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Late spring characterization of different coastal areas of the Adriatic Sea

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The objective of this study is to analyze the physical and chemical characteristics of three coastal zones of the Adriatic Sea during late spring, and to identify similarities and differences among the zones. The trophic status of the Southeastern Adriatic-Sea, dominated by the discharge from the Buna/Bojana river delta watersheds, is compared with two other Adriatic regions: the Northwestern Adriatic Sea and the Southwestern Adriatic Sea (Gulf of Manfredonia); the first is dominated by the Po River freshwater discharge and the second is one of the most productive areas of the Southwestern Adriatic.

The areas are influenced by two main Adriatic surface currents: the Eastern Adriatic Current (EAC) that flows north-westward, and the Western Adriatic Current (WAC) that flows south-eastward. The measurements of temperature, salinity, fluorescence, oxygen, nutrients and chlorophyll a in the three areas were collected and compared.

The areas showed similar physical and bio-chemical characteristics, despite the Northern Adriatic is impacted by the Po River runoff and the WAC carries out along the Western Adriatic water rich of nutrients from the northern Italian rivers. The area affected by the Po River discharge showed maximum chlorophyll and nitrogen concentrations within the river plume. Moreover, the Southwestern Adriatic Sea showed a load of nutrients and organic matter connected to substances coming from the northern Italian rivers (mainly the Po River). Similarly, in the Southeastern Adriatic-Sea, the Buna/Bojana River discharge contained relatively high values in the regional chlorophyll distribution. The three areas are directly or indirectly linked to river plume dynamics and the associated inorganic and organic inputs determine the trophic state of the areas. In particular, the Southeastern Adriatic Sea was a meso-eutrophic area; despite the most eastern side of the Adriatic was an oligotrophic basin.

Key words: dissolved nutrients, chlorophyll *a*, CDOM, river discharge, Redfield ratio, Adriatic Sea

INTRODUCTION

The quality of coastal waters is a very important and sensitive issue (RYTHER & DUNSTAN,1971; SMITH *et al.*, 2006). The chemical, physical and biological processes occurring in coastal zones can modify the marine ecosystem conditions (CAMPANELLI *et al.*, 2004, BOLDRIN *et al.*, 2009). The enrichment of water with nutrients (primarily nitrogen, silicon and phosphorus compounds) may result in the growth of algal biomass (BERNARDI AUBRY *et al.*, 2004). In particular, light and nutrient levels in the surface layer are sufficient to sustain active phytoplankton growth in similar basins (GALLEGOS & JORDAN, 1997; MCKEE *et al.*, 2002). In the Adriatic Sea, nutrient inputs come from the large surface runoff catchments, from underground water discharges, from direct urban discharges and from Aeolian inputs (CAMPANELLI *et al.*, 2011). Furthermore, the Coloured Dissolved Organic Matter (CDOM) regulates the penetration of UV light in the sea and mediates photochemical reactions; therefore it plays an important role in many biogeochemical processes on the ocean surface including primary productivity and the air-sea exchange of trace gases (MOPPER *et al.*, 1991; ARRIGO & BROWN, 1996; ZEPP *et al.*, 1998; TOOLE & SIEGEL, 2004). In fact, the absorption of blue light by CDOM overlaps the phytoplankton absorption peak near 440 nm, resulting in a competition between CDOM and phytoplankton for light in this region of the visible spectrum (WRIGLEY *et al.*, 1988; DAVIES-COLLEY, 1992; KIRK, 1994). An estimate concerning the contribution of CDOM to total Dissolved Organic Carbon (DOC) in the ocean ranges from 20% to 70% (LAANE & KOOLE, 1982) with highest values in coastal regions, where river inputs are dominant. CDOM is a useful tracer not only for carbon but also as a proxy for mixing in a wide variety of environment (COBLE *et al.* 2008).

FERREIRA *et al.* (2011) described different methods to classify the trophic states of the Mediterranean Sea. Often the regions of the ocean are classified as oligotrophic (<0.1 μgChl l^{-1}), mesotrophic (0.1-1 μgChl l^{-1}), or eutropic (>1 μgChl l^{-1}) with satellite-based ocean colour measurements of chlorophyll concentration (IOCCG, 2003). Furthermore, the Mediterranean sea is defined as oligotrophic (<0.5 μgChl l^{-1}), mesotrophic (0.5-1 μgChl l^{-1}), or eutropic (>1 μgChl l^{-1}) with measurements of chlorophyll *a* concentration (IGNATIADES, 2005). Based on these classifications the Adriatic Sea contains three eutrophic regions: the coastal region off the delta of the Po River extending southward along the western coastal region, the Gulf of Manfredonia located in the southern coastal Adriatic along the western side, and the third area in the Southeastern Adriatic Sea, along the coasts of Montenegro and Albania. The extension of these eutrophic regions can vary throughout seasons and years, depending on many environmental factors such as, for example, river discharges, atmospheric conditions, currents regime and seasonality (FISHER *et al.*, 1992; GALLEGOS & JORDAN, 1997).

The Northern and Western Adriatic Seas are clearly more influenced by river floods (MARINI *et al.*, 2002; CAMPANELLI *et al.*, 2011, GIANI *et al.*, 2012; DJAKOVAC *et al.*, 2012) and affect both the circulation through buoyancy input and the ecosystem by introducing a large amount of nutrients (DEGOBBIS *et al.*, 2000; MARINI *et al.*, 2008). The Po River provides the major buoyancy flux with an annual mean freshwater discharge rate of 1500 $m^3 s^{-1}$ (RAICICH, 1996; COZZI & GIANI, 2011). The riverine waters discharging into the Northern Adriatic form a buoyant layer that typically flows southward along the Italian coasts and is constrained close to the coast over the continental shelf, more than 50 meters deep (POULAIN & CUSHMAN-ROISIN, 2001; POULAIN *et al.*, 2001). The southward coastal flow, the Western Adriatic Current (WAC; GAČIĆ *et al.*, 1986; ZORE-ARMANDA & GAČIĆ, 1987; ARTEGIANI *et al.*, 1997a, b), is driven by the Po River buoyancy flux (low-salinity waters) and North-eastern Bora winds that characterize the region during the winter months. Bora winds causes elevated sea surface height along the western coasts, producing downwelling and the transport of coastal dense waters toward the open sea (BOLDRIN *et al.*, 2009). Runoff is also responsible for making the Adriatic a dilution basin. Eutrophication, which periodically occurs along the Italian coast of the Adriatic Sea (REVELANTE & GILMARTIN, 1976; BULJAN & ZORE-ARMANDA, 1976, SOCAL *et al.* 2008, MARINI *et al.* 2010), is mainly caused by the discharge of nutrients from the Po River. This occurs especially when the river floods. However, it can also be due to particular climatic conditions or it can occur when wind and currents push the river's waters (which normally flow out into the sea where they are then dispersed) toward the coast (CACCIAMANI *et al.*, 1992).

The Southern Adriatic Sea extends approximately from the Pelagosa sill to the Otranto Strait (ARTEGIANI *et al.*, 1997a). It is characterized by a wide depression, more than 1200 m deep, and exchanges water with the Mediterranean Sea through the Otranto Strait where the sill depth is about 800 m. The general circulation of the Southern Adriatic Sea is characterized by two coastal currents of surface waters flowing from the North along the western side and from the South along the eastern side (MANCA *et al.*, 2002; MARINI *et al.*, 2010). The WAC transports relatively fresh water along the western boundary from the North Adriatic, one of the most productive areas of the Mediterranean (CAMPANELLI *et al.*, 2011). The Gulf of Manfredonia (South-western Adriatic Sea) is located in a transition zone between the Northern and Southern Adriatic circulation. Inside the gulf, the circulation is mainly affected by winds - mainly N-NW and S-SE directions - that generate cyclonic and anticyclonic gyres (BURRAGE *et al.*, 2009). The gulf is located in a sheltered area characterized by eutrophic water (CHIAUDANI *et al.*, 1982; DAMIANI *et al.*, 1988. FOCARDI *et al.*, 2009) compared to the ones at lower concentration of nutrients in the Southward area (BELLO *et al.*, 1982; CHIAUDANI *et al.*, 1982). The biochemical and hydrological characteristics of the gulf are affected by coastal morphology, land inputs and Adriatic general circulation. In contrast with the Northern Adriatic Sea, river discharges are not abundant. The main river flowing into the gulf is the Ofanto with an average flow of 13.9 m^3s^{-1} (SIMEONI, 1992). Other minor rivers that flow into the gulf are torrent-like and practically dry in summer. The gulf of Manfredonia can be considered a complex area under the potential threats of various wastes mainly deriving from urban and agricultural activities (FIESOLETTI *et al.*, 2005).

The current along the Eastern coast (SEAd-SouthEastern Adriatic current) comes from the central Mediterranean Sea (Ionian Sea), one of most oligotrophic areas in the world (YACOBI *et al.*, 1995), and it transports the Ionian Surface Water (ISW) along the eastern boundary northward into the Adriatic Sea. Such water masses have different features, as the Adriatic surface waters show lower salinity and higher nutrient concentrations, whereas the Ionian surface waters are saltier, warmer and poorer in nutrients (FONDA-UMANI, 1992; ZAVATARELLI *et al.*, 1998, ZORE-ARMANDA *et al.*, 1999; MARINI *et al.*, 2008). As a consequence, the South Adriatic Sea is distinctly oligotrophic, except for the Italian coastal areas affected by the nutrient-rich waters descending southward (ORLIC *et al.*, 1992). However, MARINI *et al.* (2010) show how the Eastern coastal side (Montenegrin and Albanian areas) presents eutrophic waters as well. In the Southeastern Adriatic Sea, in addition to the flow from the Buna/Bojana River, several additional rivers contribute to the freshwater flux including the Drini, Mati, Ishimi, Erzeni, Shkumbini, Semani and Vjosa Rivers. The Buna/Bojana River has the largest single discharge (about 700 m^3 s^{-1}) and the combined discharge of all of the Albanian rivers is about 1250 m^3 s^{-1} (UNEP, 1996). The Buna/Bojana River is the South Eastern Adriatic counterpart to the Po River in the Northwestern Adriatic. Several of the coastal plumes from the Albanian and Montenegrin rivers are readily distinguished in the chlorophyll satellite image, but the largest chlorophyll feature is off the Buna/Bojana delta.

The goal of this study is to characterize the trophic states that occur along the South Eastern coastal region of Albania and Montenegro (SEAM) and compare them with the South Western and North Western Adriatic Seas (SWAd and NWAd) in order to understand the similarities and/or differences between the physical and bio-chemical regimes of the three areas and how these features could affect the trophic states. Whilst there are many studies regarding the trophic characterization in NWAd, only a few works analyse these processes in SWAd and SEAM. Poor data are available regarding physical and bio-chemical features (i.e. chlorophylls and Redfield ratio). In particular, simultaneous observations for the three regions do not exist yet.

This study analyses the physical-chemical characteristics only during late spring (ARTEGIANI *et al.*, 1997a) since the coastal areas during this period are generally characterized by phytoplankton growth and by a high load of nutrients carried from river discharge that could trigger local eutrophication processes (D'ELIA *et al.*, 1986; CLOERN, 1987; FISHER *et al.*, 1992; PENNOCK & SHARP, 1994; GALLEGOS & JORDAN, 1997).

A better knowledge of the physical-chemical characteristics of these areas could be useful enabling the countries to assess the coastal zones in order to apply the Marine Strategy Frameworks Directive (MSFD-2008/56/EC) and reach the Good Environment Status (GES) by 2020.

MATERIALS AND METHODS

The authors used satellite maps from NASA (available at http://reason.gsfc.nasa.gov/Giovanni) and observations *in situ* to analyse physical and chemical characteristics of the North Western, South Western and South Eastern zones of the Adriatic Sea. The characteristics include salinity, temperature, fluorescence, oxygen saturation, concentrations of Dissolved Inorganic Nitrogen (DIN), orthophosphate, orthosilicate, Colored Dissolved Organic Matter (CDOM) and chlorophyll *a*. This evidences eutrophication occurrence along the mentioned three coastal zones. The Redfield ratio was used to characterize the three coastal zones.

Data for this study were collected during the three oceanographic cruises in the Northern and Southern Adriatic Seas (Fig 1). The first cruise was conducted in the North Adriatic aboard the R/V Knorr (Woods Hole Oceanographic Institution-USA) from 25th May to 15th June 2003; the second and third oceanographic cruises were

Fig. 1. Study area showing Po River basin (North Western Adriatic-NWAd), Gulf of Manfredonia (South Western Adriatic-SWAd), and Gulf of Drini (South Eastern Adriatic-SEAM; red squares).

conducted aboard the R/V Dallaporta (CNR, Italy) in the Southeastern Adriatic Sea (from 24th June to 29th June 2008) and the Southwestern Adriatic Sea (from 8th June –to 14th June 2009).

During the cruises, n. 88 CTD (Conductivity Temperature Depth) casts and n. 354 water samples were collected and analyzed for nutrient concentration at suitable depths.

N. 78 samples of CDOM and n. 118 samples of chlorophyll *a* at the surface and 10 m deep were collected in the South Western and in the South Eastern Adriatic. Chlorophyll concentrations in the North Western Adriatic were already described by MARINI *et al.* (2008) for the same cruise.

The data were collected with a SeaBird Electronics SBE 911-plus CTD equipped with a SeaBird SBE43 oxygen sensor, SeaPoint turbidity sensor (Nephelometric Turbidity Unit-NTU), Wetlabs ECO-AFL fluorometer (R/V Knorr) and a SCUFA fluorometer on the R/V G. Dallaporta. The 24 Hz CTD data were processed according to UNESCO (1988) standards, and pressure-averaged to 0.5 db intervals. Water samples were obtained on the upcasts with a SeaBird Carousel rosette water sampler equipped with 10-L Niskin bottles. Nutrient water samples were filtered (GF/F Whatman, 25 mm, nominal pore size 0.7 µm) and stored at -22 °C in polyethylene vials. Nutrients (ammonium-NH_4, nitrite-NO_2, nitrate-NO_3, orthophosphate-PO_4 and orthosilicate-SiO_4) were analysed colorimetrically (IVANČIĆ & DEGOBBIS, 1984; PARSONS *et al.*, 1985). Absorbencies were measured with a Technicon TrAAcs 800 and with an AxFlow quAAtro AutoAnalyzers. Dissolved Inorganic Nitrogen (DIN) was calculated as the sum of NH_4, NO_2 and NO_3 concentrations.

In order to measure the CDOM absorption, water samples were filtered through 0.2 µm Nucleopore membrane filters, then stored in the dark under refrigeration (4° to 8° C) and analysed on board within 24 hours using a Perkin Elmer spectrophotometer 550A model (10 cm cuvette pathlength). Absorbance data were converted to absorption coefficient ($a_{CDOM}(\lambda)$) according to MITCHELL *et al.* (2003):

$$a_{CDOM}(\lambda) = (2.303/l)[AB_s(\lambda) - AB_{bs}(\lambda) - AB_{null}(\lambda)]$$

where l is the cuvette pathlength, $AB_s(\lambda)$ is the optical density of the filtrate sample relevant to purified water, $AB_{bs}(\lambda)$ is optical density of a purified water blank treated like a sample relevant to purified water, and $AB_{null}(\lambda)$ is the apparent residual optical density at a long visible or near infrared wavelength where absorption by dissolved material is assumed to be zero. Chlorophyll *a* was measured by filtering 3 l samples through 47 mm GF/F filters and immediately extracted with 5 ml of acetone at –22 °C. The analyses were carried out at the ISMAR-CNR laboratory with a Dionex UHPLC equipped with a UltiMate 3000 RS pump, a PDA100 Photodiode Array Detector (wavelength range: 190–800 nm), a RF 2000 Fluorescence Detector (wavelength range: 200-650nm), a C18 reversed phase column (4.6 mm x 150 mm, 3 µm particle size), an ACC3000 Auto sampler and a 100 µl sample injection loop. Cholorophyll *a* concentrations were determined using a modification of the procedure developed by WRIGHIT *et al.* (1991).

RESULTS AND DISCUSSION

Physical and chemical characteristics of three coastal zones

The monthly satellite maps of surface chlorophyll *a* from NASA (Fig. 2) are useful for a preliminary characterization of the areas during the periods studied. Figure 2 shows a strong front in the three areas, and the coastal chlorophyll *a* concentrations range between 0.3 and 10 µgChl l^{-1}. The NWAd shows maximum values (> 10 µgChl l^{-1}) of chlorophyll *a* concentrations compared to the other ones, and the area appears the widest.

In order to better characterize the areas, 37.5 isohaline is used to delineate the offshore ambient water from the along shore water influenced by rivers. Table 1 shows the correlations among the different parameters in the three areas. Table 2 summarizes the mean values and their standard deviations for the different water masses in the areas.

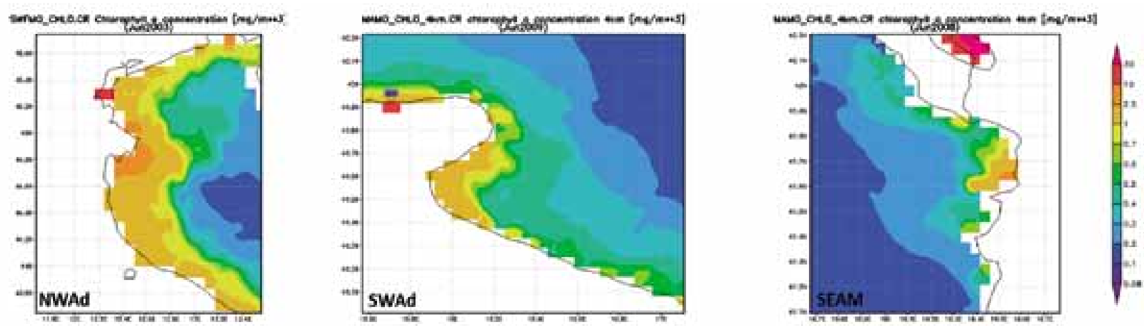

Fig. 2. SeaWiFS images of chlorophyll a concentration (provided by NASA) for the periods 1-30 June 2003, 1-30 June 2008 and 1-30 June 2009 showing the three sub-basins North Western Adriatic (NWAd), South Western Adriatic (SWAd) and South Eastern Adriatic (SEAM).

Table 1. Linear relationships among Salinity (S), Dissolved Inorganic Nitrogen (DIN), Ortosilicates (Si(OH)4), Chlorophyll a (Chl a), aCDOM440, Oxygen percentage saturation (O2%). The relationships are relative to the surface, to the bottom, to the S < 37.5 and to the S > 37.5 in the three sub-basin of the Adriatic Sea (South Eastern Adriatic-SEAM, South Western Adriatic-SWAd, and North Western Adriatic-NWAd). R^2 is the variance, n is the number of data used for the computation and P indicates the confidence level. The positive relationships are marked in bold characters. R indicates that the hypothesis of a linear relationship should be rejected at 5% confidence level.

	SEAM			SWAd			NWAd		
	All area	S<37.5	S>37.5	All area	S<37.5	S>37.5	All area	S<37.5	S>37.5
S vs DIN	R	R	R	R^2=0.62 n=60 P<0.001	R^2=0.74 n=43 P<0.001	R	R^2=0.20 n=39 P<0.001	R^2=0.36 n=28 P<0.001	R
S vs $Si(OH)_4$	R	R^2=0.31 n=38 P<0.001	**R^2=0.25 n=214 P<0.001**	R^2=0.19 n=60 P<0.001	R^2=0.18 n=41 P<0.005	R	**R^2=0.18 n=39 P<0.005**	R	**R^2=0.48 n=10 P=0.005**
S vs Chl *a*	R	R^2=0.53 n=38 P<0.001	R	R	R	R	R^2=0.59* n=18 P<0.001	R*	R*
S vs $a_{CDOM}440$ m^{-1}	R^2=0.18 n=50 P<0.001	R^2=0.46 n=21 P<0.001	R	R	R	R	----	----	----
S vs O_2 %	R	R	R	**R^2=0.48 n=58 P<0.001**	**R^2=0.18 n=41 P<0.005**	R	R^2=0.84 n=18 P<0.001	R^2=0.88 n=7 P<0.001	R
O^2% vs DIN	R	R^2=0.13 n=34 P<0.005	R	R^2=0.28 n=58 P<0.001	R^2=0.14 n=40 P<0.005	R	R	R	R
Chl a vs $a_{CDOM}440$ m^{-1}	R	**R^2=0.48 n=16 P<0.001**	R	R	R	R	----	----	----

* Chl *a* measured *in vivo* as fluorescence.

North Western Adriatic

The satellite image for the NWAd shows a strong color front along the Western boundary that separates the higher-chlorophyll coastal water from the more oligotrophic mid-basin and Eastern boundary Adriatic waters. Offshore the Po River's mouth, the surface layer is characterized by low salinity and high temperature (Fig. 3). The bottom layer was not shown because there are data only along a transect in front to Po mouth. POULAIN *et al.* (2001) show how the Po plume extended much more eastward in late spring than in winter due to the reduction of the vertical mixing. However, the plume extended southward along the Italian coast (MARINI *et al.*, 2008). The distribution of nutrient concentrations (Fig. 3) shows that, under well-defined stratification conditions, the DIN values are higher on the surface layer (10-12 µmol l^{-1}), where the lowest salinity is observed, and on the bottom of shallow stations, not shown. Also the chlorophyll *a* concentrations show higher values (10-15 µg l^{-1}, MARINI *et al.*, 2008) at the stations with lowest salinity. The orthosilicate distribution shows low concentrations in the surface layer (< 2 µmol l^{-1}) and high values on the bottom (Table 2). The distribution of orthosilicates does not appear controlled by river inputs. In particular, the highest values (>15 µmol l^{-1}) are observed where salinity is >38. In the fresher water of the Po plume (Salinity 31-35.) the nutrient concentrations are variable. The oxygen distribution (not shown) is influenced by river discharge and shows the higher saturation values (130-140 %) in the fresh water core of the plume. This feature is confirmed by a reverse correlation found between O_2 and salinity (Table 1).

The negative correlation found between DIN versus S<37.5 and positive between orthosilicate versus S>37.5 seems to confirm that the load of nitrogen is mainly controlled by river discharge, whilst the silicic is controlled by other processes such as sinking and mineralization. Moreover, in NWAd the column water stratification is high and separates the bottom

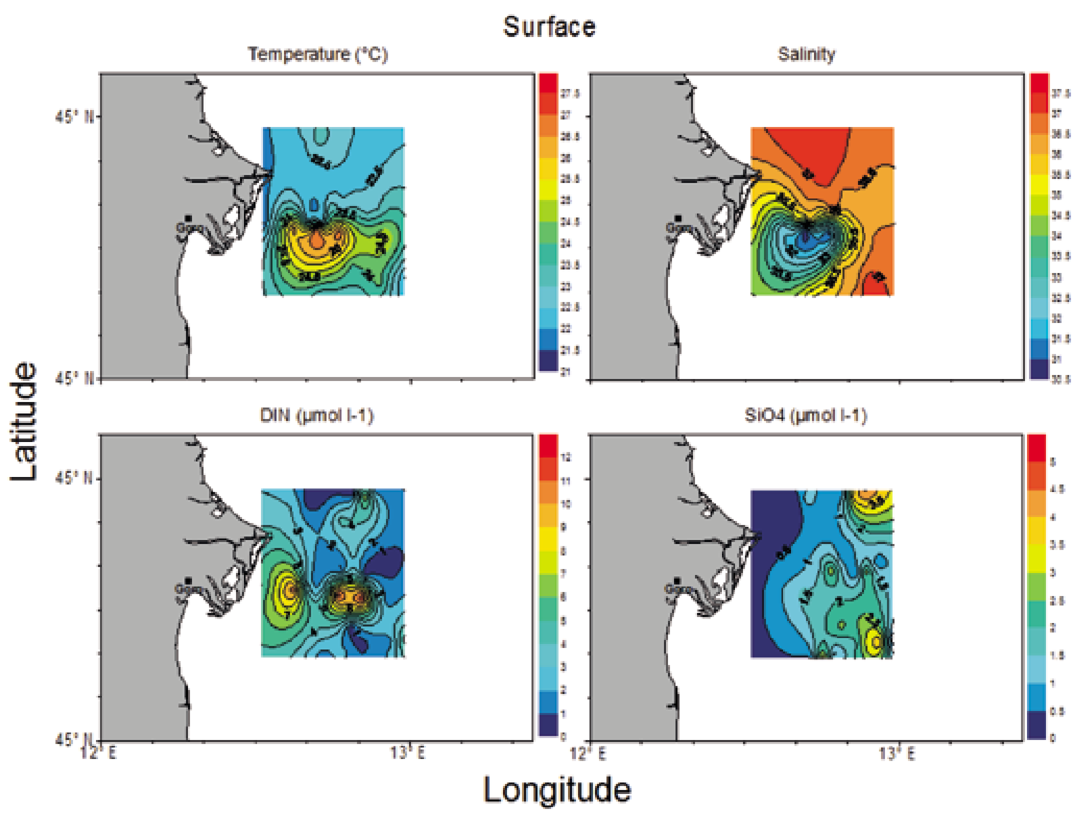

Fig. 3. Surface distributions of Temperature (T°C), Salinity, Dissolved Inorganic Nitrogen-DIN (µmol l^{-1}) and Orthosilicate (µmol l^{-1}) in the North Western Adriatic Sea (NWAd)

Parameter	Depth	SEAM			SWAd			NWAd		
		All area	S<37.5	S>37.5	All area	S<37.5	S>37.5	All area	S<37.5	S>37.5
T°C	surface	25.5±1(49)	25.5±1.1 (39)	17.2±3.7 (215)	22.6±0.7(22)	21.8±1.3 (43)	15±2.1 (19)	23.3±1.2(27)	23.1±1.6 (28)	13.0±2.8 (11)
	bottom	15.2±2(49)			17.5±3.6(22)			11.2±2.3(6)		
S	surface	37.2±0.8(49)	36.8±0.5 (39)	38.5±0.3 (215)	35.9±0.5(22)	36.3±0.6 (43)	38.1±0.2 (19)	36±1.6(27)	36±1.6 (28)	37.9±0.1 (11)
	bottom	38.7±0.2(49)			37.5±0.8(22)			37.9±0.2(6)		
O_2 sat %	surface	94.2±1.3(49)	94.2±1.4 (39)	89.5±13.3 (215)	102.4±1.5(22)	102.8±1.9 (41)	107.3±3.4 (19)	141.2±17.5(6)	134.6±23.6 (7)	95.3±11.4 (11)
	bottom	82.8±7.3(49)			105.5±3.3(22)			90.1±8.1(6)		
DIN/P	surface	48.5±52.1(45)	98.5±107.7 (34)	49.6±60.2 (200)	93.3±72.3(22)	91.2±61.2 (41)	42.3±37.9 (19)	21.9±19.3(27)	22.0±19.0 (28)	19.1±14.9 (28)
	bottom	46.2±43.3(44)			80.1±60.2(20)			23.8±18.6		
Si/P	surface	47.5±37.4(49)	36.3±20.1 (38)	31±28.4 (214)	127.8±70.4(22)	104.8±57.2 (41)	68.9±32.9 (19)	17.4±15.5(27)	18.0±15. (11)5	58.2±44.9 (11)
	bottom	43.7±40.7(49)			87.1±58.2(20)			84.6±37.9		
DIN µmol l^{-1}	surface	6.9±7.1(45)	6.6±7.3 (34)	2.3±1.6 (200)	5.1±2.3(22)	4.3±2.3 (41)	1.5±1.5 (19)	2.7±2.9(27)	2.7±2.9 (28)	2.8±2.3 (11)
	bottom	9.3±6.9(44)			2.6±1.8(20)			3.8±2.8(6)		
$Si(OH)_4$ µmol l^{-1}	surface	2.4±1.5(49)	2.6±1.7 (38)	2.3±1.6 (214)	7.9±3.7(22)	6.1±3.4 (41)	4.3±1.7 (19)	1.7±1.3(27)	1.7±1.3 (28)	8.2±5.6 (11)
	bottom	4±1.6(49)			4.2±1.6(20)			11.4±4.8(6)		
PO_4 µmol l^{-1}	surface	0.1±0.1(49)	0.1±0.1 (38)	0.1±0.4 (214)	0.06±0.07(22)	0.06±0.06 (41)	0.07±0.04 (19)	0.1±0.04(27)	0.1±0.04 (28)	0.13±0.04 (11)
	bottom	0.2±0.1(49)			0.04±0.03(20)			0.1±0.05(6)		
Chl *a* µg l^{-1}	surface	0.25±0.29(25)	0.22±0.24 (22)	0.37±0.52 (26)	0.36±0.37(22)	0.26±0.31 (40)	0.10±0.15 (18)		˜1-15 (Marini et al. 2008)	
	bottom	----			0.09±0.1(19)					
a_{CDOM}440 m^{-1}	surface	0.6±0.6(23)	0.6±0.5(21)	0.4±0.5(29)	0.6±0.3(12)	0.6±0.3(20)	0.6±0.2(2)	-----	-----	-----

Table 2. Mean values and standard deviations of Temperature (T), Salinity (S), Density (D), Oxygen Saturation (O_2 sat) Dissolved Inorganic Nitrogen (DIN), Orthophosphate (PO_4), Orthosilicate ($Si(OH)_4$), a_{CDOM}440, in situ chlorophyll a (Chl a), ratios between DIN, Orthophosphate (P) and Orthosilicate (Si). The values are relative to the surface, to the bottom, to the S < 37.5 and to the S > 37.5 in the three sub-basin of the Adriatic Sea (South Eastern Adriatic-SEAM, South Western Adriatic-SWAd, and North Western Adriatic-NWAd). The number of data used for the computation is reported in brackets.

waters with high orthosilicates concentrations from the surface ones. The absence of the Bora wind and the strong bottom currents during the summer period results in an isolation of the bottom layer that occurs usually in late summer/ early autumn causing the phenomena hypoxia on the bottom of the Northern Adriatic basin (MARINI *et al.*, 2004; BOLDRIN *et al.*, 2009).

Considering all the data collected, salinity and fluorescence are significantly correlated (R^2=0.59, n=18, P<0.001). This confirms that the trophic state of the waters is mainly controlled by fresh water input. Unfortunately, analyzing the separated water masses (Table 1), the data available were few, and this does not allow a good significant correlation. In particular, the phytoplankton growth is probably due to nutrient uptake coming from river discharge together with other favourable environmental conditions of the period (i.e. relatively high temperature, high light radiation, low water mixing). No data are available for CDOM absorbance in this area.

South Western Adriatic

The satellite image for the SWAd shows, in the same seasonal period, high chlorophyll values inside the gulf. A relatively strong gradient is observed between the coast and offshore region as detected in the Po plume area.

Surface salinity and temperature (Fig. 4) increase slightly from North to South highlighting that the prevalence of freshwater comes from the Northern coast (MARINI *et al.* 2008; Fig. 4). On the other hand, the salinity and temperature at the bottom show a gradient from coast to offshore (salinity increase and temperature decrease). These features indicate that the summer stratification separates the surface layer (more influenced by the input coming from the Northern coast driven by the WAC) from the bottom layer. Furthermore, a month before the cruise, exceptional Po River floods (from 29th April to 5th May) with a maximum of 7091 m^3 s^{-1} (2nd May) occurred (Idro-Meteo-Clima Arpa ER: http://www.arpa.emr.it/sim/osservazioni_e_dati/dexter). The presence of the surface salinity gradient is probably due to these floods. The whole area is oxygen saturated as expected in late spring (Fig. 4). Higher chlorophyll *a* values (0.5-1 µg l^{-1}; Fig. 5) are observed near the Southern coast (Ofanto River mouth). The DIN values are slightly higher on the surface layer - especially in the northern side of the gulf (7-8 µmol l^{-1}) and in the area in front of the Ofanto River mouth (5-6 µmol l^{-1}) than on the bottom layer. The highest DIN values (Fig. 5) coincide with the lowest salinity signal as confirmed by the correlation found between DIN versus S<37.5 (R^2=0.74, n=43, p<0.001). The orthosilicate concentrations (Fig. 5) show highest values (12-14 µmol l^{-1}) on the surface of the stations located near the coast. The surface layer shows the highest values also offshore where high DIN values (4-5 µmol l^{-1}) are detected. The correlation found between orthosilicate and S<37.5 stresses that the load of nutrients come from the Northern coast. Furthermore, the positive correlation found between O_2 and S together with negative correlations of S versus DIN and O_2 versus DIN confirm this feature. The surface water masses that are fresher, richer in nutrients and less oxygenated are mixed with the water masses present in the gulf that are saltier, poorer in nutrients and more oxygenated.

The $a_{CDOM}440$ values (Fig. 5) range between 0.1 and 1.1 m^{-1} and show the highest values in the southern part of the area where the Ofanto mouth is located. No correlations are found between $a_{CDOM}440$ and other parameters. These features indicate that probably the organic matter comes from different factors. In fact, it is well known, that the abundance and distribution of CDOM in many coastal waters are dominated by terrestrial inputs coming from rivers and runoffs as decomposition of terrestrial organic matter yields light-absorbing compounds such as humic and fulvic acids (HØJERSLEV, 1982; CARDER *et al.*, 1989; DEL VECCHIO & BLOUGH, 2004).

The area does not have a main river and the trophic system is probably due to multiple factors. The trophic characteristics of this area seem to be mainly influenced by the amount of organic and inorganic matter coming from the North Adriatic Sea, and by how much substance

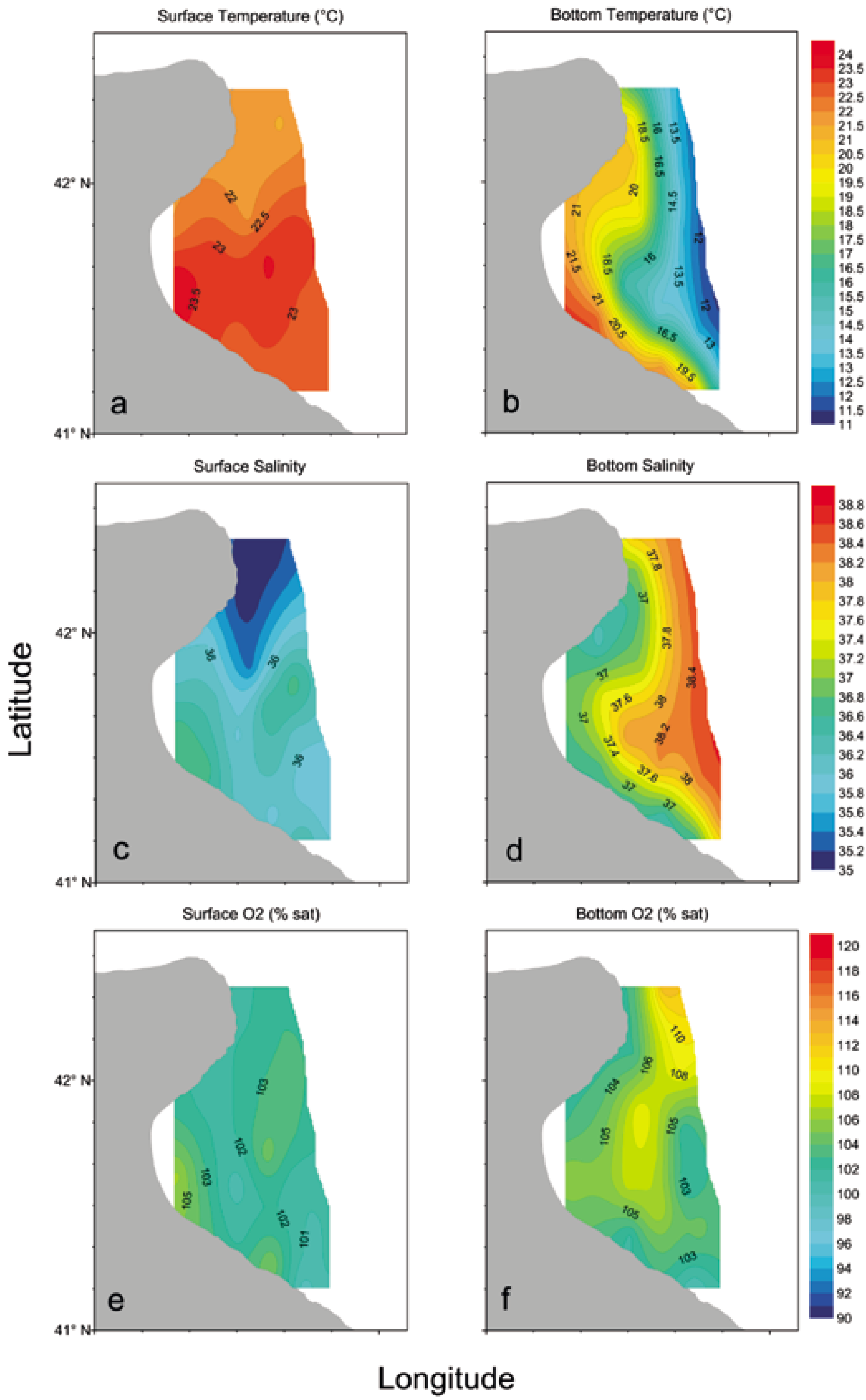

Fig. 4. Surface (a, c, e) and bottom (b, d, f) distributions of Temperature (T°C), Salinity, Oxygen percentage saturation (%) in the South Western Adriatic Sea (SWAd)

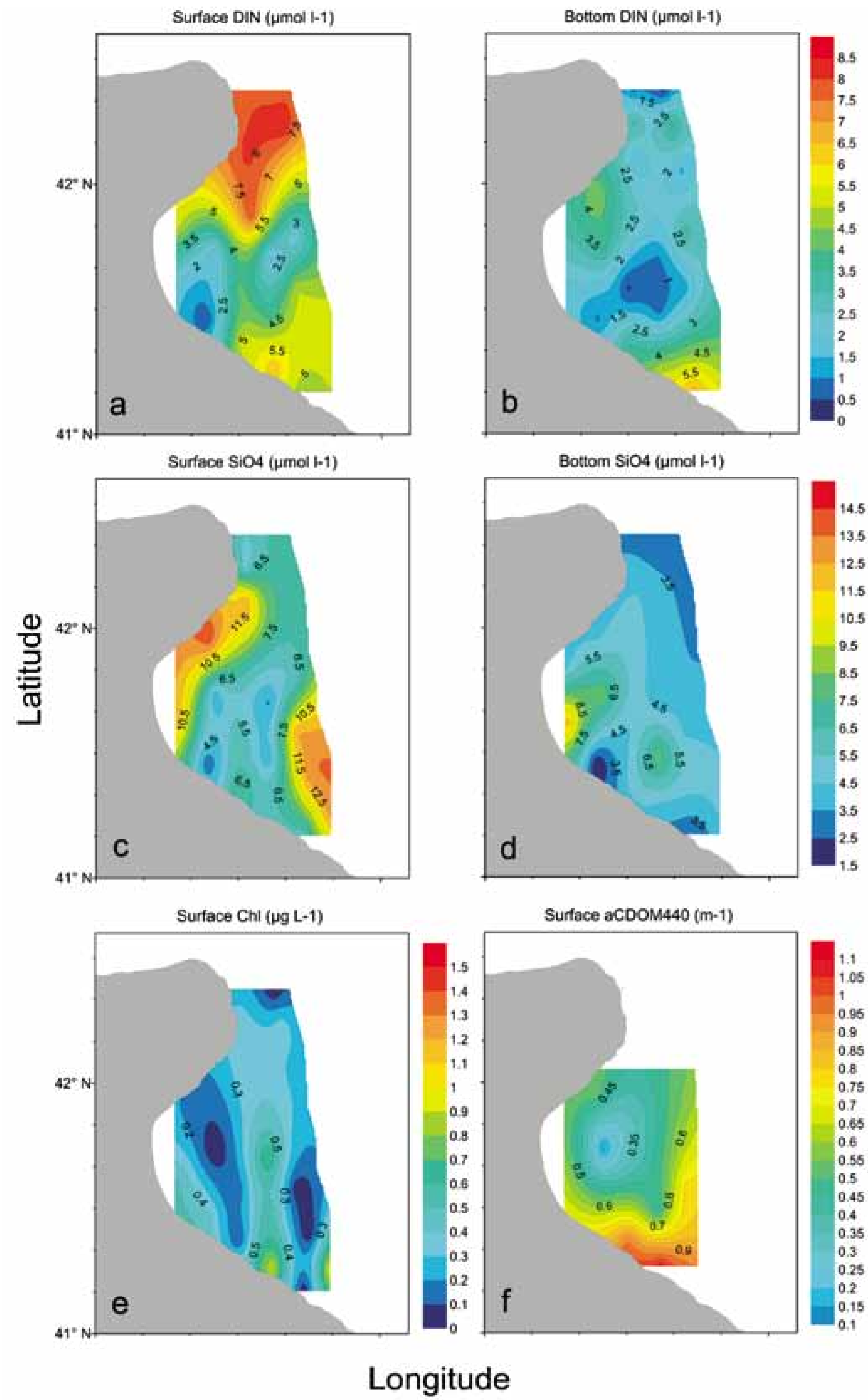

Fig. 5. Surface (a, c) and bottom (b, d) distributions of Dissolved Inorganic Nitrogen-DIN (µmol l^{-1}) and Orthosilicate (µmol l^{-1}) in the South Western Adriatic Sea (SWAd). The panels e and f show surface distributions of chlorophyll a (µg l^{-1}) and $a_{CDOM}440$ (m^{-1}) respectively

is uptake along the way. An exceptional Po River discharge could influence the basin more than local rivers inputs. In fact, CAMPANELLI *et al.* (2011) showed how relevant floods can modify for months the physical and chemical characteristics of the waters in the Northern and Central Adriatic Sea. The local circulation affected by winds (BURRAGE *et al.*, 2009) probably plays a main role in the redistribution of the organic and inorganic matter coming from the North Adriatic as well as that coming from local inputs.

South Eastern coastal region of Albania and Montenegro

The satellite image for the SEAM shows in June 2008 high chlorophyll *a* concentrations along the coast and in particular inside the Gulf of Drini (1-2.5 μgChl l^{-1}).

The salinity map (Fig. 6) shows that the Buna/Bojana River does not particularly influence the area as found by MARINI *et al.* (2010) during April 2006 when, probably, the river discharge is higher. The mean discharge in June during the years 1965-85 was about 550 m^3 s^{-1} instead of 881 m^3 s^{-1} in April (UNEP, 1996).

However, a less salty water mass is evident alongshore compared to the offshore one. The station in front of the Buna/Bojana River shows a surface salinity of 36.9 and temperature of 23.8°C (Fig. 5a,c). The entire area is slightly under saturated, especially on the bottom. Highest chlorophyll *a* values (0.8-1.2 μg l^{-1}; Fig. 7) are observed inside the Gulf of Drini and offshore the Boka Kotorska Bay. The distributions of DIN and orthosilicates (Fig. 7) show maximum values higher than 15 μmol l^{-1} and 2 μmol l^{-1} respectively. A core of freshwater mass (salinity 35.3-35.9) is detected South of the river plume probably coming from river discharge during the previous days and probably moving toward the centre of the gulf by local gyres (MARINI *et al.*, 2010). In the same area, the highest values of $a_{CDOM}440$ (1.6-2.3 m^{-1}; Fig. 7) are observed and this could be a signal of richness of organic matter coming from the river. The surface DIN and orthophosphate distributions are patchy showing a local maximum in the Buna/Bojana River mouth and in the Southern side of the area respectively. The surface distribution of orthosilicates shows a local maximum southward the Buna/Bojana River mouth as expected if river-born nutrients are injected in the coastal area and not used by the primary producers. The bottom nutrient distributions are patchy from the DIN values. The concentrations of orthosilicate and orthophosphate show the maximum values on the bottom of the deepest stations offshore. On the other hand, the orthosilicate values show a negative correlation with S<37.5 and positive correlation with S>37.5.

Patterns of chlorophyll *a* versus S<37.5, $a_{CDOM}440$ versus S<37.5 and consequently chlorophyll *a* versus $a_{CDOM}440$ are well correlated (P<0.001) while DIN versus salinity shows uncorrelated patchy structures inside the freshwater influenced area. The local freshwater input is important for evaluating the trophic state of the basin as observed in NWAd. However, the load of nutrients coming from the rivers seems to influence mainly the amount of silicic rather than nitrogen during the sampling period. The chlorophyll *a* concentrations measured during the three cruises show values of the same order of magnitude to that retrieved from satellite images. Nonetheless, the measurements of chlorophyll *a* are smaller compared to satellite data as expected in coastal areas where the optical complexity is highly variable (DIERSSEN, 2010; BLONDEAU-PATISSIER *et al.* 2014).

According to the classification of IGNATIADES (2005), only the NWAd area is mostly eutrophic during the late spring sampling. The SWAd and the SEAM areas show mainly mesothrophic conditions in coastal stations and only a few of them appear eutrophic.

Redfield Ratio

It is well known that under aerobic conditions the assimilation and the regeneration of nutrients occur in constant ratios ($DIN:Si(OH)_4:PO_4$ = 16:15:1) RICHARDS 1958 and REDFIELD *et al.* 1963. In coastal and shelf areas, the Redfield ratios can be significantly different from the standard values (which were originally calculated for open

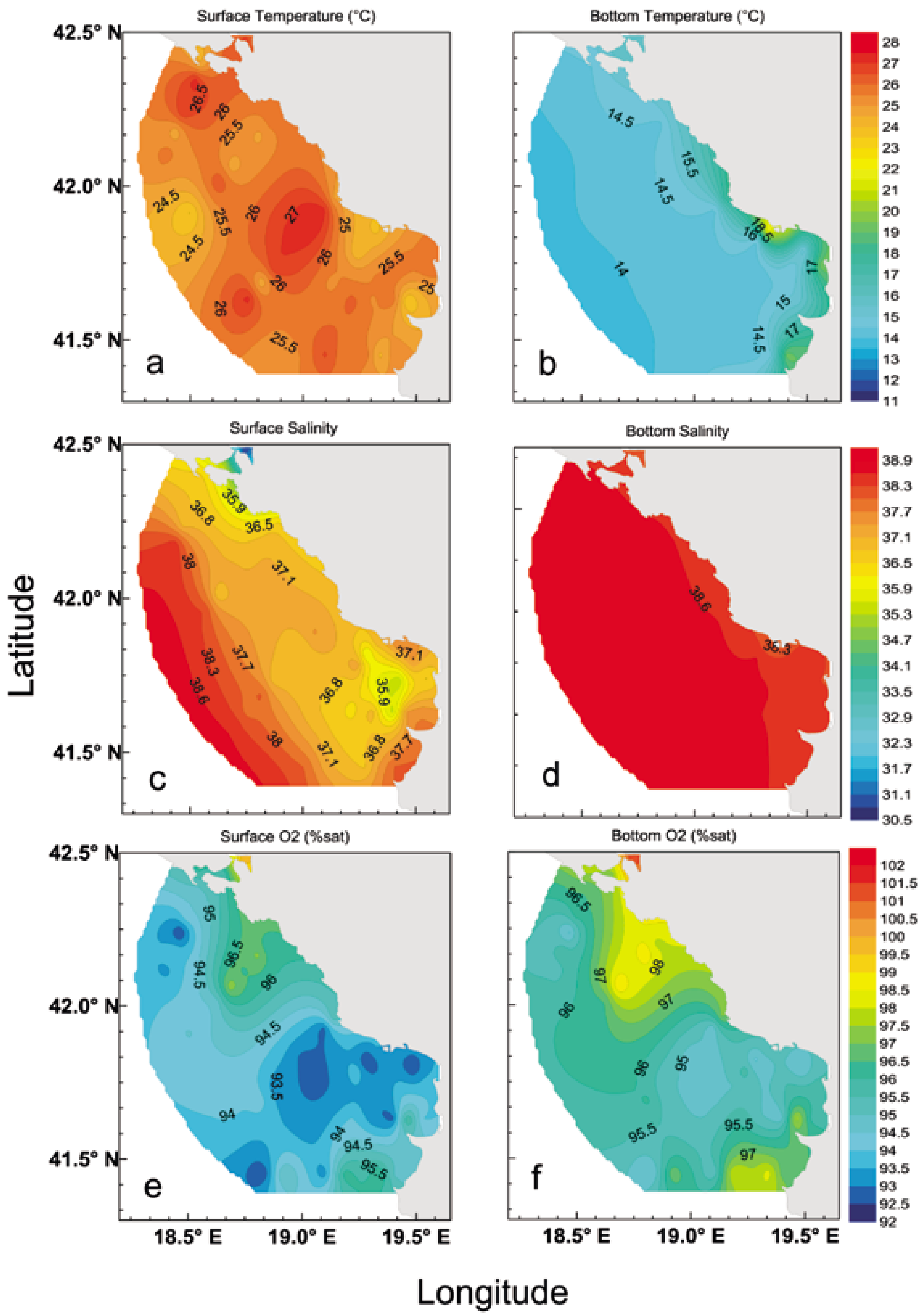

Fig. 6. Surface (a, c, e) and bottom (b, d, f) distributions of Temperature (T°C), Salinity, Oxygen percentage Saturation (%) in the South Eastern Adriatic Sea (SEAM)

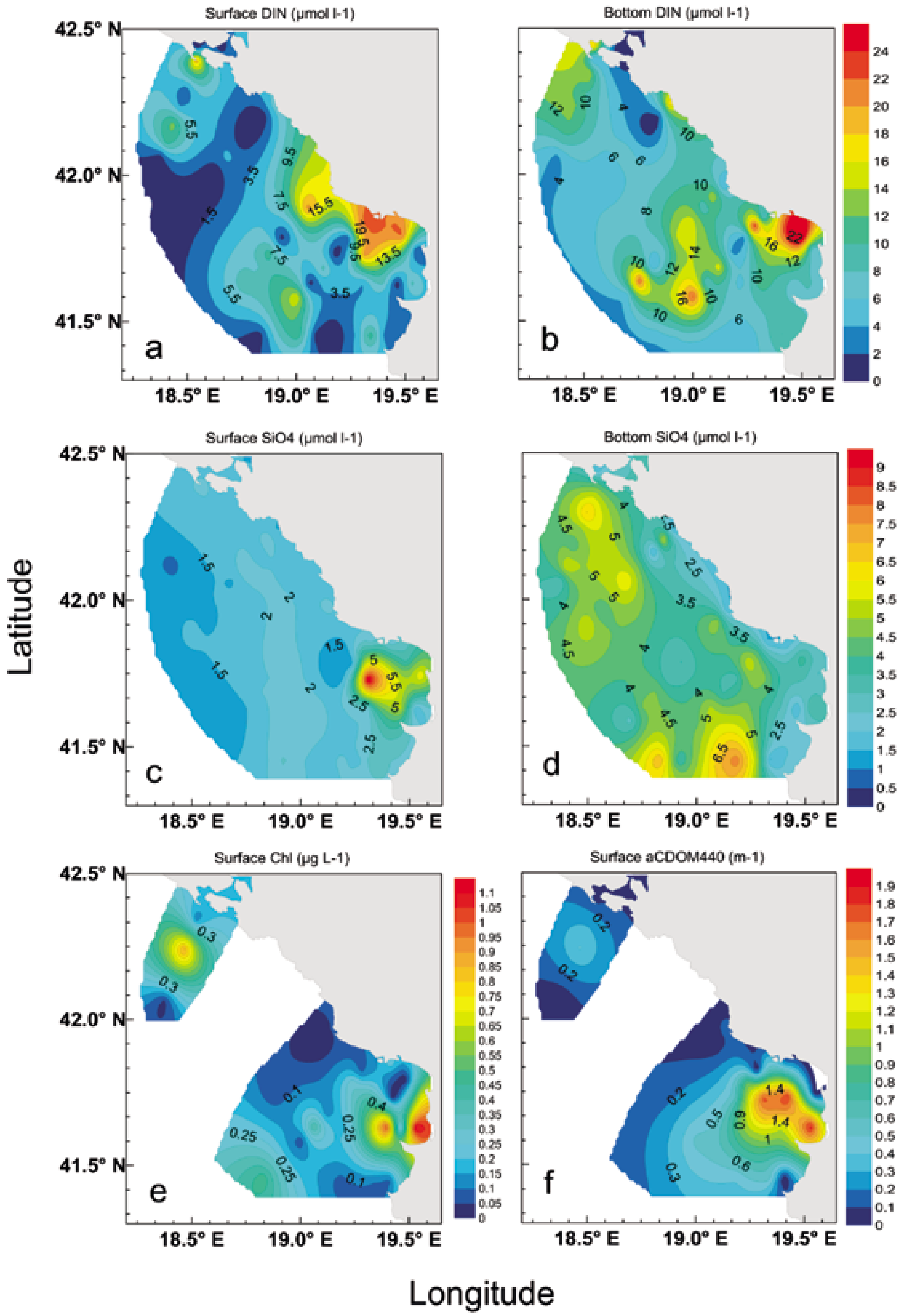

Fig. 7. Surface (a, c) and bottom (b, d) distributions of Dissolved Inorganic Nitrogen-DIN (µmol l^{-1}) and Orthosilicate (µmol l^{-1}) in the South Eastern Adriatic Sea (SEAM). The panels e and f show surface distributions of chlorophyll a (µg l^{-1}) and $a_{CDOM}440$ (m^{-1}) respectively

sea regions) depending on local factors such as the amount and the nature of continental inputs or the influence of regenerative processes which occur in the sediments. DEGOBBIS (1990), ZAVATARELLI *et al.* (1998), MARINI *et al.* (2008) and CAMPANELLI *et al.* (2011) calculated the Redfield ratios relevant to water masses having different characteristics as oxygen saturation percentage and salinity ranges for the Adriatic Sea. In this work, the Redfield ratios ($DIN:PO_4$, $Si(OH)_4:PO_4$,) are calculated at the surface, on the bottom and at different salinity ranges for the three areas (Table 2). It was observed that the standard deviations associated with the Redfield ratios are high, close to the average value itself. This demonstrates the high variability of the data and of the biological and physical processes controlling the nutrient level in the three coastal areas.

The N:Si:P ratio at the surface in the SEAM is 48:47:1 and on the bottom is 46:44:1.The analysis of these ratios at different S ranges show that N:P ratio is double where $S<37.5$. This feature is due to higher DIN values detected in the area influenced by fresh water than in the saltier waters.

In the SWAd, the N:Si:P ratios relevant to the surface and the bottom are twice those calculated in the SEAM. On the other hand, the analysis of the two water masses with different salinity show the N:P ratios similar to the SEAM, and the Si:P ratios are highest for both water masses. The different Redfield ratios found depend both on the lowest concentrations of orthophosphate and nitrogen and on the highest values of silicates measured as regards the SEAM area. Moreover, a very low orthophosphate concentration present in the SWAd can be due to uptake by primary producers along the Italian coast before the water masses reach this basin.

In the NWAd, the N:Si:P ratio is lower than the other sub areas. In particular, the N:Si:P ratio relevant to the surface, is 32:17:1. Normally, the volume flux from the Po River system is twice the volume flux from the Buna/Bojana River system. On the other hand, MARINI *et al.* (2008) showed that during the previous months of the 2003 cruise the Po river discharge was one third of the means of the period. The low Po river discharge of the period can be the cause of these ratios due primarily to low nitrogen and silicate concentrations in respect to the other two basins. On the other hand, the nutrient levels in the Northern and Southeastern Adriatic are normally controlled by river inputs (MARINI *et al.*, 2010; CAMPANELLI *et al.*, 2011). The analysis of the water masses with different salinity show mostly the same patterns with lower Redfield ratio respect to other areas.

These ratios indicate high concentrations of nitrogen and orthosilicate in respect to phosphorus in the three areas and mainly in the SWAd and SEAM. The three areas appear phosphorus limited. However, among the three basins, the NWAd shows the better conditions of assimilation and regeneration of nutrients probably supported by low Po River discharge during the previous months of the cruise.

CONCLUSIONS

The data evidence the direct and indirect importance of river discharges for the trophic state of the Adriatic systems. In particular, the physical and chemical characteristics of NWAd and SEAM appear directly influenced by local river discharges. The SEAM is mainly influenced by the freshwater system of the Buna/Bojana River and other minor rivers (Mati and Ishimi) and the NWAd is mainly influenced by the Po River discharge. These features are evidenced by negative correlations found between chlorophyll *a* (or fluorescence) values versus salinity. The SWAd is indirectly influenced by the amount of freshwater richer in nutrients and organic matter coming from the North Adriatic Sea and by how much substance is uptake along the way. The high Po river discharges could influence the trophic state of this area even though it is located at about 250 nM South as regards the Po river mouth. The local gyres present in the SWAd play a main role in the redistribution of these substances coming from the North Adriatic inside the gulf.

The fresh water signal is mainly connected to load of orthosilicate in the SEAM and to load of nitrogen in the NWAd and SWAd. In these two areas, the load of nitrogen is probably due to the hydrographic basin of the Po River that is impacted by a great agriculture system of North Italy.

The measurements of chlorophyll *a* collected during the cruises show that only the NWAd area is mostly eutrophic in the late spring. The SWAd and SEAM areas show mainly meso-throphic conditions in coastal stations and only a few stations appear eutrophic.

The Redfield ratio shows that the three basins are phosphorus limited in respect to nitrogen and orthosilicate concentrations, in particular the SWAd and SEAM. This study analyzed the three areas in order to better understand their physical and chemical characteristics during late spring.

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Karakterizacija različitih obalnih područja Jadrana u kasno proljeće

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SAŽETAK

Cilj ovog istraživanja je analiza fizikalnih i kemijskih svojstava triju obalnih područja Jadrana u kasno proljeće i ustanovljenje sličnosti i razlika među zonama. Trofički status jugoistočnog Jadranskog mora, pod utjecajem dotoka slatke vode iz sliva rijeke Bune / Bojane, je u ovom radu uspoređen s druge dvije jadranske regije: sjeverozapadnim Jadranom i jugozapadnim Jadranom (zaljev Manfredonia) u prvom dominiraju pražnjenja rijeke Po, dok je drugi jedno od najproduktivnijih područja jugozapadnog Jadrana.

Područja su pod utjecajem dviju glavnih površinskih struja Jadranskog mora: istočne jadranske struje (EAC) koja teče prema sjeverozapadu i zapadne jadranske struja (WAC) koja teče prema jugoistoku. Podaci o izmjerenoj temperaturu, slanosti, fluorescenciji, kisiku, hranjivim tvarima i klorofilu *a* su sakupljeni i uspoređeni za sva tri područja. Istraživana područja su pokazala slične fizičke i bio-kemijske karakteristike, unatoč činjenici da je sjeverni Jadran pod utjecajem dotoka rijeke Po, a zapadna jadranska struja (WAC) nosi duž zapadnog Jadrana vodu bogatu hranjivim tvarima iz talijanskih rijeka na sjeveru. Područje pogođeno dotokom rijeke Po pokazalo je maksimum koncentracije klorofila i dušika unutar rijeka. Štoviše, u jugozapadnom Jadranu količina hranjivih tvari i organske tvari je povezana s tvarima koje dolaze iz sjevernih talijanskih rijeka (uglavnom rijeke Po).

Slično tome, u jugoistočnom dijelu jadranskog mora, dotok rijeke Bune / Bojane sadržavao je relativno visoke vrijednosti klorofila na nivou regionalne distribucije. Tri područja su izravno ili neizravno povezana s dinamikom riječnih perjanica, te organskim i anorganskim riječnim unosom koji određuje trofičko stanje područja. Konkretno, jugoistočno Jadransko more je mezo-eutrofično područje; unatoč većoj istočnoj strani Jadrana koij je bio oligotrofan bazen.

Ključne riječi: otopljene hranjive tvari, klorofil *a*, CDOM, dotok rijeka, Redfield omjer, Jadransko more