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## Hypoxia and dissolved oxygen trends in the northeastern Adriatic Sea (Gulf of Trieste)

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## ABSTRACT

Physical and chemical data collected in three stations, with time series ranging from 1983, 1986 and 1989 to 2016, were analyzed in order to detect trends and frequency of occurrence of hypoxia events in bottom waters of the Gulf of Trieste (Adriatic Sea). The results of the analysis of 30-years data show a tendency toward increasing oxygen concentration in the bottom waters, nevertheless two hypoxic events were recorded during the summers of 2015 and 2016 even in a relatively shallow area of the Gulf. The spatial and temporal extent of these events was analyzed by coupling oceanographic surveys with automatic oceanographic measurements. During both summers, the area was characterized by high seawater temperature (up to 28.4 °C at the surface) and salinity (38.1 at the bottom) and a marked stratification of the water column, which prevented the mixing of oxygen-rich surface water with oxygen-poor deep water. The main contribution to oxygen depletion in the bottom waters was attributed to plankton respiration (54–61%) and to benthic oxygen consumption (39–46%), which exceeded the oxygen produced by planktonic and benthic microalgae and the one diffused from the overlying oxygenated water. These events of marked oxygen depletion in shallow coastal ecosystems are possibly favored by the positive temperature trend in bottom waters, coupled with the increase in riverine discharges in late spring, limiting vertical mixing and bottom water renewal.

## 1. Introduction

Dissolved oxygen (DO) concentrations in coastal areas have been decreasing in many regions over the past decades mainly due to land and river based anthropogenic nutrient inputs, with the evolution of massive agriculture and the use of fertilizers (Diaz and Rosenberg, 2008; Rabalais et al., 2010; Zillén et al., 2008; Breitburg et al., 2018). River borne nutrient enhance marine primary production and consequently increase phytoplankton biomass, part of which sinks to the seabed where it is used by the benthic community or buried. Its decomposition due to bacterial remineralization reinforces the DO consumption in bottom waters and leads to oxygen depletion. There are additional processes regulating the seasonal dynamics of bottom DO, one of them is the occurrence and the duration of the water column stratification, which isolates the bottom water from exchange with oxygen-rich surface water. Increase in seawater temperature enhanced by global warming, and altered regimes of wind, precipitation and runoff can deeply affect the water column stratification or combine to form stable water masses near the bottom that become hypoxic when they

are isolated from re-oxygenation with surface waters (Diaz, 2001; Keeling et al., 2010; Vaquer-Sunyer et al., 2012). Many studies worldwide have demonstrated that seawater warming can increase the susceptibility of marine organisms to low oxygen levels, reducing the abundance of benthic fauna, altering nutrient and carbon cycling and shifting the marine systems toward heterotrophy (Altieri and Gedan, 2015; Carstensen et al., 2014; Rabalais et al., 2010; Vaquer-Sunyer and Duarte, 2011).

In coastal areas, where the physical processes are generally more dynamic and complex compared to open ocean, the complexity of interacting processes makes it difficult to identify specific causes. DO concentration depends on multiple factors, such as hydrological conditions affecting gas solubility, air–water exchange, water vertical stratification, pelagic and benthic metabolism. The net balance between oxygen production and consumption is a key factor affecting changes in dissolved oxygen concentration in coastal waters. In some oligotrophic systems, respiration of both eukaryotic plankton and bacterioplankton tend to exceed gross primary production (Del Giorgio et al., 1997). These features combine to form stratified or stable water masses

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near the bottom that become hypoxic when they are isolated from re-oxygenation with surface waters (Diaz, 2001).

Shallow waters, semi-enclosed circulation and river-borne nutrient discharges characterize the northernmost part of the northern Adriatic, the Gulf of Trieste (Cossarini et al., 2012; Cozzi et al., 2012; Lipizer et al., 2011; Malačič and Petelin, 2009). As a result of the combination of all these factors, in the past massive phytoplankton blooms, hypoxia and anoxia (Cabrini et al., 2012; Degobbi et al., 2000; Faganeli et al., 1985; Aleffi et al., 1992; Faganeli and Ogrinc, 2009) have been observed in the northern Adriatic continental shelf and in the Gulf of Trieste. The type of hypoxia mostly observed in the study area is a seasonal hypoxia (Djakovac et al., 2015; Malej and Malačič, 1995).

Many thresholds for hypoxia in differing units have been used (Hofmann et al., 2011), mostly based on the effects observed on the biota. In the present work we adopted, according to Riedel et al. (2008) and Vaquer-Sunyer and Duarte (2008), the terms hypoxic, moderately hypoxic and oxygen stressed condition to indicate waters with DO concentrations below  $45 \mu\text{mol O}_2 \text{ L}^{-1}$  ( $1.43 \text{ mg O}_2 \text{ L}^{-1}$ ),  $62.5 \mu\text{mol O}_2 \text{ L}^{-1}$  ( $2 \text{ mg O}_2 \text{ L}^{-1}$ ) and  $143.8 \mu\text{mol O}_2 \text{ L}^{-1}$  ( $4.6 \text{ mg O}_2 \text{ L}^{-1}$ ), respectively. Waters with oxygen concentrations below  $4.6 \text{ mg O}_2 \text{ L}^{-1}$ , would be expected to maintain most of the populations, except the 10% most sensitive species, therefore this oxygen level could thus be considered as a precautionary limit to avoid catastrophic mortality events (Vaquer-Sunyer and Duarte, 2008).

Several studies reported long-term records of oxygen content in coastal (Alvisi and Cozzi, 2016) and offshore areas (Justic et al., 1987; Djakovac et al., 2015; Degobbi et al., 2000; Giani et al., 2012) of the northern Adriatic. The interpretations of trends over 20 years or less, need to be performed with greatest caution, as the annual-to-decadal variations are substantial, and influence the determination of long-term trends.

After a period of frequent hypoxic events at the end of 1980s/start of 1990s, oxygen stressed conditions became rare in the decade

2004–2014. Recently, in 2015 and 2016, a reappearance of stressed oxygen conditions was identified by means of oceanographic surveys and continuous automatic measurements at fixed stations.

In the present study, we address two main questions: which is the time scale for development of the seasonal depletion of dissolved oxygen in the Gulf of Trieste and which are the major factors influencing its time evolution. Based on the hypothesis that both physical and biological processes regulate dissolved oxygen dynamics, we analyze the effects of riverine inputs, stratification, vertical diffusion as well as of biological activities (respiration and production) from both planktonic and benthic compartments, and we estimate the time needed to reach oxygen-stressed and also hypoxic conditions. Ultimately, we focus on the effect of temperature increase on planktonic and benthic respiration, in light of the vulnerability of these processes to overall warming.

The analysis of this data and the comparison of the available time series of oceanographic observations carried out in the study area were performed in order to understand the long-term evolution of summer oxygen depletion.

## 2. Study area

The Gulf of Trieste is a shallow and semi-enclosed basin (maximum depth: 25 m; surface area:  $500 \text{ km}^2$ ) located in the northeastern part of the Adriatic Sea (Fig. 1), which accounts for 2.6% of the NAd surface ( $18900 \text{ km}^2$ , considering the limit on the 50 m isobaths). The area is influenced by Isonzo River discharges (mean flow of  $82 \text{ m}^3 \text{ s}^{-1}$ ), which contributes to about 90% of the freshwater inputs (Cozzi et al., 2012) and is characterized by a significant interannual variability and pronounced seasonal variability with two high-discharge periods in spring ( $122 \text{ m}^3 \text{ s}^{-1}$ ) and late autumn ( $198 \text{ m}^3 \text{ s}^{-1}$ ) and two lower runoff seasons in winter and summer (Comici and Bussani, 2007).

Beside the buoyancy effects of the Isonzo River plume, the hydrodynamics of the Gulf is driven by winds (southeasterly Scirocco and

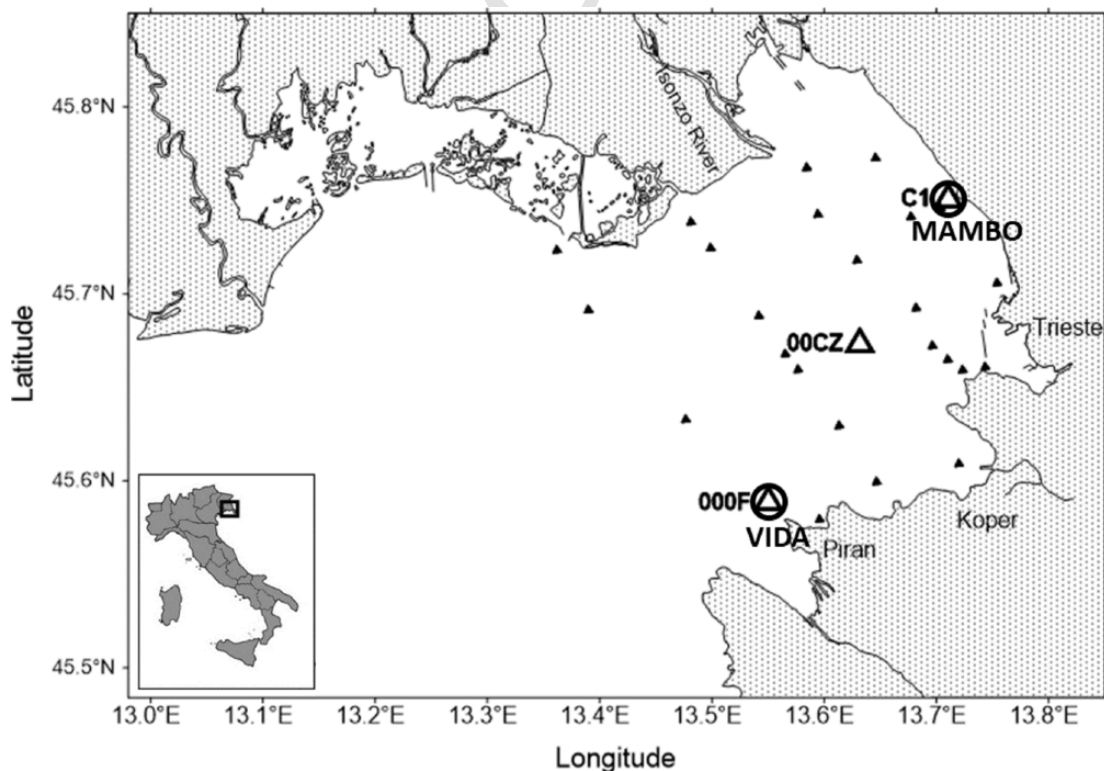


Fig. 1. Study area and position of the sampling stations. The stations monitored in summer 2015 and 2016 are represented by black triangles; the stations where long-term series are monitored by open triangles and the oceanographic buoys by circles.

northeasterly Bora), tides and water masses exchanges with the Adriatic Sea (Falcieri et al., 2016). The circulation can be subdivided in three layers, the surface layer (0–5 m deep), which is mainly wind driven, and the intermediate (5–10 m deep) and the lower (10–bottom) layers which follow a general cyclonic circulation (Stravisi, 1983). Residual currents are in the range 1–3 cm s<sup>-1</sup>, but total currents as high as 30 cm s<sup>-1</sup> are found in the upper layer, because of the effects of tides and wind stress (Mosetti and Purga, 1990; Mosetti and Mosetti, 1990). The outflow of seawater mostly occurs along the northern coast, however, intense and frequent wind conditions can produce highly variable and even opposite circulations at the surface layer (Malačič and Petelin, 2009) and modify the vertical structure of the water column (Querín et al., 2007). The Gulf of Trieste is also under the influence of the Eastern Adriatic Current (EAC), a current flowing northwards along the Croatian coast, advecting warmer and saltier waters coming from the Ionian Sea (Poulain and Cushman-Roisin, 2001) and playing an important role on the biogeochemical composition of the waters of the area (Lipizer et al., 2011, 2012). The ingression of EAC is more frequent in the cold seasons, when a cyclonic circulation is present.

The climate seasonal cycle in the area determines the high variability of seawater temperature, total irradiance and water column stratification during the year (Malačič and Petelin, 2001). Hydrology, biogeochemistry and productivity are mainly influenced by the river load, which is the major allochthonous source of freshwater and nutrient in the area (Cozzi et al., 2012). In addition to river born nutrient, also wastewater discharges contribute to increase the N and P and organic carbon and organic nitrogen loads in the Gulf (Cozzi et al., 2008, 2014; Mozetič et al., 2008). The freshwater inputs and the variability of the circulation pattern, which influence the distribution of the nutrient, have a significant impact also on plankton community structure and their productivity, but also on events of hypoxia/anoxia (Malej and Malačič, 1995), which have characterized the area in the past.

### 3. Material and methods

Monthly main physical and chemical parameters (temperature, salinity, dissolved oxygen, density anomaly and chlorophyll a) at stations C1, 000F and 00CZ during the years 2015–2016, were analyzed in order to describe the environmental characteristics during the observed oxygen depletion periods.

High frequency temporal variability of MAMBO and VIDA buoys data during August 2015 and 2016, were used to better interpret the short-term dissolved oxygen variations. The evolution of the oceanographic features in bottom waters of the Gulf in July and August 2015 and 2016 was followed by means of 28 stations.

Trends in water properties (temperature, salinity, dissolved oxygen, chlorophyll a and AOU) from 1983/1989 (depending on the station) to 2016 in the three long-term monitoring stations were examined, in order to determine the processes driving the changes in dissolved oxygen concentrations and the occurrence of hypoxia events.

#### 3.1. Field sampling and measurements

The oceanographic dataset analyzed in this study included ~15,500 data collected at three long-term monitoring stations at different depths and summer CTD profiles of 28 stations distributed in the study area during two years (2015–2016).

##### 3.1.1. Long-term monitoring stations

The long-term surveys of oceanographic properties (Table S1) of the Gulf of Trieste as well as the 2015–2016 period are part of Slovenian and Italian national monitoring programs. Two stations in the southern (000F and 00CZ) and one in the northern (C1) part of the Gulf were sampled monthly. Time series of stations 000F, 00CZ and C1 covered

periods of up to 33 years—1983–2016, 1989–2016 and 1986–2016 (with a break between 1991 and 1998), respectively. In 2006, station C1 has been included in the Italian network of long-term ecological research sites (LTER-Italy) as part of the northern Adriatic LTER site. In 2016, the station 000F was included in the LTER-Slovenia network.

Station C1 is located in relatively shallow waters (17.5 m) in the north-eastern part of the Gulf, 200 m far from the coast and 11.5 km far from Isonzo River mouth. The other two stations, 00CZ and 000F, are located in the central and southern part of the Gulf (Fig. 1). Station 00CZ (bottom depth of 25 m) is 7 km far from the coast and 13 km from Isonzo River mouth while station 000F (bottom depth of 22 m) is 1.3 km far from the coast, 21 km from Isonzo River mouth but only 5 km from other smaller rivers.

The University of Trieste and the Marine Biology Laboratory carried out regular surveys of oceanographic parameters at station C1 from 1986 to 2005 when OGS took over the sampling.

In the earliest period of the Italian time series (C1), i.e. from 1986 to 1990, data of temperature and salinity were obtained with the Beckmann RS 5-3 Salinometer (Cabrini et al., 1994). From 1990 onwards, data of temperature, salinity, and oxygen concentration and saturation were obtained using an Idronaut Ocean Seven (models 401 and 316) or a SBE 19plus SEACAT multiparametric probes, calibrated every 6–12 months.

Prior to 1991, salinity of bottle samples was determined by chlorinity titration (Grasshoff et al., 1999), while temperature was measured using Niskin reversing thermometers at the two Slovenian stations (000F and 00CZ). After 1991, vertical profiles of temperature, salinity, density and dissolved oxygen were obtained using two fine-scale CTD probes. The first probe, designed by the University of Western Australia for ecological fieldwork, was used from 1991 to 2007, while from 2007 onwards the Microstructure Profiler MSS90 (Sea & Sun Technology GmbH) was used. Both probes were calibrated once a year.

The general sampling frequency at the three long-term stations was once per month, although weekly and biweekly samplings occasionally occurred. In order to obtain a homogenized dataset, when more than one sampling was performed in one month, the data of that month were averaged. Water samples were collected at discrete depths, depending on the sampling period and station depth.

##### 3.1.2. Analyses

At station C1 the dissolved oxygen data was determined by Winkler method (Grasshoff et al., 1999), while at stations 000F and 00CZ the DO was measured by Winkler method until 2008. From 2008 onwards only the CTD probe equipped with a AMT DO optode was used to measure DO concentrations. During the period from June 2007 until december 2008 both methods were used. The AMT DO optode was calibrated during the regular CTD calibrations which were carried out against „WINKLER titration“ (iodometric titration) as reference.

Chlorophyll a concentrations, corrected for phaeopigments, were determined fluorometrically (Holm-Hansen et al., 1965) in 90% acetone extracts on Turner Designs fluorimeters, Model 112 until 2005 and Trilogy from 2006 onwards for the stations 000F and 00CZ. On the contrary, on station C1 Chlorophyll a concentrations have been measured by spectrophotometry from April 1986 to July 1990 and by spectrofluorometry from October 1998 onwards, according to Lorenzen and Jeffrey (1980), using PerkinElmer LS50B or JASCO FP 6500 spectrofluorometers. Rates of oxygen utilization were estimated from the changes in DO during 24 h incubations in the dark at in situ temperature ( $\pm 1$  °C). Dissolved oxygen concentrations were determined in triplicate bottles at the beginning and at the end of the incubation by Winkler method (Grasshoff et al., 1999). The relative standard deviation of replicated analyses was <10%. Respiration rates were expressed in  $\mu\text{mol O}_2 \text{ L}^{-1} \text{ h}^{-1}$ .

### 3.1.3. Summer 2015 and 2016 oceanographic surveys

Twenty-eight stations distributed along the Gulf of Trieste (Fig. 1) were monitored for the DO concentration and consumption during the summer months. Hydrological data analyzed for this study refers to monthly CTD profiles collected in July and August 2015 and 2016 (Table S1). Of all these stations, 18 were monitored by ARPA FVG by means of the CTD probe Idronaut Ocean Seven 316 *plus*, 1 by OGS using the SBE 19plus SEACAT and 9 by NIB by means of the Microstructure Profiler MSS90. All the CTD profiles were averaged at 0.25 m.

### 3.1.4. Automatic buoy measurements

Close to C1 station, near-real-time data of temperature, salinity, dissolved oxygen and meteorological variables were acquired by MAMBO meteo-oceanographic buoy, operative since 1998, (<http://nettuno.ogs.trieste.it/mambo/>; Lipizer et al., 2017; Ravaioli et al., 2016), equipped with surface meteorological sensors for atmospheric temperature, pressure, humidity and wind speed and direction (Young mod. 05106) and underwater CTD sensors (SBE37-ODO at 1.5 m depth, SBE-16 at 15 m). On VIDA buoy a CTD (SBE, Seacat 16plus at 2.5 m) and oxygen sensor (Aandera, Oxygen optode 4835 at 23 m) are installed (<https://www.nib.si/mbp/en/oceanographic-data-and-measurements>).

### 3.1.5. Isonzo River discharges

Daily averaged flow rates ( $\text{m}^3 \text{s}^{-1}$ ) of Isonzo River were provided by ARPA FVG and by ACEGAS-APS spa for the period 1998–2016. Wind data for August 2016 were measured by ARPA FVG-OSMER at PALOMA buoy.

### 3.1.6. Duration of the daily solar irradiance

The duration of the daily solar irradiance was estimated from data measured during August 2015 and August 2016 at Pier Fratelli Bandiera in the Gulf of Trieste by ARPA FVG-OSMER (<http://www.meteo.fvg.it>).

## 3.2. Data analysis

### 3.2.1. Oxygen consumption estimates

Stratification is a precondition for hypoxia to occur, thus, the depth of the deeper pycnocline for each of the 28 stations during August 2015 and 2016 was calculated. The pycnocline depth was defined as the vertical position in the water column (depth,  $z$ ) where the square of Brunt-Väisälä frequency ( $N^2$ , eq. (1)) was at its maximum value (Pond and Pickard, 1983; Testa and Kemp, 2014) as follows:

$$N^2 = [g/(\rho z)] * [\delta\rho/\delta z] \quad (1)$$

where  $g$  is gravity,  $\rho_z$  is the water density at depth  $z$  and  $\delta\rho/\delta z$  is the density gradient at depth  $z$ , using a 0.25 m window around  $z$ .

The Apparent Oxygen Utilization (AOU) was calculated as the difference between equilibrium saturation concentration in water and the measured DO concentration (Pytkowicz, 1971), providing an approximation to the balance between biological processes of primary production and respiration.

At each station the mean DO concentrations under the pycnocline was calculated by trapezoidal method every 0.25 m and then integrated for the thickness of the water layer. The spatial distribution was obtained by interpolating the integrated DO values with ordinary kriging method on a 2D grid, covering the studied area. The volume under pycnocline was calculated, as the volume comprised between the depth of pycnocline and the depth of seafloor. All the interpolations were performed using Surfer 9 program (Goldensoftware, USA).

To calculate the total DO (tDO) for each month, the mean integrated DO concentration was multiplied by the volume under pycno-

cline. The DO consumption ( $\text{DO}_c$  in  $\text{mmol O}_2$ ) was calculated as the difference between the tDO calculated in July and in August.

The time needed by respiratory and oxidative processes over the 24 h (to consume the  $\text{DO}_c$  under pycnocline) was also estimated.

The time ( $T_d$ , in days) for the occurrence of the summer oxygen depletion was estimated dividing the  $\text{DO}_c$  by  $R$  (net daily oxygen consumption in  $\text{mmol O}_2 \text{d}^{-1}$ ), defined as:

$$T_d = \text{DO}_c / R$$

$$R = PR$$

- \*  $V + \text{SOC}$
- \*  $A - PP$
- \*  $V - BPP$
- \*  $A - F$
- \*  $A$

calculated as the sum of the planktonic respiration (PR), and sediment oxygen consumption (SOC: benthic respiration and sediment chemical oxidation) minus DO produced by planktonic primary production (PP), and benthic primary production (BPP) over the mean irradiance time during August (12.7 h and 12.8 h for 2015 and 2016, respectively) and vertical DO diffusion (F) through the pycnocline, multiplied per area ( $A$ ,  $\text{m}^2$ ) or volume ( $V$ ,  $\text{m}^3$ ).

The vertical flux (F) of the DO through the pycnocline was estimated according the Ficks law:

$$F = -K_z \delta[\text{O}_2] / \delta z \quad (2)$$

where  $\delta[\text{O}_2]$  is the dissolved  $\text{O}_2$  concentration ( $\mu\text{mol O}_2 \text{L}^{-1}$ ) difference across the pycnocline,  $\delta z$  is the thickness of the diffusive layer through the pycnocline (m), which was assumed to be of 1 m, and  $K_z$  is the vertical eddy diffusivity ( $\text{m}^2 \text{s}^{-1}$ ) defined as follows:

$$K_z = a \varepsilon N^{-2} \quad (3)$$

The buoyancy frequency  $N$  was calculated as reported above.

For “ $a$ ”, the value of 0.25 from Denman and Gargett (1983), and for “ $\varepsilon$ ”, the value of  $10^{-7} \text{m}^2 \text{s}^{-3}$  according to Justic et al. (2002) were adopted.

### 3.2.2. Statistical analyses

Statistical analyses of trends over time were performed by applying Spearman's rank order correlation using the software STATISTICA 7 (Statsoft, USA).

## 4. Results

### 4.1. Long-term seasonal oxygen depletion and trends during summer

The monthly distribution of DO in bottom waters obtained from 33-, 27- and 22- year time series at stations 000F, 00CZ and C1 (Fig. 2a) clearly shows the marked seasonal depletion reaching the lowest values between August and October in the deepest station (00CZ). The lowest mean concentrations were found in September for 00CZ and 000F ( $150$  and  $198 \mu\text{mol O}_2 \text{L}^{-1}$  respectively) and in August for C1 station ( $186 \mu\text{mol O}_2 \text{L}^{-1}$ ). Low DO concentrations observed during August 2015–2016 (at C1  $97$  and  $99 \mu\text{mol O}_2 \text{L}^{-1}$  in 2015 and 2016; at 000F  $135 \mu\text{mol O}_2 \text{L}^{-1}$  in 2016; at 00CZ  $135$  and  $113 \mu\text{mol O}_2 \text{L}^{-1}$  in 2015 and 2016) are lower than the first quartile for all the stations. Also in June 2016, the observed DO ( $144 \mu\text{mol O}_2 \text{L}^{-1}$ ) in 00CZ station is considered as an extreme value.

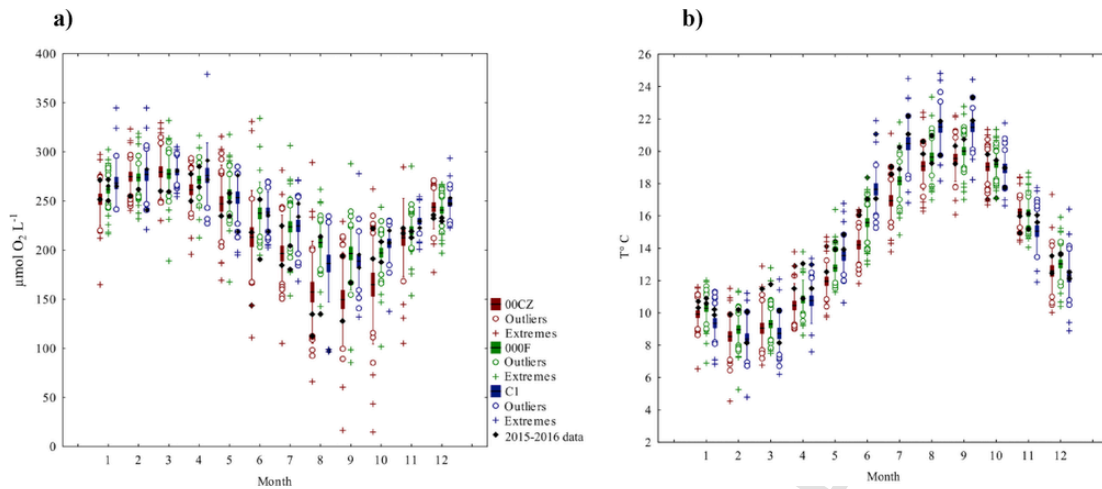


Fig. 2. Dissolved oxygen (a) and temperature (b) climatology in bottom waters at 000F, 00CZ and C1 stations. Boxes represent the interquartile range (25th to 75th percentile), the horizontal line is the mean, circles represents the outliers and crosses are extreme values (that are  $>$  or  $<$  than 1.5 and 3 times the interquartile range, respectively).

Over the whole investigated period, hypoxic conditions ( $< 45 \mu\text{mol O}_2 \text{ L}^{-1}$ ) were recorded only at the 00CZ station during September 1995 and October 1995 and 2001, while DO stressed conditions ( $< 143.8 \mu\text{mol O}_2 \text{ L}^{-1}$ ) were observed frequently at all sampling stations from June to November. The highest number of events (34) was observed at 00CZ station (Fig. 3a), while at the stations 000F and C1 only 5 events were registered. The analysis of the temporal distribution of DO stressed conditions indicated that these events were highly scattered across the whole study period and among the stations (Fig. 3b). A cluster of hypoxic ( $< 45 \mu\text{mol O}_2 \text{ L}^{-1}$ ) or moderately hypoxic events ( $< 62.5 \mu\text{mol O}_2 \text{ L}^{-1}$ ) was observed in the bottom layers of the station 00CZ between 1990 and 2001 (Fig. 3b). In contrast, DO concentrations lower than  $92 \mu\text{mol O}_2 \text{ L}^{-1}$  were not observed after 2001. In the period 2004–2016 only 20 events of DO stressed conditions occurred, with a minimum of  $111 \mu\text{mol O}_2 \text{ L}^{-1}$ . However moderate hypoxic conditions were found during the surveys carried out in the study area in August 2015 ( $53 \mu\text{mol O}_2 \text{ L}^{-1}$ ) and 2016 ( $48 \mu\text{mol O}_2 \text{ L}^{-1}$ ) in the (Fig. 3b), as will be presented in the chapter 4.3. The temporal distribution of the five events registered at 000F station was more homogeneous, three until 1994 and two after 2007, while in C1 station four of the five events were registered in 2011–2016, however it has to be considered the lack of the data in the period (1991–1998). Except for two events registered at 00CZ in June 2016 and October 2011, during the period 2011–2016 the hypoxia events occurred mainly in August and September.

Temperature climatology (Fig. 2b) in bottom waters also denotes a marked seasonality, with the maximum values observed from July to September. Data recorded in 2015 and 2016 were mostly exceed the mean climatological values and the most of these values were higher than the third quartile from January to August.

Based on the climatology a seasonal window for hypoxia prone months was selected, to give a better description of low oxygen conditions: the months considered were from August to October. For the temperature trend analysis also July was included, considering it as a preconditioning phase (Table 1). The trends of temperature, DO, apparent oxygen utilization (AOU), Chlorophyll a and salinity for the three long-term stations are reported in Table 1. Despite large variability, several parameters showed significant long-term trends. In the upper 20 m of water column at stations 000F, 00CZ and C1, temperature, salinity and AOU display significant ( $p < 0.05$ ) positive correlation with time, whereas DO and Chlorophyll a show a significant opposite trend. On the contrary, in deep waters DO increases with time, whereas AOU decreases, though only at 00CZ station ( $> 24 \text{ m}$ ).

#### 4.2. Riverine freshwater discharges

The Isonzo river flow oscillated between a monthly mean discharge of  $7.5$  and  $405 \text{ m}^3 \text{ s}^{-1}$ . During both summers 2015 and 2016, the discharges were at minimum (Fig. 4). During the winter 2015 the freshwater discharges were scarce with respect to the 1998–2016 climatology, while the winter discharges in 2016 were mostly higher compared to the same climatology. On the contrary high discharges were typical for both autumns, during September–October 2015, and October–November 2016. On average the monthly discharges in 2016 were 2.5 fold higher than in 2015 particularly in spring, when they were up to 3 folds higher.

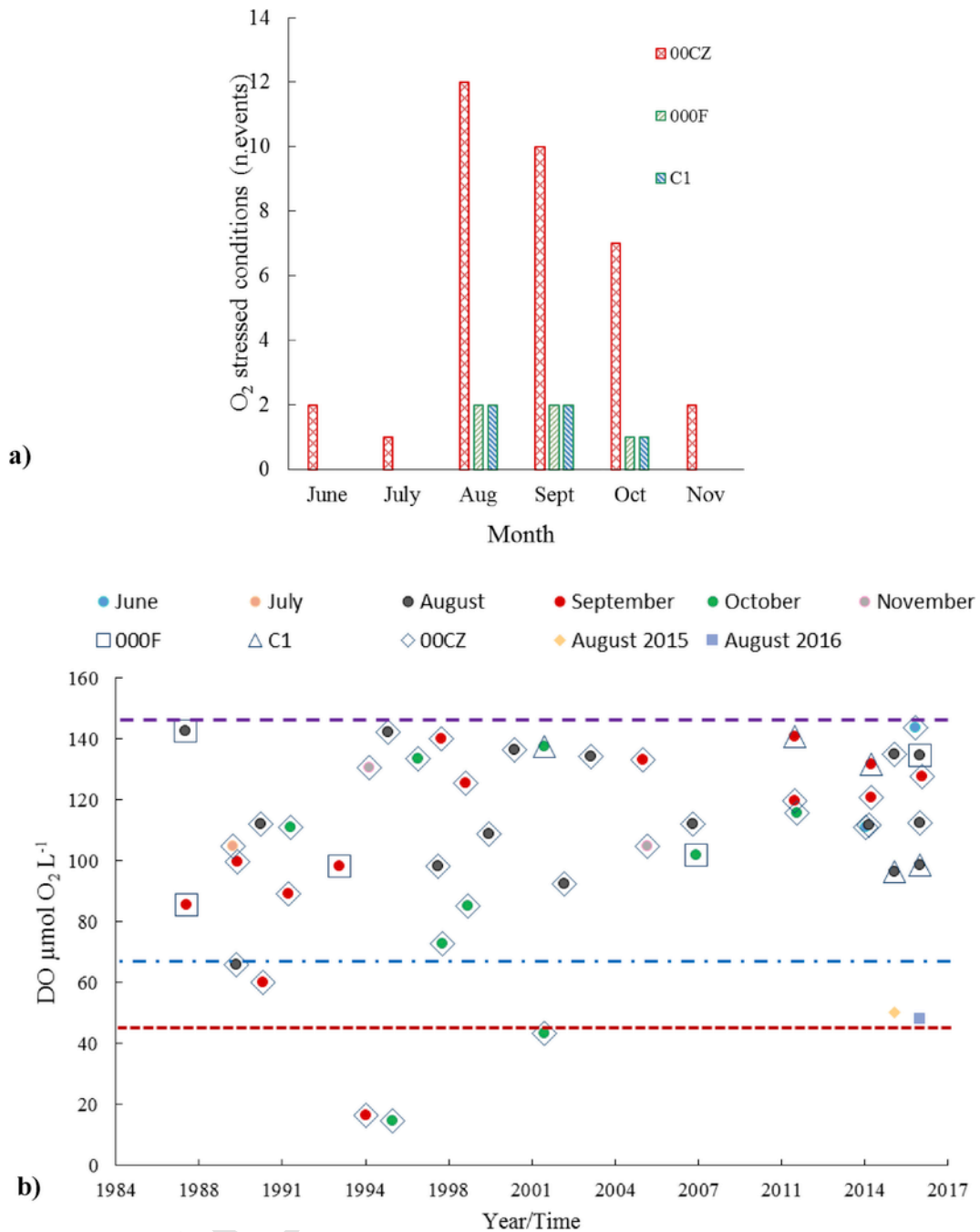
#### 4.3. Recent seasonal hypoxic events (2015–2016)

##### 4.3.1. Monthly variability of thermohaline properties and dissolved oxygen

The temperature profiles of the three long-term stations in the period 2015–2016 showed a marked seasonal variation ranging from  $8.2$  to  $28.3^\circ\text{C}$ , both extremes observed at C1 station in February and July 2015, respectively (Fig. 5). In general, the maximum values were observed in July at the surface, while the lowest values characterized the whole water column in January/February. The maximum surface temperatures were detected in summer 2015; however, during summer 2016 the deeper thermocline and higher bottom temperatures, which lasted until September, were observed. Surface temperatures were relatively comparable across the entire Gulf, while the depth of the thermocline varied greatly between stations. During July 2015, temperatures reached values higher than  $25^\circ\text{C}$  down to  $10 \text{ m}$  depth, with peaks of  $28^\circ\text{C}$  in the  $3.5 \text{ m}$  surface layer at C1 station. Notably high temperatures ( $> 25^\circ\text{C}$ ) were observed also at the stations 000F and 00CZ (down to depths of  $8.9$  and  $3.2 \text{ m}$ , respectively). During 2016, the maximum temperature ( $> 26^\circ\text{C}$ ) was reached in July at C1 station from surface down to  $6.5 \text{ m}$  depth. Values higher than  $25^\circ\text{C}$  were observed down to  $11 \text{ m}$  depth at C1,  $3.9 \text{ m}$  at 000F and  $1.4 \text{ m}$  at 00CZ stations. Bottom temperatures were higher during 2016 at all stations. Approximately  $20^\circ\text{C}$  were measured at 000F and 00CZ stations (at  $22$  and  $25 \text{ m}$  depth) from July until September, while in the same period of 2015 the temperature was about  $19^\circ\text{C}$ . In C1 station at  $17 \text{ m}$  depth the maximum ( $23.1^\circ\text{C}$ ) was registered during September 2016.

Salinity varied strongly among stations, due to differences in riverine waters advection, related to the location of the stations (Fig. 5). The stations C1 and 00CZ were more influenced by the freshwater inputs, while the 000F station, the most eastern one, showed the highest





**Fig. 3.** a) Number of events with oxygen stressed conditions ( $DO < 143.8 \mu\text{mol O}_2 \text{ L}^{-1}$ ) in bottom waters observed in 000F (1983–2016), 00CZ (1989–2016) and C1 (1986–1990; 1998–2016) stations and b) low oxygen concentrations distribution over time. The upper boundary for oxygen stressed, moderately hypoxic and hypoxic conditions are indicated by violet, blue and red dashed lines, respectively. The DO minima measured in the summer 2015 and 2016 surveys are reported in the insert graph b). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

salinity values, in particular at the bottom. Haline stratification was present during spring and summer months with peaks in May and June 2016, when the river discharges were the highest. The duration of the stratification period varied from one year to another: 2015 was characterized by a longer period of stratification and fresh water influence especially in 00CZ station, while in 2016 the stratification was more pronounced but limited to the months of May, June and July.

The minimum salinity measured at surface of the C1 station in May 2016 (28.5) was not observed in the other two stations. On the contrary, the extremely high salinity ( $>38$ ) observed at bottom during the

winter months and in September 2016 in the stations 000F and 00CZ was not detected at C1 station.

The DO dynamics in the period 2015–2016 reflected the bottom-water ventilation in winter related to wind-induced mixing, and thermal stratification and DO depletion in summer (Fig. 6). During cold weather in December and January of both years, water DO remained constant. The biological activity led to the increase in DO concentrations from February to May, while a considerable decrease appeared in June, which eventually resulted in bottom-water oxygen stressed conditions with different evolution at the three station and in both years.

During August 2015, an extraordinary DO stressed condition was observed at C1 station, with values lower than  $105 \mu\text{mol L}^{-1}$  over the

**Table 1**

Linear regression between Temperature, Dissolved Oxygen (DO), Apparent Oxygen Utilization (AOU), Chlorophyll a and salinity (Sal), and time/year. Values in bold are considered as statistically significant.

Parameter (unit)	Station	Depth (m)	P	r	Slope (unit y <sup>-1</sup> )	Period		
						(years)	(months)	
Temperature ( °C)	00CZ	< 20	<b>0.050</b>	<b>0.103</b>	<b>0.032</b>		Jul-Aug-Sept-Oct	
		<= 5	0.105	0.111	0.034	1989-2016		
		>= 24	0.061	0.183	0.039			
	000F	< 20	0.001	<b>0.145</b>	<b>0.038</b>		1983-2016	
		<= 5	0.040	0.126	0.033			
		>= 21	<b>0.009</b>	<b>0.201</b>	<b>0.031</b>			
	DO ( μmol O <sub>2</sub> L <sup>-1</sup> )	C1	<= 15	0.000	<b>0.084</b>	<b>0.023</b>		1986-2016
			<= 5	<b>0.034</b>	<b>0.052</b>	<b>0.016</b>		
			< 20	<b>0.001</b>	<b>-0.194</b>	<b>-0.522</b>		
00CZ		<= 5	<b>0.003</b>	<b>-0.233</b>	<b>-0.562</b>		1989-2016	
		>= 24	<b>0.004</b>	<b>0.317</b>	<b>2.028</b>			
		< 20	<b>0.000</b>	<b>-0.226</b>	<b>-0.484</b>			
000F		<= 5	<b>0.000</b>	<b>-0.337</b>	<b>-0.629</b>		1983-2016	
		>= 21	0.638	0.041	0.135			
		<= 15	<b>0.000</b>	<b>-0.380</b>	<b>-1.122</b>	1986-90/1999-2016		
C1	<= 15	<b>0.050</b>	<b>-0.137</b>	<b>-0.698</b>	1999-2016			
	<= 5	0.000	<b>-0.491</b>	<b>-1.133</b>	1986-90/1999-2016			
	<= 5	0.200	-0.127	-0.473	1999-2016			
Sal	00CZ	< 20	<b>0.013</b>	<b>0.150</b>	<b>0.023</b>		Aug-Sept-Oct	
		<= 5	0.082	0.137	0.023	1989-2016		
		>= 24	<b>0.000</b>	<b>0.428</b>	<b>0.023</b>			
	000F	< 20	<b>0.000</b>	<b>0.355</b>	<b>0.036</b>		1983-2016	
		<= 5	<b>0.000</b>	<b>0.368</b>	<b>0.041</b>			
		>= 21	<b>0.000</b>	<b>0.573</b>	<b>0.032</b>			
	Chlorophyll a ( μg L <sup>-1</sup> )	C1	<= 15	<b>0.000</b>	<b>0.075</b>	<b>0.011</b>		1987-2016
			<= 5	<b>0.005</b>	<b>0.087</b>	<b>0.016</b>		
			< 20	<b>0.000</b>	<b>-0.227</b>	<b>-0.026</b>		
00CZ		<= 5	<b>0.001</b>	<b>-0.260</b>	<b>-0.026</b>		1989-2016	
		>= 24	0.711	-0.042	-0.006			
		< 20	<b>0.004</b>	<b>-0.160</b>	<b>-0.014</b>			
000F		<= 5	<b>0.004</b>	<b>-0.207</b>	<b>-0.015</b>		1983-2016	
		>= 21	<b>0.045</b>	<b>-0.206</b>	<b>-0.018</b>			
		<= 15	<b>0.000</b>	<b>-0.289</b>	<b>-0.027</b>	1986-90/1999-2016		
C1	<= 15	0.612	-0.035	-0.005	1999-2016			
	<= 5	<b>0.000</b>	<b>-0.338</b>	<b>-0.024</b>	1986-90/1999-2016			
	<= 5	0.272	-0.107	-0.011	1999-2016			
AOU ( μmol O <sub>2</sub> L <sup>-1</sup> )	00CZ	< 20	<b>0.007</b>	<b>0.162</b>	<b>0.440</b>		1989-2016	
		<= 5	<b>0.011</b>	<b>0.200</b>	<b>-0.026</b>			
		>= 24	<b>0.003</b>	<b>-0.336</b>	<b>-2.178</b>			
	000F	< 20	<b>0.002</b>	<b>0.160</b>	<b>0.349</b>		1983-2016	
		<= 5	<b>0.000</b>	<b>0.292</b>	<b>0.539</b>			
		>= 21	0.361	-0.082	-0.268			
	C1	<= 15	<b>0.000</b>	<b>0.337</b>	<b>1.114</b>	1987-90/1999-2016		
		<= 15	<b>0.032</b>	<b>0.149</b>	<b>0.804</b>	1999-2016		
		<= 5	<b>0.000</b>	<b>0.435</b>	<b>1.131</b>	1987-90/1999-2016		
	<= 5	0.120	0.154	0.612	1999-2016			

whole water column, with the minimum of 96 μmolL<sup>-1</sup> observed at bottom. No evidence of oxygen depleted waters was observed at the 000F station; while 00CZ station was characterized by low bottom DO concentrations (135 μmolL<sup>-1</sup>). Bottom DO stressed conditions were observed during summer 2016 at all the studied sites. The lowest value (98 μmolL<sup>-1</sup>), observed at C1 station, was limited to August, while at 000F station low bottom DO concentrations were detected in August (135 μmolL<sup>-1</sup>) and September (167 μmolL<sup>-1</sup>). On the contrary, at 00CZ station the bottom waters were characterized by DO concentrations lower than 143 μmolL<sup>-1</sup> during the whole summer period, from June to September, except for July.

Density anomaly (Fig. 6) varied seasonally ranging from 20.6 to 29.3 kg m<sup>-3</sup>. The lower values corresponded to surface waters in late spring and the maximum to bottom waters in winter of both years. Both surface warming and fresh water influenced the decrease of the density anomaly and led to increased stratification, which tended to reduce the mixing with the bottom waters and to increase the energy

necessary to mix the water column. Low bottom DO generally matched with the month subsequent to the deeper pycnocline onset, which prevented the mixing with the oxygen saturated surface layers. Chlorophyll a seasonal variations presented in Fig. S1, show low concentrations during winter months and slightly higher values from spring to autumn, in the range of 0–2 μg L<sup>-1</sup>. High concentrations were observed during summer 2016, at 000F (3.9 μg L<sup>-1</sup>) during July, whereas at C1 and 00CZ stations in August (3.1 μg L<sup>-1</sup> and 10.9 μg L<sup>-1</sup> respectively). These maxima deepen with the increase of the distance from the coast. Notwithstanding these high chlorophyll a concentrations, the AOU were positive in all stations indicating the prevalence of respiratory processes.

#### 4.3.2. Short-term variability of thermohaline properties, dissolved oxygen and wind intensity in August 2015 and 2016

The most evident features in the daily evolution during August 2015 in the northern part of the Gulf of Trieste (MAMBO buoy) were

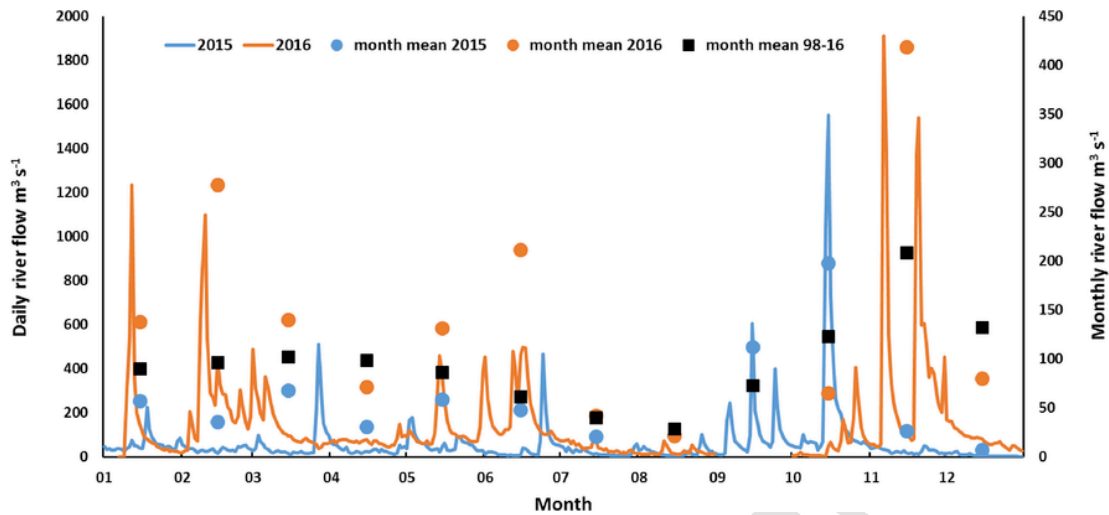


Fig. 4. Isonzo river daily discharge for the years 2015 and 2016 and mean monthly discharge for the years 2015 and 2015 and for the period 1998–2016.

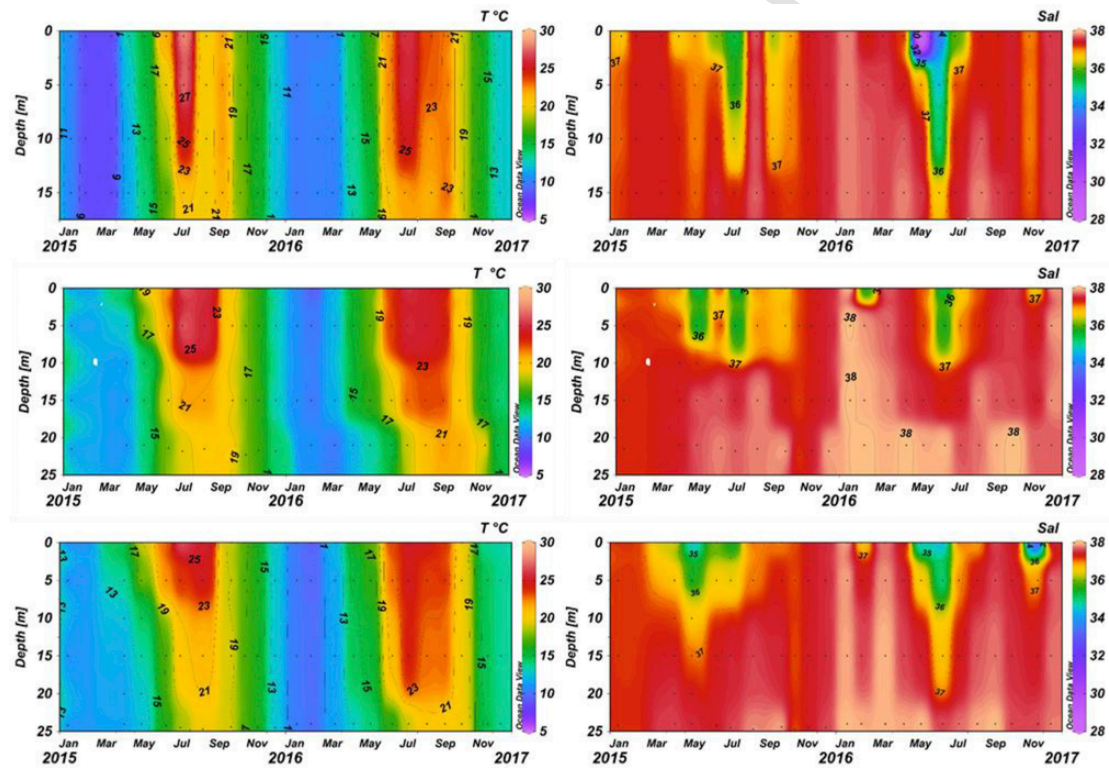


Fig. 5. Temperature (T °C) and salinity (Sal) temporal variations (2015–2016) in the water column at sites C1 (top), 000F (middle) and 00CZ (bottom).

the slight increase of the temperature and salinity from the 3rd to the 14–15th August at surface (Fig. 7b and c), followed by a decrease of the temperature until the 26th, when abrupt changes were detected in a few hours, which were more marked in the surface waters. Surface salinity increased (+1.23) and surface temperature and DO decreased (−3.6 °C and −121 μmol L<sup>-1</sup>, respectively), followed by a quick re-establishment of former conditions.

Strong thermocline and halocline separated high-temperature and low-salinity surface waters from lower-temperature and high-salinity bottom waters.

At bottom, DO concentrations were almost in equilibrium with the surface until the 14th when the concentrations decreased to less than 45 μmol L<sup>-1</sup> in a 10-days period (Fig. 7d). The DO stressed condition lasted for 3 days, from 23rd to the 26th. Starting with the 26th DO

concentrations increased, reaching in few days the concentration of the surface oxygenated waters. Moderately intense ENE wind, with speed up to 12 ms<sup>-1</sup>, characterized the first part of the month (August 3rd to 11th, Fig. 7a). From 11th to 26th wind intensity decreased, while on 26th a strong event of Bora wind (ENE) occurred with intensities of up to 14 ms<sup>-1</sup>, which led to the mixing of the whole water column and the subsequent re-oxygenation of bottom waters.

Also in the southern part of the Gulf (VIDA buoy, Fig. 8) during August 2015 there was a strong thermocline, with surface temperature mainly higher than 25 °C and bottom temperature of 19.58 °C. Surface salinity was quite constant (mean 36.94) except for a minimum of 35.53 observed on 3rd of August 2015 and a three days of high salinity (> 37.5) from 22nd to 25th. In 2016, surface salinity was characterized by higher values (mean 37.27). DO concentrations at bottom during



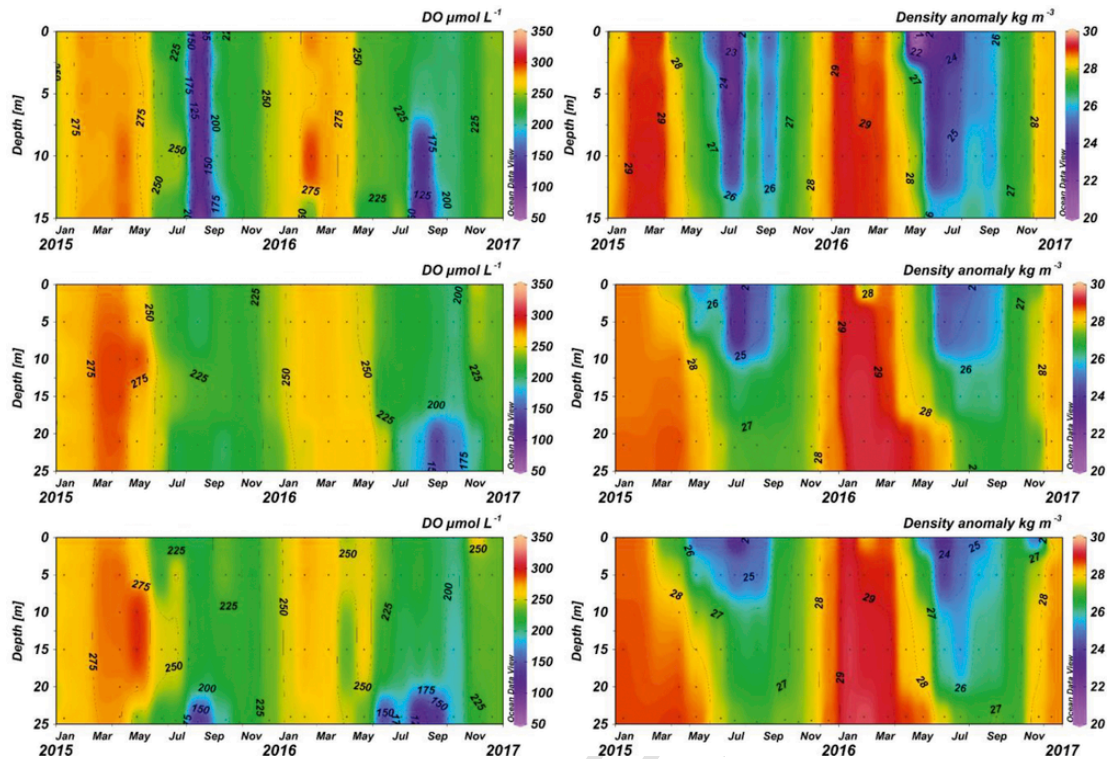


Fig. 6. Dissolved oxygen (DO) and density anomaly temporal variations in the water column at sites C1 (top), 000F (middle) and 00CZ (bottom), during 2015 and 2016.

2015 were constant at  $225 \mu\text{mol L}^{-1}$  except for a 6 days period (2 - 8th of August) when it decreased to  $150 \mu\text{mol L}^{-1}$ . This decrease was concomitant with surface low salinity and lower bottom temperature.

In 2016 mean DO concentration was  $220 \mu\text{mol L}^{-1}$  until the 14th August when it sharply decreased to  $75 \mu\text{mol L}^{-1}$ . This event was coupled with the decrease of bottom temperature and of surface salinity. Low DO  $< 150 \mu\text{mol L}^{-1}$  lasted for 10 days. After August 23rd, when another sharp decrease in DO ( $50 \mu\text{mol L}^{-1}$ ) was observed, DO remained quite constant at  $100 \mu\text{mol L}^{-1}$ .

The decline in DO concentration was apparently gradual. However, analyses of the high frequency measurements revealed that this decline might be occasionally interrupted by brief events of both rapid depletion and ventilation (Figs. 7 and 8). Day to week variability was driven by wind-mixing events. This is particularly evident in the time series of MAMBO buoy data in 2015, when surface DO abruptly decreased, after which surface values of DO, temperature and salinity, equalled those measured in the bottom waters, indicating upwelling of colder, saltier and DO depleted waters. On VIDA buoy a bottom DO decrease from 2 to 8 August 2015 (Fig. 8A) and from 14 to 22 and from 23 to 31 August 2016 (Fig. 8B) were observed. The sudden increase in the oxygenation of bottom waters on the 22 August 2016 was driven by NE Bora wind mixing (Fig. 7e).

#### 4.3.3. Oceanographic features in bottom waters during summers 2015 and 2016: spatial variations

The August 2015 survey, covering 28 stations, was performed in three days (20th, 21st and 26th) and showed a pronounced coastal warming with the maximum temperature ( $25.8^\circ\text{C}$ ) of bottom waters observed in the north-western shallow coast (Fig. 9), where freshwater inflows determined low salinity (35.7) at surface. In the deep (22–23 m) central-eastern area the temperature was around  $19^\circ\text{C}$  and the salinity reached values higher than 37.7. In the same area moderate hypoxia developed in the bottom waters, with the minimum of  $52.7 \mu\text{mol O}_2 \text{ L}^{-1}$ . Coastal warming in the bottom waters in north-western part of the Gulf, observed from the 9th to 17th of August 2016 was

less marked than in 2015 with maximum temperature of  $24.4^\circ\text{C}$  and minimum salinity of 36.4. Temperatures of about  $20^\circ\text{C}$  and maximum salinity (37.9) were observed in the deepest central area (24–25 m), where also the bottom hypoxia occurred (minimum DO  $48 \mu\text{mol L}^{-1}$ ).

Fig. 9.

#### 4.3.4. Dissolved oxygen inventory in the bottom waters during summers 2015 and 2016

Total dissolved oxygen (tDO) consumption from July to August was calculated for both summers 2015 and 2016, when the study area was monitored across a network of 28 stations. The volume of water considered in the DO calculations was dependent on the deeper pycnocline depth and was estimated as  $1.82 \text{ km}^3$  and  $2.12 \text{ km}^3$  during 2015 and 2016, respectively. The volume of oxygen stressed condition (DO  $< 143.8 \mu\text{mol L}^{-1}$ ) accounted for 6% and 8% of the water below the pycnocline. The mean depth of  $\text{O}_2$  depleted bottom waters was 15.9 and 14.5 m in summer 2015 and 2016, respectively.

The mean DO concentrations under pycnocline, were  $268$  and  $168 \mu\text{mol L}^{-1}$  in July and August 2015, respectively, and  $211$  and  $155 \mu\text{mol L}^{-1}$  in July and August 2016, respectively. Therefore the  $\text{DO}_e$  consumed from July to August was  $1.82 \times 10^{11} \text{ mmol}$  in 2015 and  $1.19 \times 10^{11} \text{ mmol}$  in 2016.

To assess the balance between DO consumption and production, the various sources and sinks of DO were quantified and compared with the observed change in DO over the studied period. The schematic representations of oxygen supply and consumption in the bottom layer is represented in Fig. 10. Advective transport was not considered due to the relatively long residence time of the waters in Gulf of Trieste during summer (Cantoni et al., 2003). The main processes considered in the DO balance were planktonic and benthic primary production, plankton respiration, sediment oxygen consumption and the vertical diffusive flux from the upper more oxygenated water mass towards the bottom waters. The horizontal diffusion of oxygen was not considered due to the absence of data on a wider spatial scale.

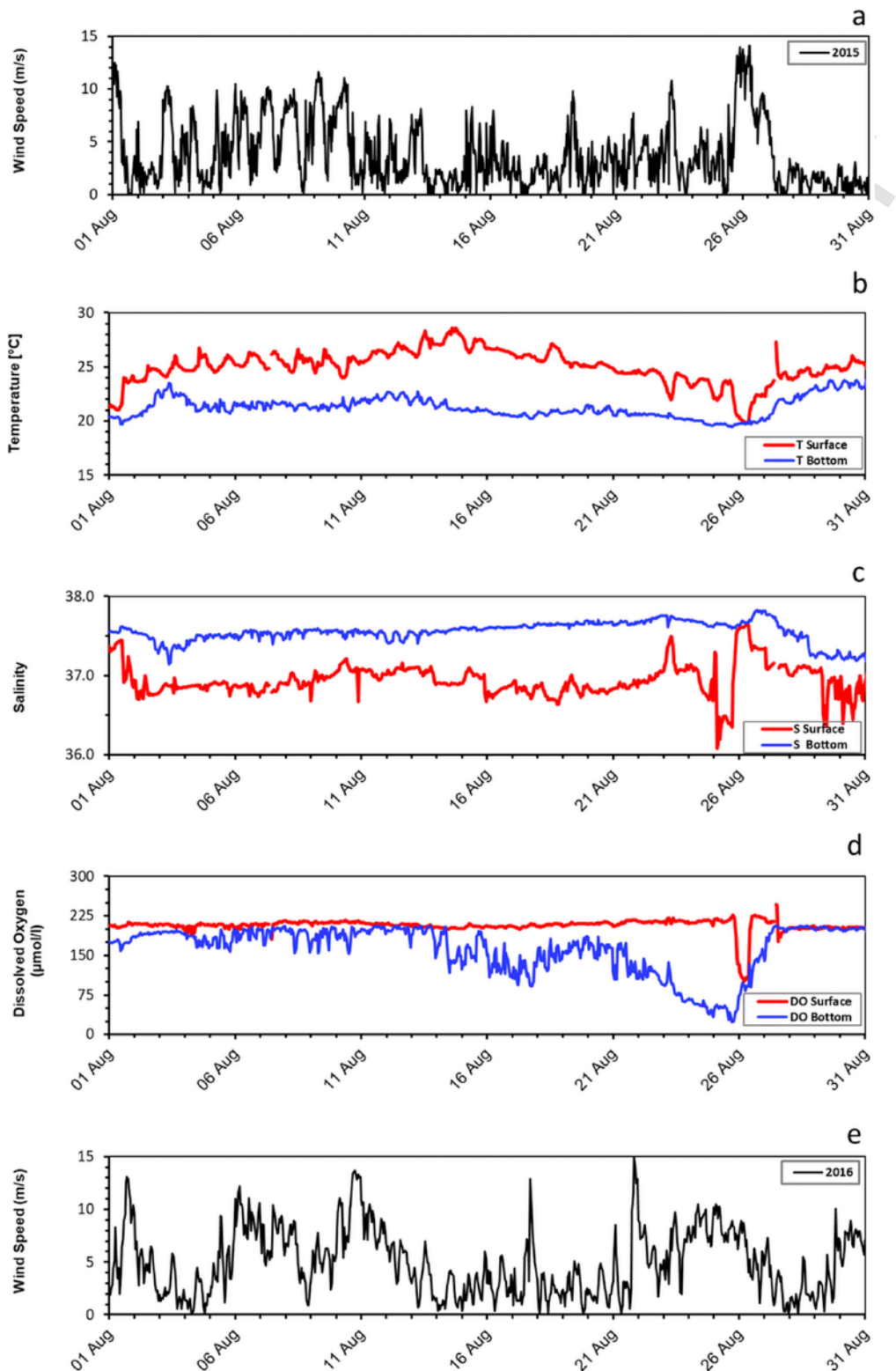
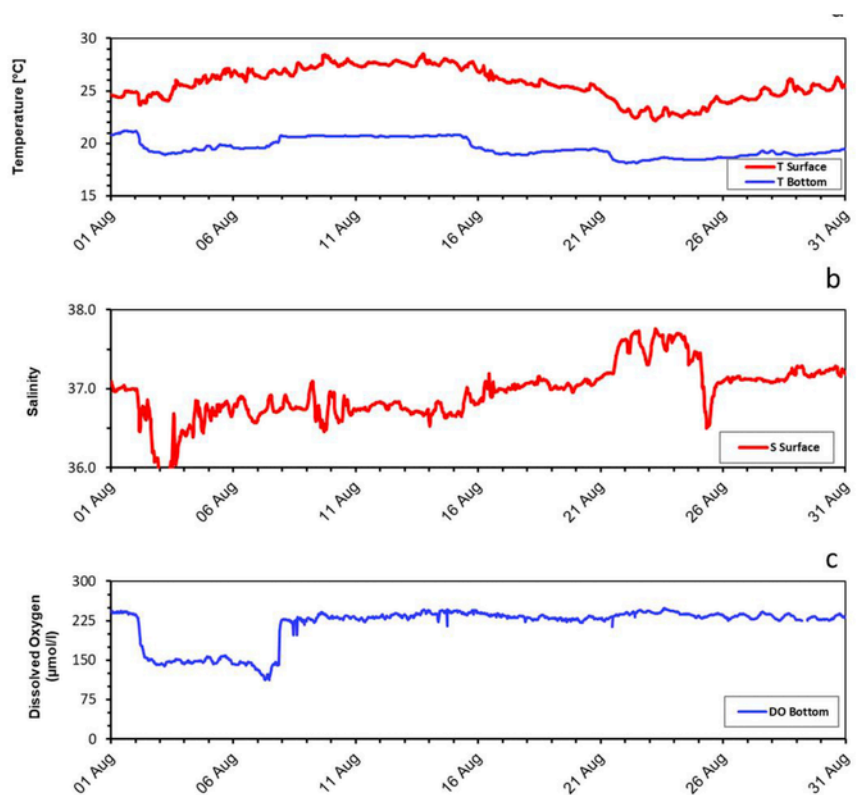


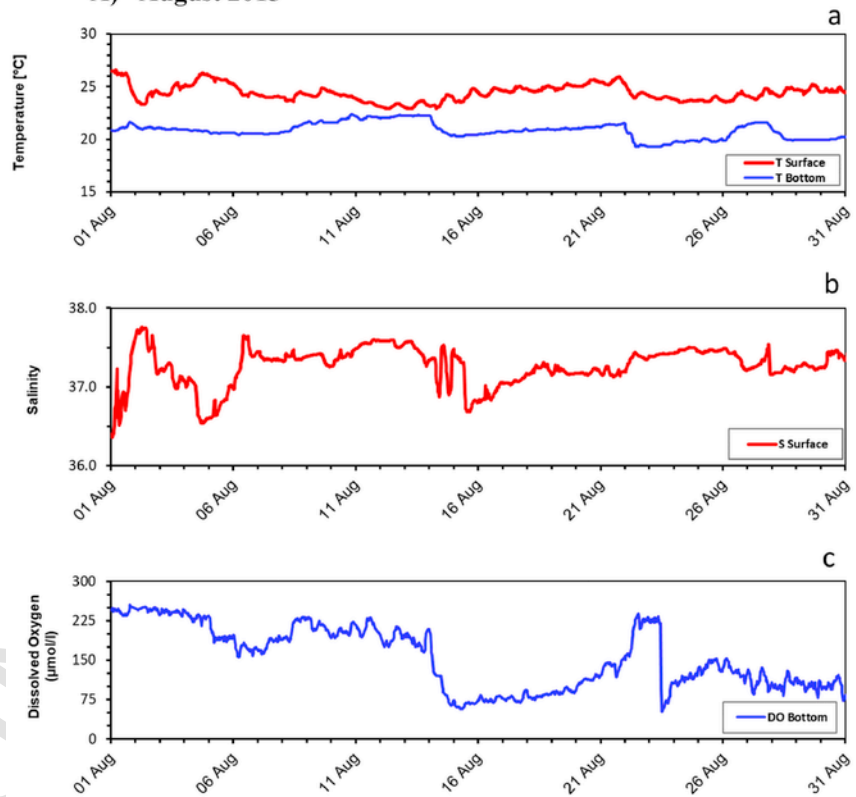
Fig. 7. Wind speed (a), seawater temperature (b), salinity (c) and dissolved oxygen (d) measured at MAMBO buoy during August 2015 (Red line: 1.5 m depth, blue line: 15 m depth). Wind speed measured at PALOMA (e) during August 2016. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Plankton gross primary production was assumed to be  $1.92 \text{ mg C m}^{-3} \text{ h}^{-1}$  (Cibic, unpublished data, measured at 20m during August 2012) similar to estimates reported by Talaber et al. (2018) for August 2010 and 2011 in the southeastern part of the Gulf ( $1.57 \pm 0.65 \text{ mg C m}^{-3} \text{ h}^{-1}$ ). Benthic gross primary production was supposed to be

$10 \text{ mg C m}^{-2} \text{ h}^{-1}$  (Cibic et al., 2008), which was similar to those of Faganeli et al. (1991) and Herndl et al. (1989), measured at 000F station. Benthic and plankton primary production were converted from carbon to oxygen unit assuming a  $-O_2:C$  ratio of 1.34 (Körtzinger et al., 2001). Plankton respiration of  $0.573 \mu\text{mol O}_2 \text{ L}^{-1} \text{ h}^{-1}$  and  $0.365 \mu\text{mol}$



**A) August 2015**



**B) August 2016**

**Fig. 8.** Temperature (a), salinity (b) and dissolved oxygen (c) measured at VIDA buoy during: A) August 2015 and B) August 2016. (Red line: 2.5 m depth, blue line: 23 m depth). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

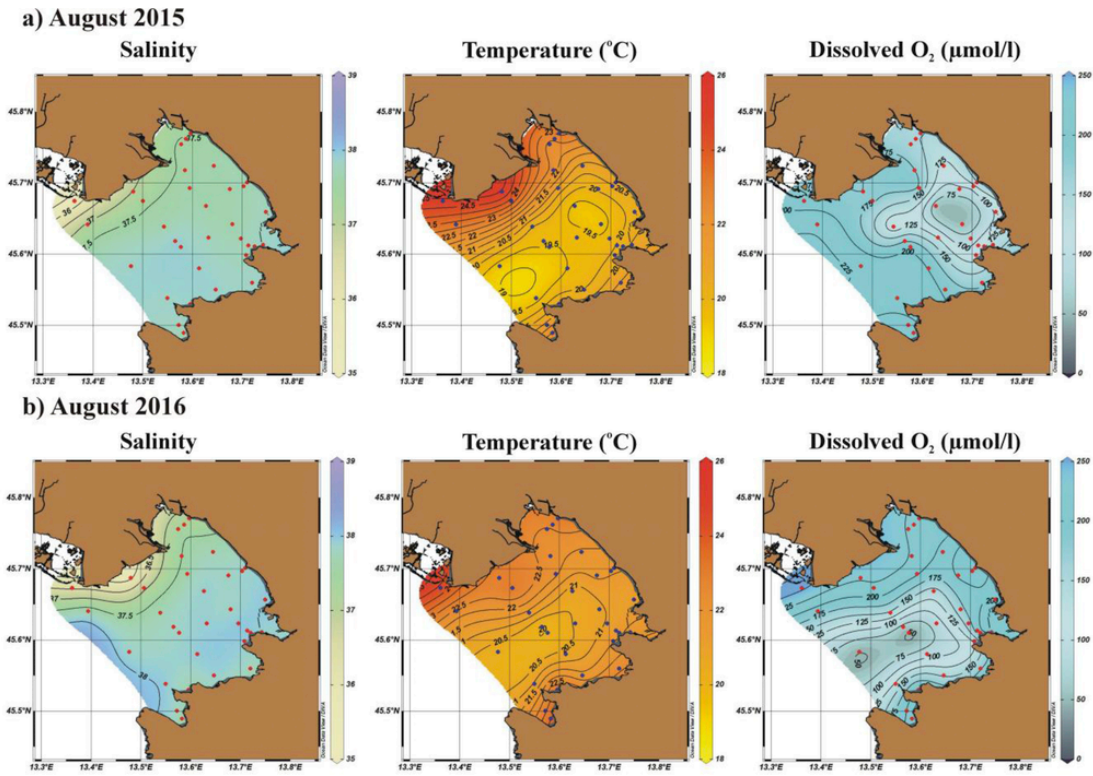


Fig. 9. Salinity, temperature and dissolved oxygen in bottom waters of the Gulf of Trieste in August 2015 (a) and 2016 (b). Dots denote the position of the stations. The maps were produced using Ocean Data View (Schlitzer, R., Ocean Data View, <https://odv.awi.de>, 2018).

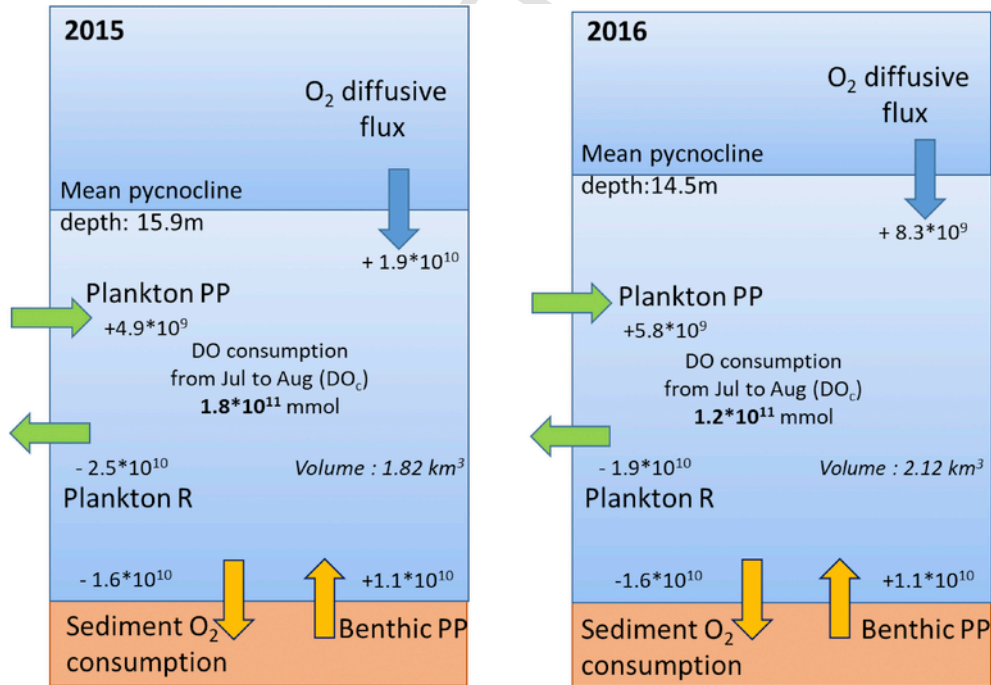


Fig. 10. Scheme of the total dissolved oxygen consumption ( $DO_c$  in mmol), production and vertical diffusive fluxes in the water column during summer 2015 (left) and 2016 (right). Rates are expressed in  $mmol O_2 d^{-1}$ .

$O_2 L^{-1} h^{-1}$  (Fig. S2) were measured at C1 station at  $-15m$  during July 2015 and 2016 respectively, and were similar to those observed by Fonda Umami et al. (2012) during August 1999–2005. For the sediment oxygen consumption was used a mean value of  $25.3 mmol O_2 m^{-2} d^{-1}$  measured by Bertuzzi et al. (1996) in the Gulf of Trieste. As evidenced

by Fig. 10 the dominant biological process was plankton respiration ( $2.5 \times 10^{10} mmol O_2 d^{-1}$  in 2015 and  $1.9 \times 10^{10} mmol O_2 d^{-1}$  in 2016), which exceeded the  $DO$  derived by plankton primary production ( $4.9 \times 10^9 mmol O_2 d^{-1}$  in 2015 and  $5.8 \times 10^9 mmol O_2 d^{-1}$  in 2016).  $DO$  consumption exceeded the production also in the sediments ( $1.6 \times 10^{10} mmol O_2 d^{-1}$  vs.  $1.1 \times 10^9 mmol O_2 d^{-1}$ ). A not negligible



contribution to DO inventory was given also by vertical flux through the pycnocline, with  $1.9 \times 10^{10}$  and  $8.3 \times 10^9$  mmol O<sub>2</sub> d<sup>-1</sup> during 2015 and 2016, respectively.

Fig. 10.

## 5. Discussion

### 5.1. Long-term trends

The Gulf of Trieste is a shallow basin subjected to riverine inputs, strong seasonal variations in temperature and salinity, and intense wind regime. The river-borne nutrient discharges coupled to the circulation regime, which occasionally determines a closed circulation and the entrainment of waters in the northernmost part of the sub-basin, have caused episodic late summer – early autumn hypoxic and anoxic events during the 1970s, 1980s and beginning of the 1990s (Faganeli et al., 1985; Malej and Malačič, 1995), causing mortality of benthic fauna (Stachowitsch, 1991).

In the present work, the long-term Chlorophyll a trend (Table 1) confirmed the previously described decreasing trends in phytoplankton biomass (Mozetič et al., 2010, 2012) and abundance (Cabrini et al., 2012) in the Gulf of Trieste.

Lower phytoplankton biomass can be one of several factors that may contribute to less oxygenated surface waters in the upper mixed layer (Table 1). The consequent decrease of organic matter sedimentation lead to a lower consumption of oxygen in bottom waters during summer-early autumn period, resulting in an increase in bottom DO (Table 1). In addition, the warming trend might have enhanced oxygenation of the upper waters.

A similar trend was observed for the DO in the open northern Adriatic waters (Djakovac et al., 2015). The increasing trend of DO in bottom waters and fewer recent hypoxic/low DO events (Fig. 3, Table 1) coincide with the oligotrophication evidenced in the Gulf of Trieste (Solidoro et al., 2009) and also in the open northern Adriatic (Solidoro et al., 2009; Mozetič et al., 2010; Giani et al., 2012). This was attributed to a marked decrease in the continental discharge of nutrient (Cozzi et al., 2012), notwithstanding the increase of riverine discharges occurred after the marked drought in the mid-2000. Besides the situation observed in the Gulf of Trieste, improvement in oxygen conditions in bottom waters as a consequence of a reversal in trophic trends has also been reported in some areas of the Baltic Sea, which has been affected by eutrophication the last 50–100 years (Andersen et al., 2017; Caballero-Alfonso et al., 2015; Larsson et al., 1985).

Furthermore, a significant increasing trend of the seawater temperatures has been observed ranging from +0.16 to +0.38 °C per decade (Table 1). This trend is significant for the upper to intermediate layer extending to the depth of 20 m. The observed temperature increase is in line with satellite observations (Shaltout and Omstedt, 2014), which evidenced a warming of 0.35 °C per decade (1982–2012) in the Mediterranean Sea, being the most pronounced in spring. A significant positive trend in temperature was observed also at sea surface temperature in the Gulf of Trieste by Raicich and Colucci (2019), and in other areas of the Adriatic Sea (Djakovac et al., 2015; Giani et al., 2012; Grbec et al., 2018; Vilibić et al., 2019). Both physical and biological processes can affect oxygenation of seawater. The seawater temperature increase could contribute to the deoxygenation of surface waters by 2.3% (max) in 30 years or 0.76% per decade.

However, increasing temperature could be more relevant for the DO balance in seawater through the biological processes. The direct effect of warming on plankton manifests as increasing metabolic rates of both phytoplankton and zooplankton, and a growing imbalance between photosynthesis and respiration rates as temperature increases (Lewandowska et al., 2014). Heterotrophic processes are more sensitive to temperature than autotrophic ones (Lopez-Urrutia et al., 2006;

O'Connor et al., 2009), leading to higher grazing rates by zooplankton, which consequently intensify the top-down control of phytoplankton biomass under warmer conditions (O'Connor et al., 2009; Sommer and Lewandowska, 2011). On the other hand, the autotrophic processes can be limited by high temperatures. This was observed in the Gulf of Trieste when extreme summer temperatures above 28 °C induced a decline in surface photosynthesis although the effect of supraoptimal irradiance through photoinhibition could not be discarded (Talaber et al., 2014).

### 5.2. Stratification and oxygen consumption below the pycnocline

In winter 2015, the waters were more oxygenated and colder throughout the water column and for a longer time with respect to 2016 (Figs. 5 and 6). In the bottom layer, the DO decreased with the onset of stratification in June; this was more evident during 2016 in the deeper stations (00CZ and 000F) when also higher salinity at bottom was observed.

Temperatures at the bottom were higher in August 2016 than in August 2015 (Fig. 9). The high differences of temperature and salinity between the surface and the bottom waters in both years determined a marked water column stratification, which contributed to the segregation of bottom waters where oxygen was progressively consumed.

During 2016, the Isonzo River discharges were exceptionally high until March and from May to June (Fig. 4) and contributed to the development of a strong water column stratification (stations C1 and 00CZ). During 2016, bottom DO depleted waters occurred in the 00CZ station already in June and lasted until September.

Considering O<sub>2</sub> production and consumption rates reported in Fig. 10, it was calculated that it would take 28 days to consume tDO in summer 2015, whereas only 13 days would be needed in summer 2016. In order to reach conditions of moderate hypoxia (DO < 62.5 μmol L<sup>-1</sup>), 58 and 34 days would have been needed in summer 2015 and 2016, respectively.

The oxygen consumption estimates in the area during August 2015 ( $4.1 \times 10^{10}$  mmol O<sub>2</sub> d<sup>-1</sup>) and 2016 ( $3.5 \times 10^{10}$  mmol O<sub>2</sub> d<sup>-1</sup>), which exceeded oxygen production ( $1.6 \times 10^{10}$  and  $1.7 \times 10^{10}$  mmol O<sub>2</sub> d<sup>-1</sup> respectively during 2015 and 2016) indicated that the main contribution to oxygen depletion can be attributed to benthic and plankton respiration (Fig. 10).

Plankton respiration accounted for 53–61% of total DO (DO<sub>e</sub>) decrease, whereas sediment oxygen consumption contributed 39–46%. Faganeli and Herndl (1991) showed that the sediment DO consumption in the study area is temperature dependent and follows the Arrhenius equation, which relates the DO consumption (J<sub>O<sub>2</sub></sub>) to temperature:  $\ln J_{O_2} = -5922.98/T + 23.55$  ( $r^2 = 0.64$ ,  $n = 22$ ). Adopting this equation an increase of 1.13 °C in 30 years would increase the sediment DO consumption by 6.7%.

The temperature effect on plankton respiration (PR) in estuaries could be fitted, by combining temperature and chlorophyll (chl) according to the equation of Hopkinson and Smith (2005):  $\log PR$  (mmol C m<sup>-3</sup> d<sup>-1</sup>) =  $0.39 + 0.08T$  (°C) +  $0.45 \log chl$  (mg m<sup>-3</sup>) ( $r^2 = 0.49$ ,  $p < 0.001$ ). If we consider that a temperature increase of 1.14 °C (Table 1, station 000F) and a decrease of Chlorophyll a concentration of 0.40 mg m<sup>-3</sup> (Table 1, station 000F) occurred in 3 decades we could estimate that a 2.6% reduction of plankton respiration could have occurred. This decrease in respiration could explain the increase of DO in bottom waters, and the lower number of hypoxia events observed (Fig. 3b). However during the 2000s also a marked decrease of the river borne nutrient due to a pronounced drought (Cozzi et al., 2012; Mozetič et al., 2012) contributed to the reduce organic carbon availability in the Gulf of Trieste and therefore also a lower oxygen consumption due to oxidative processes. Nevertheless, particular conditions of prolongation or strengthening of stratification can lead to hy-



oxic events despite declining eutrophication, as described in similar systems, because of the long-term temperature increase and temperature-enhanced oxygen consumption in the bottom water (Lennartz et al., 2014). Also a recent temporal reconstruction of past hypoxia events occurred in the Gulf of Trieste attributed a key role to the stratification with respect to the nutrient supply (Tomašových et al., 2017, 2018).

In the Gulf of Trieste, there is a strong seasonal variation in the primary production/respiration ratio, which can vary from 1.68 in spring to 0.14 in autumn (Fonda Umani et al., 2012) with an annual average of 0.89. The warming and the oligotrophication trends (Mozetič et al., 2010) could induce a shift toward a higher prevalence of heterotrophic metabolism with respect to net primary production as also predicted for the global ocean (Regaudie-de-Gioux and Duarte, 2012).

## 6. Conclusions

Long-term DO increase and AOU decrease have been evidenced in the deepest waters of the northeastern Adriatic Sea (Gulf of Trieste).

The warming of surface waters, which is significant down to 20 m depth, contributes to the deoxygenation by decreasing the DO solubilization and to the unbalance between primary production and respiration.

Long-term chlorophyll *a* decrease in the water column, coupled with deoxygenation induced by temperature increase, contributes to a decreasing trend of DO in surface waters.

Dissolved oxygen stressed conditions in the bottom waters are triggered by local conditions, which favour the production and retention of organic matter in the Gulf, coupled with the seasonal stratification. Thirteen to twenty-eight days of oxygen consumption in bottom waters during summer conditions like in 2015 and 2016, can lead to DO stressed conditions, whereas 34–58 days would be necessary to reach the hypoxic conditions.

According to the estimated oxygen budget, in summer planktonic respiration exceeds by 3–5 folds phytoplankton production and is the most intense biological process influencing the oxygenation of the water column.

Future increasing temperature trends could enhance planktonic and benthic respiration, which could play a major role, being a key driver of widespread hypoxia in the Gulf.

Further investigations of the key biogeochemical processes are necessary to better understand the response of the ecosystem under climate-induced changes.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.dsr2.2019.06.002>.

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