencijala i procesa adsorpcije ili desorpcije ortofosfata u pornoj vodi sedimenta.

Ključne riječi: sediment, redox potencijal, organska tvar, srednji Jadran