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Recent evolution of the physical–chemical characteristics of a Site of National Interest—the Mar Piccolo of Taranto (Ionian Sea)—and changes over the last 20 years

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Abstract The Mar Piccolo of Taranto, classified as a 'Site of National Interest' (SIN), is a semi-enclosed basin divided into two inlets with lagoon features and sea influences, seriously affected by anthropic activities. In the framework of the RITMARE project, a study has been carried out to evaluate the functionality of this ecosystem. As part of this work, measurements of the water abiotic parameters were performed in order to assess the physical–chemical features of this area after the activation, in the last decade, of treatment plants for various urban and industrial dumping. Seawater intrusions and continental inputs, as well as several submarine freshwater springs, clearly affect physical–chemical characteristics of the water column in the two inlets. This finding suggests that small-scale patterns in water circulation have the potential to influence the chemical properties of the seawater. The comparison with a 20-year dataset reveals a drastic decrease in nutrient concentrations after the year 2000, validating the functionality of the treatment plants. The reduction of nutrient inputs into the basin (up to −90 % in the first inlet characterized by lower hydraulic residence time) has changed the biogeochemical characteristics of the Mar Piccolo from being relatively eutrophic to moderately oligotrophic.

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Introduction

Coastal areas, lagoons and transitional areas form unique transitional systems as they are closely linked to both marine and terrestrial factors. The increase of municipal and industrial waters discharge, as consequence of the growth of human population and the development of agriculture, aquaculture and industrial activities, has led to environmental degradation to both water column and benthic habitats in these fragile areas. One of the worldwide largest issues caused by the increase of anthropogenic inputs is eutrophication, especially in areas with limited water exchange and restricted flushing, as estuaries (Cerco and Noel 2007; Mallin et al. 2005; Lopes et al. 2007), salt marshes and lagoons (Magni et al. 2008; Souchu et al. 1998; Velasco et al. 2006). Several studies have provided evidence of the sensitivity of marine systems to changes in nutrient loading and it has been highlighted that the intensity and frequency of eutrophication-related water quality problems are often (but not always) correlated with the supply rates of N and P to the receiving waters (Smith et al. 2006 and references therein). As reported for various coastal systems within the past four decades (Pinckney et al. 2001; Kemp et al. 2005; Cloern and Dufford 2005), also many Italian estuarine and coastal waters have changed from balanced and productive ecosystems to ones experiencing sudden trophic changes, biochemical alterations and a deterioration in the quality of natural habitats.

The identification of this problem has prompted management of discharges, through the construction, implementation or relocation (e.g. in the New River Estuary, North Carolina, Mallin et al. 2005; in Massachusetts Bay, Oviatt et al. 2007; in the Boston Harbor, Taylor et al. 2011) of treatment plants and has allowed the reduction of organic matter and nutrient inputs (Conley et al. 2002).

This is the case of the area of Taranto, which during the 1960s was inundated by an intense industrialization process, with the construction of a large industrial district that completely changed the inner natural marine and land environment. The Mar Piccolo basin, in addition to the inlets of waters from the inland high-cultivated region and the municipality sewage pipes, became affected by numerous industrial and military wastewater discharges. Also the extensive fishing and aquaculture (Cardellicchio et al. 2006), in particular mussel culture, have led to the reduction of the environmental quality. Indeed, Mar Piccolo houses the biggest mussel farm in Italy, with plants widely distributed in both the inlets covering the 61 % of the total surface producing about 30, 000 tons year^{-1} (Cardellicchio et al. 2015). Even if the extensive mussel cultivation is considered to have low impacts compared to fish farming, as it does not require any inputs of feeds, and bivalves can act as a buffer against eutrophication processes by controlling the phytoplankton biomasses, the intense filtration, coupled with the production and the subsequent deposition of faeces and pseudofaeces, increases inputs of labile organic matter to the superficial sediment. This organic matter load, which can be two to three times higher underneath the mussel farm compared to ambient outside the farm, fuels mineralisation processes, stimulating both aerobic and anaerobic metabolism, and nutrient recycling back to the water column by enhancing benthic fluxes (Nizzoli et al. 2005; Souchu et al. 2001; Christensen et al. 2003). Furthermore, the use of the waters in the cooling system of the steel factory quickened the circulation and reduced the flushing times of the waters in the basin to 2–3 weeks and increased the salinity due to the input of waters from the Mar Grande (Caroppo et al. 2012; Umgiesser et al. 2007). These numerous anthropogenic activities influenced the biogeochemical characteristics of waters and sediments, making the area seriously polluted by heavy metals and organics (Cardellicchio et al. 2007; Petronio et al. 2012). Moreover, the increase in the rate of supply of organic matter, the nutrients loading and the scarce hydrodynamism (De Serio et al. 2007) determined strong eutrophication events in the area (Alabiso et al. 1997, 2005; Caroppo and Cardellicchio 1995).

In 1998, with the Italian Legislative decree 426, the area of Mar Piccolo was declared a Site of National Interest for its high pollution. Under this initiative, the Italian Government enacted laws, in September 2001, in order to plan the remediation and environmental cleaning up. Since then, 7 of the 14 municipal discharges were fitted out with treatment plants or relocated to the Gulf of Taranto, with the consequent lowering of nutrient discharges and the improvement of the water quality.

Numerous studies have been done on the Mar Piccolo basin to estimate the impact of the anthropic activities on its physical–chemical characteristics up to the year 2009 (Alabiso et al. 1997, 2005, 2006; Caroppo and Cardellicchio 1995; Cavallo et al. 1999; Giacomini and Alabiso 2006; Umgiesser et al. 2007; Zaccone et al. 2005).

In order to evaluate the effectiveness of the treatment plants and the relocation of the sewage discharges for the reduction of eutrophication and the improvement of water quality of the Mar Piccolo of Taranto, two surveys in 2013 and two in 2014 have been performed, and data obtained were compared with a 20-year dataset. The aim was to achieve an overall physical–chemical evaluation of the environmental conditions of this area, useful for the planning of integrate long-term remediation actions required by the Water Framework Directive (WFD 2000/60/EC), which addresses all surface waters and groundwaters, and the Marine Strategy Framework Directive (MSFD 2008/56/EC), which establishes a framework for marine environmental policy.

Materials and methods

Study site

The Mar Piccolo of Taranto is an inner and semi-enclosed shallow sea located in the northern area of the Taranto Town (Fig. 1). It has a surface area of 20.72 km^2 and is divided by a promontory in two smaller basins named First and Second Inlet (FI and SI). The area is characterized by shallow waters; maximum depths are reached in the centre of the FI (15 m) and in the central part of the SI (10 m) (Pastore 1993).

The FI is directly connected with Mar Grande through two connection channels: the Navigabile channel and the Porta Napoli channel. The fluxes of water through these inlets are generally weak and depend on the difference of density between the two basins. Most of the water inputs derive from numerous small surface watercourses and 34 submarine freshwater springs, called 'Citri', which influence the salinity and the temperature of both inlets (Vatova 1972). The two most important 'Citri' for the freshwater discharges are Citro Galeso in the FI (0.6 m^3 s^{-1}) and Citro Copre in the SI (0.1–1.2 m^3 s^{-1}) (Umgiesser et al. 2007). As more than 80 % of the province of Taranto is used for farming, in particular for the cultivation of wheat, cereal crops and fodder (Calabrese et al. 2014), freshwater inputs carry chemicals drained from the surrounding agricultural soils in the basin (Caroppo et al. 2008; Di Leo et al. 2010). Furthermore, until the year 2000, the discharges of 14 sewage pipes from the nearby towns amounted to 0.21 m^3 s^{-1}, whereof 85 % in the SI (Caroppo et al. 2008).

The basin is generally characterized by low velocity currents (about 5–10 cm s^{-1}) driven by the sea tides, with the

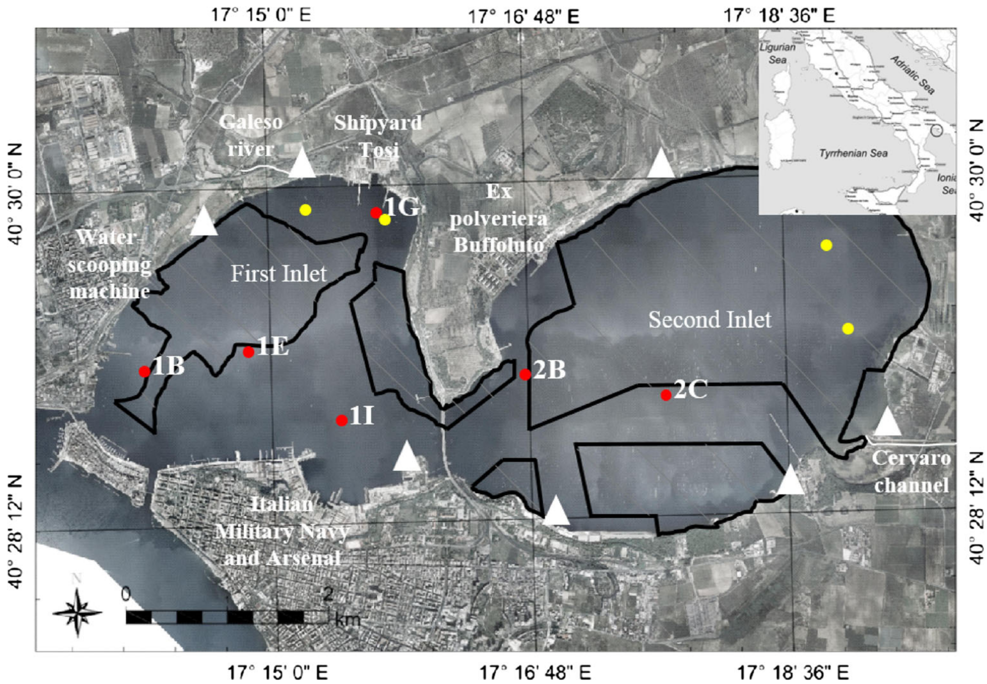


Fig. 1 Study area and location of stations sampled during 2013–2014 in the Mar Piccolo of Taranto. *White triangles* represent the active sewage outfalls, *yellow circles* are the principals freshwater springs 'Citri' and the *black lines* define the mussel farming areas. *Red circles* represent 2013-2014 sampling stations

maximum reached in the two connecting channels with the Mar Grande (up to 30–40 cm s^{-1}) (Umgiesser et al. 2007). From modelling studies (De Pascalis 2013), the dominant currents in the Mar Piccolo show two different components at surface and at 6 m depth. At surface (−1 m), the dominant current flux flows from the SI to the FI and discharges in the Mar Grande through the Navigabile and Porta Napoli channels. This flow generates clockwise currents inside both inlets. On the other hand, at 6 m depth, the current from the Mar Grande flows across the two channels into the FI and then enters in the SI.

The two inlets are characterized by different levels of confinement (Alabiso et al. 2006), i.e. by a different degree of connection to the sea and of sea water renewal time (Melaku Canu et al. 2012). In particular, the SI, due to the limited hydrodynamism and the low water exchange with the nearby Mar Grande, represents the most confined part of the system (Cardellicchio et al. 2007). The morphological characteristic of this inlet, together with the human activities, could be the reason of the reported increase of the fluctuation of nutrients, high water stratification in summer and hypoxia in the lower water layers (Alabiso et al. 2006; Caroppo et al. 2008).

Sampling strategy and analysis

Water samples were seasonally collected in June and October 2013 and in February and April 2014 at six different stations (Fig. 1). Sampling sites were chosen in order to better characterize the different areas of the subbasins. Four stations were located in the First Inlet: 1B, between the channels that connect the Mar Piccolo with the Mar Grande and the area of the cooling water intake (water-scooping machine); 1E, in the middle of the basin; 1G, near the freshwater submarine springs, Galeso River discharges and the former shipyard 'Tosi'; 1I, between the Navy Arsenal and Italian Military Navy and the connection with the Second Inlet. In the Second Inlet, two stations were sampled: the first near the Punta Penna Bridge at ex Polveriera Buffoluto (2B) and the second in the centre of the basin in correspondence of a long-term monitoring site (2C).

Depth profiles of temperature, salinity, oxygen concentration and saturation were recorded by a Sea Bird SBE 19 Plus Seacat multiparametric probe in June 2013 and April 2014, and with a Idromar IP050D multiparametric probe in October 2013. Unfortunately, during February 2014 survey, due to technical problems with multiparametric probes, depth profiles of the hydrological parameters were not recorded. Salinity (at surface and bottom of the six stations) and temperature (at the surface and bottom of stations 1B, 1I and 2C) were immediately measured on board on seawater samples with the conductivity method (CDM83 conductivity meter from Radiometer Copenhagen) while oxygen data are missing.

During each survey, discrete water samples were collected at surface (−1 m) and at bottom, using 5-L Niskin bottles. Subsamples were analysed for dissolved inorganic nutrients (nitrite N-NO_2, nitrate N-NO_3, ammonium N-NH_4, phosphate P-PO_4 and silicate Si-$Si(OH)_4$), dissolved organic and inorganic carbon (DOC, DIC), particulate organic carbon and particulate nitrogen (POC and PN), chlorophyll *a* and phaeopigments (chl-*a* and phaeo).

Samples for DIC analyses were collected minimizing gas exchange with atmosphere, treated with a mercuric chloride solution in order to prevent biological activity and stored refrigerated until analyses. Samples for dissolved inorganic nutrients and DOC were filtered on board on pre-combusted Whatman GF/F filters and kept frozen (−20 °C) until laboratory analysis. Dissolved inorganic nutrients were determined with a segmented flow Bran+Luebbe AutoAnalyzer 3 following standard colorimetric methods (Hansen and Koroleff 1999). The detection limits of nutrient concentrations reported by the analytical methods are 0.02, 0.02, 0.04, 0.02 and 0.02 μM, respectively, for $N\text{-}NO_2$, $N\text{-}NO_3$, $N\text{-}NH_4$, $P\text{-}PO_4$ and $Si\text{-}Si(OH)_4$. The accuracy and precision of the analytical procedures at low concentrations are checked annually through the quality assurance programme QUASIMEME and the relative coefficient of variation for five replicates was less than 5 %. Internal quality control samples were used during each analysis.

DIC and DOC were determined using the Shimadzu TOC-V CSH analyser. For DIC, samples were injected into the instrument port and directly acidified with phosphoric acid (25 %). For DOC analysis, water samples were previously acidified (automatically into instrument syringe, 2 %–6 M HCl) and after CO_2 elimination, the concentration was determined using a high temperature catalytic method (Sugimura and Suzuki 1988). Phosphoric acidification for DIC and combustion conducted at 680 °C on a catalyst bed for DOC, generated CO_2 that was carried to a non-dispersive infrared detector (NDIR). Analysis from a minimum of three injections showed a variation coefficient <2 % and the reproducibility of the method tested with replicate field sampling was between 1.5 and 3 %. DOC results are periodically referenced against the international community of DOC analysts by using consensus reference material (CRM—University of Miami). The instrumental limit of detection (with high sensitivity measurement kit) is 0.33 μM, while it was 1–2 μM defined from measurement of certificated low carbon water (University of Miami) treated in the same way as samples. Analytical results from certified reference seawater of Quasimeme Laboratory Performance Study indicated a good agreement between determined concentrations and the certified values.

Subsamples for chlorophyll *a* analysis were stored in the dark and kept at 4 °C until filtration through 47 mm Whatman GF/F filters that were then stored frozen (−20 °C) until laboratory analysis. Pigments were extracted overnight (4 °C) with 90 % acetone from the homogenate filter and determined spectrofluorometrically according to Lorenzen and Jeffrey (1980). The measurements of chl-*a* and phaeo were performed, respectively, before and after acidification with two drops of HCl 1N using JASCO FP 6500 spectrofluorometer. The coefficient of variation for three replicate samples was lower than 5 %, and the detection limit, defined as twice the standard deviation of three blank filters treated in the same way as samples, was 0.002 and 0.068 μg L^{-1} for chl-*a* and phaeo, respectively. The procedures were quality controlled and monitored by participation in the QUASIMEME intercalibration programme.

POC and PN were measured using an elemental analyser CHNO-S Costech mod. ECS 4010 applying the methods performed by Pella and Colombo (1973) and Sharp (1974). Two subsamples of about 0.5 L each were filtered on 25-mm Whatman GF/F pre-combusted filters and were stored frozen at −20 °C. Before analysis, the filter was treated with the addition of 200 μl of HCl 1N to remove the carbonate and then dried in oven at 60 °C for about 1 h with the similar method of Lorrain et al. (2003). Before the analysis, the filter was inserted in a 10×10-mm tin capsule. Known amounts of standard acetanilide (C_8H_9NO—Carlo Erba; assay≥99.5 %) were used to calibrate the instrument. The detection limit for PN and POC, defined as twice the standard deviation of the blank (5–10 blank 25-mm filters), were 0.01 μmol-N L^{-1} and 0.001 μmol-C L^{-1}, respectively. The relative standard deviations for three replicates of internal quality control sample replicates were lower than 10 %. The accuracy of the method is verified periodically against the certified marine sediment reference material PACS-2 (National Research Council Canada).

Historical datasets (1991–2009)

The data obtained during the four-season surveys in the years 2013–2014 were compared with older data collected in the area in the periods between 1991 and 2009. This historical data are available from separate datasets deriving from different projects (with different sampling points) on hydrobiochemical and plankton distribution in the Mar Piccolo.

- March 1991–February 1992, surface and bottom monthly data from one station in each inlet of the basin (Caroppo and Cardellicchio 1995).
- June 1993–July 1994, monthly surface data from four stations in the FI and three stations in the SI (Alabiso et al. 1997).
- January 1996–December 2004, surface and bottom data at seven stations (four in the FI and three in the SI) (Alabiso et al. 2005, 2006; Giacomini and Alabiso 2006).
- January 2005–October 2009, surface samples of the same seven stations (Alabiso, unpublished data)

As, starting from 2000, the number of sewage pipes has been progressively reduced (Caroppo et al. 2010), the whole dataset was subdivided in two sampling periods: 1991–2000 and 2001–2009. Only the surface data were considered in the elaboration of the dataset because there was too little data from bottom depth.

The monthly evolution of the two groups of data for each inlet is represented by a graphical depiction, using box and whisker plots. This kind of plot represents the distribution of data around the median, symbolized by the central line, the box gives the interval between 25 and 75 % percentiles, the segment indicates the range and the points the outliers. For the 2013–2014 dataset, the surface data were averaged for each inlet and graphically drawn as red diamonds in the second group of data.

Data elaboration and statistical analyses

Graphical representations and statistical analyses were performed using Golden Software Grapher 9, R statistical software (R Development Core Team 2011) and Primer-E Software package v7.0 (Plymouth Marine Laboratory, UK) according with Clarke and Warwick (2001). Different statistical analyses were performed on data in order to define trends and significant differences in the study area among the investigated periods and between inlets. The normality of the data was assessed with the Shapiro–Wilk test. Due to their non-normal distribution, a non-parametric approach was adopted. Spearman rank correlation analyses were performed on all the measured parameters, in order to examine significant relationships between the variables. Statistically significant differences among surveys and inlets for each parameter were tested with the ANOVA Kruskal–Wallis rank sum test. Principal component analysis (PCA), used to investigate patterns in the relative common variables over the stations and to compare the present situation with the former datasets, was performed on normalized variables after z-standardization. Tests for significant differences between the inlets and the surveys for the monitored variables were performed using the two-way crossed analysis of similarities (ANOSIM) test, which was performed considering all the studied variables, except for the parameters "Depth" and "Temperature" which could influence the statistics.

In order to assess the differences in water characteristics in response to the implementation of the treatment plants, a ANOSIM test was performed. The statistics was applied for the evaluation of the differences between the period 1991–2000 and 2001–2009 and between these two datasets and the data collected on 2013–2014.

R statistics for PCA and ANOSIM were interpreted according to Clarke and Warwick (2015): $R<0.25$=no differences in variables pattern; $0.25<R<0.50$=variables among the stations are overlapping but differ to a certain degree; $R>0.50$=parameters among the stations are different.

Results

Hydrology

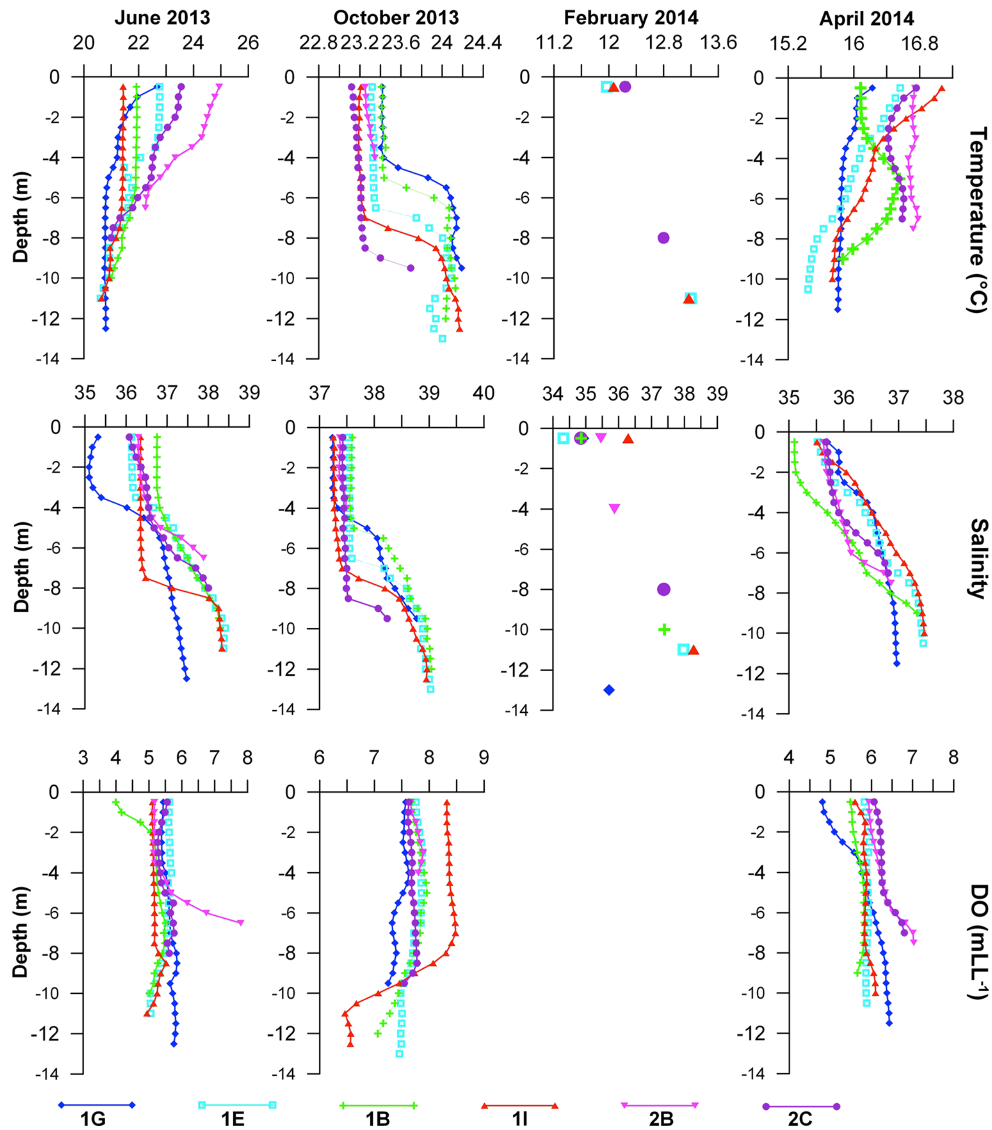
Even if some data from February 2014 survey are lacking, general trends of hydrological parameters can be inferred. During 2013–2014, temperature, as expected, showed a marked dependency on seasonal conditions (Fig. 2). Surface maxima were registered in June in the SI (24.25±0.98 °C) while at the bottom the highest temperatures were measured, at both inlets, in October (23.91±0.33 °C). Minima were reached, at both inlets, in February, with values of 12.09±0.14 and 13.06±0.22 °C, at surface and bottom, respectively. In June, the water column was generally characterized by thermal stratification favoured by the increasing air temperature, with surface values in the FI lower than in the SI, and similar temperature at the bottom waters of both inlets. In the same month, the maximum surface–bottom gradient (2.5 °C) was registered at the SI. During October, a seasonal reverse thermocline developed in both inlets at depths varying from 4 to 7 m. In April, a strong decrease of temperature was detected in both inlets, and the water column resulted quite homogeneous but SI showed weakly higher values than FI.

At each survey, vertical profile of salinity (only surface and bottom data for February survey) showed a positive surface–bottom gradient (Fig. 2). Both at surface and bottom, the maximum of salinity was reached in October (37.60 and 39.04, respectively) and the minimum in February (34.32 and 35.71, respectively).

In June, due to the different influence of freshwater springs in the area, the two inlets were characterized by a wide range of salinity values and by marked stratification. The halocline depth was quite variable: from 3 to 8 m, in the FI, and at 4 m, in the SI. In October, the first 4–5 m of the water column was homogenous (~37.5), while the variability persisted in the deeper waters, where the halocline was still present. In February, the surface mean salinity lowered to 35.12±0.68 with the minimum at St. 1E and the maximum at St. 1I. The bottom average salinity was 37.10±1.07, with the minimum in the St. 1G and the maximum in 1I. Water column stratification weakened in April when, with the exception of St. 1B (S=35.10), the surface salinity averaged 35.69±0.13, even if vertical profiles showed a slight increase.

In June, dissolved oxygen (DO) concentrations (Fig. 2) varied from ~5 to ~6 mL L^{-1} with the exceptions of the strong depletion evidenced at surface of St. 1B (3.99 mL L^{-1}) and of the strong increase up to 7.79 mL L^{-1} in the deeper layer of St. 2B. In October, the two inlets were definitely more oxygenated with DO mean concentrations of 7.43±1.29 mL L^{-1}. Vertical profiles resulted homogeneous in all stations with the only exception of the St. 1I, characterized by waters enriched in DO at surface and depleted at bottom. In April, the study area showed a general decrease in DO concentrations widely ranging from 4.80 mL L^{-1}, at surface of St. 1G, to 7.03 mL L^{-1} at bottom of St. 2B. No occurrence of anoxia was evidenced during the studied period. Unfortunately,

Fig. 2 Physical–chemical profiles of temperature, salinity and dissolved oxygen (DO) in the Mar piccolo of Taranto during June and October 2013 and February and April 2014



dissolved oxygen (DO) data are not available for the February 2014 survey.

Analysis of the former data sets showed a clear seasonal pattern with winter temperature, salinity and oxygen minima and summer maxima both during 1991–2000 and 2001–2009. This temporal evolution was observed at both inlets (Fig. 3). The dataset 2001–2009 was characterized by a large number of outliers in respect to the other group of data. No significant difference in temperature was observed at both inlets between the two considered periods, while the salinity showed significant differences ($p<0.05$) evidencing a general increase, in the second period, especially during summer. For oxygen, too little data were available before the 2001, therefore, the data are represented as a line. Observing the two graphical representations, no clear differences appeared, except for the month of December, characterized by a higher oxygen saturation, after 2000.

Biogeochemical properties of the water column

Seasonal variations of biogeochemical parameters measured during 2013–2014 are graphically shown in Figs. 4 and 5. DOC data are available only for June 2013 and April 2014. On average, concentrations were more heterogeneous and higher during June (119±19 μM) with a peak in St. 1G reaching 155 μM. The highest values, however, were observed in St. 2C in April (164 and 145 μM, at surface and at bottom, respectively) even if, excluding this station, the study area was characterized by a great homogeneity in DOC distribution and, on average, lower values (88±9 μM).

The distribution of DIC was similar in June, February and April with values ranging from 2648 to 2961 μM, while in October, higher values were detected in the whole study area (3289±90 μM). During all surveys, the highest concentrations were observed at surface in relation to the salinity minima. POC and PN spatial and temporal patterns were highly

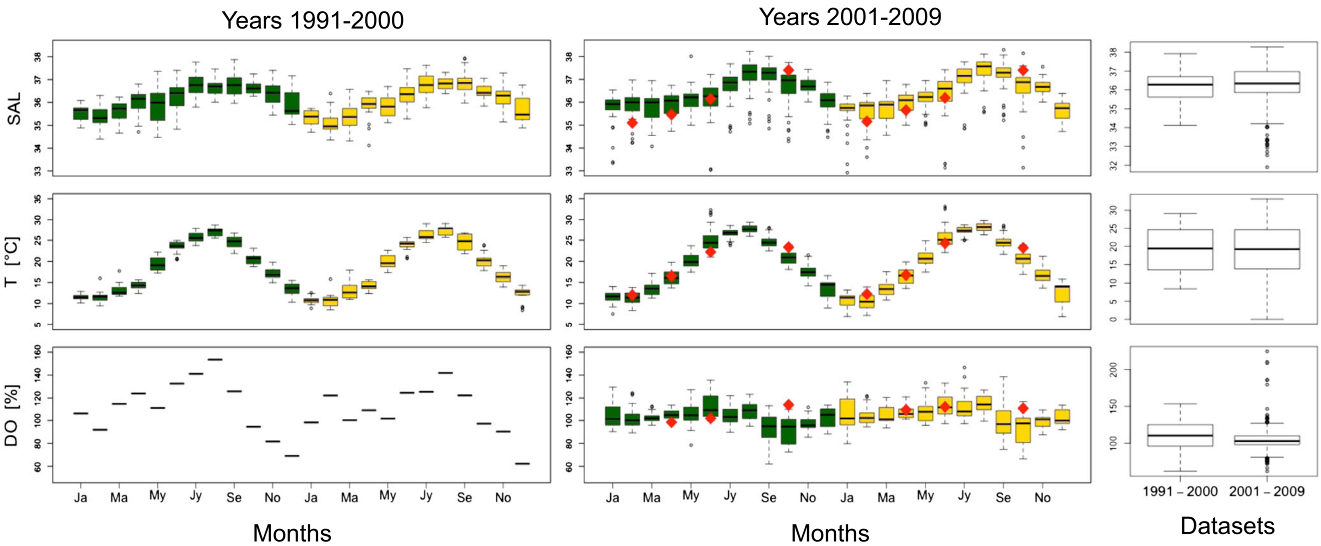


Fig. 3 Box and whiskers plots showing the variability of the monthly values of salinity, temperature and oxygen (SAL, T, DO) in the two different periods (1991–2000 and 2001–2009) at the surface water of the First (*green*) and Second Inlet (*yellow*). On the right, box and whiskers plots showing the variability of the two sets of historical analysed data. *Boxes* represent the interquartile range (25th to 75th percentile), the *horizontal line* is the median, the *ends of the whiskers* are the 5th and 95th percentiles and the *points* are the outliers. *Red diamonds* represent average values of 2013–2014 data

variable with concentrations ranging from 7.87 to 24.06 μM and from 1.02 to 3.52 μM, respectively (Fig. 4). In general, maxima of both parameters were observed in October, while minima were reached in February. The high correlation ($p<0.05$) found between POC and PN indicates a common source of C and N for the entire study area. The average molar ratio of Corg/Ntot (6.94±0.62) (Table 1) was very close to the Redfield ratio and inversely related with DOC ($p<0.05$) suggesting a more autochthonous marine origin of organic matter. The highest values of the ratio (>8) were measured at surface waters of stations more subject to continental input: 1G, in October and April, and 2C in February (Fig. 4). Chl-*a* showed a clear seasonality, with spring maxima (2.15±1.09 μg L^{-1}) and winter minima (0.68±0.69 μg L^{-1}); also spatial differences between the two inlets were found, with higher concentrations reached at the bottom waters of the SI. Phaeopigments, which represent the pigment degradation products, exhibited a different trend showing spring maxima, summer minima and similar values in October and February (Fig. 4). Chl-*a*/Phaeo ratio ranged between 0.27 and 4.68. The highest values and the wider variability were found in June.

Inorganic nutrient distribution showed a wide spatial and temporal variability (Fig. 5). Among nitrogenous species, nitrate concentrations ranged from 0.04 μM, minimum measured in June at the surface of St. 2B, to 36.92 μM, maximum detected at the surface of St. 1G, in April. In June, the water column was characterized by low bottom concentrations (<0.74 μM) at both inlets, while at surface, values ranged between 1.70 and 7.41 μM in the FI and were lower than 0.10 μM in the SI. A slight increase of concentrations, both at surface and at bottom, was detected at either inlets in October, followed by a sharp increase, especially at the surface, in February when a relative maximum of 19.92 μM was reached at St. 1B. In April, the two inlets differed substantially, with the FI clearly influenced by the continental input rising the N-NO_3 surface concentrations, and the SI characterized by quite homogeneous lower values along the water column.

Nitrite was detected in the range of 0.02–0.54 μM, and as for nitrate and ammonium, the highest concentrations characterized the surface waters, in February.

Ammonium concentrations varied from undetectable (at some sampling point, in April) to 3.14 μM (maximum reached at the surface of St. 2C, in February). During June, the two inlets were generally characterized by relatively low N-NH_4 concentrations (range 0.48–0.85 μM). Values increased in October, especially at bottom, where concentrations of two to three times higher (up to 2.27 μM) were reached. An opposite trend characterized February when the maximum concentrations of the study period (higher than 2.30 μM) were observed at surface. In April, at most of the stations, N-NH_4 values were close to or under the detection limit, never reaching values higher than 0.67 μM.

Dissolved inorganic nitrogen (DIN), as sum of ammonium, nitrite and nitrate, was characterized by a seasonal pattern, with lower concentrations in summer, due to the uptake of autotrophic organisms, and higher concentrations in winter, as result of the scarce biological activity and land runoff (Table 1).

At both inlets, N-NO_3 was the main component of DIN during October, February and April constituting from 49 to

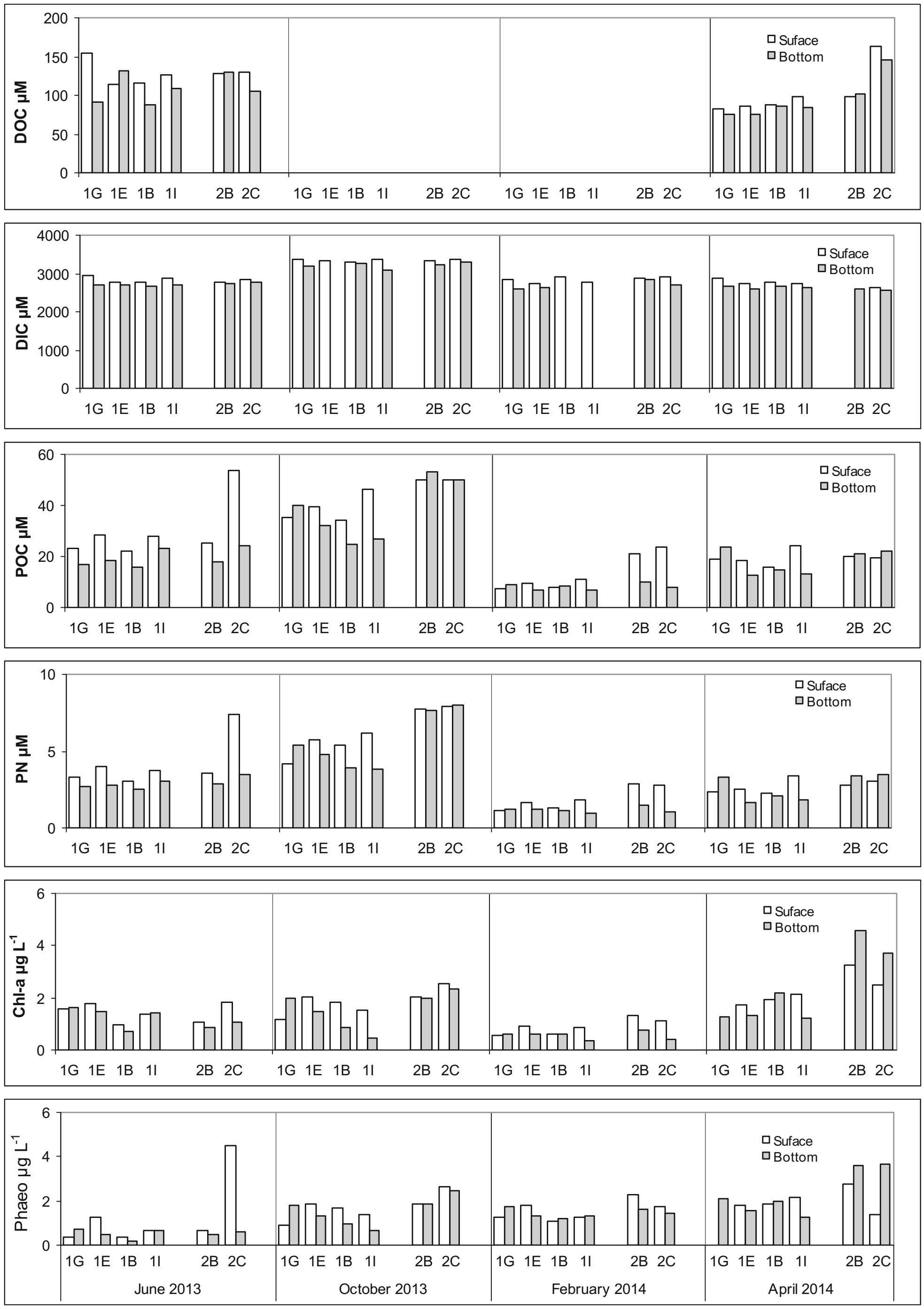


Fig. 4 Surface and bottom concentrations of DOC, DIC, POC, PN, chl-*a* and phaeo in the Mar Piccolo of Taranto during the four sampling surveys (June and October 2013, February and April 2014)

99 %, with the only exception encountered in October at the bottom of St. 2C, when N-NH_4 contributed up to the 67 %. In June, a great variability was observed between the two inlets. In the FI, N-NO_3 predominated at surface while at the bottom N-NH_4 was the main component (>51 %). The only exception was encountered at the bottom of St. 1I where N-NO_3 reached the 58 %. In the SI, the main component was N-NH_4 (>85 %) except for the bottom of St. 2C where predominate the N-NO_3. Nitrite represented less than 6 % of DIN ranging from 0.6 to 5.8 %.

Phosphate varied between under detection limit and 0.65 μM. The seasonal variability was higher than that of other nutrients, showing winter maxima and spring/summer minima. During June 2013 and April 2014, in fact, P-PO_4 concentrations were depleted to low values, often at or near the limits of detection. Temporal pattern at surface seemed to be more definite than in the bottom layer and among the sites, the SI experienced the highest amplitude of the annual phosphate cycle.

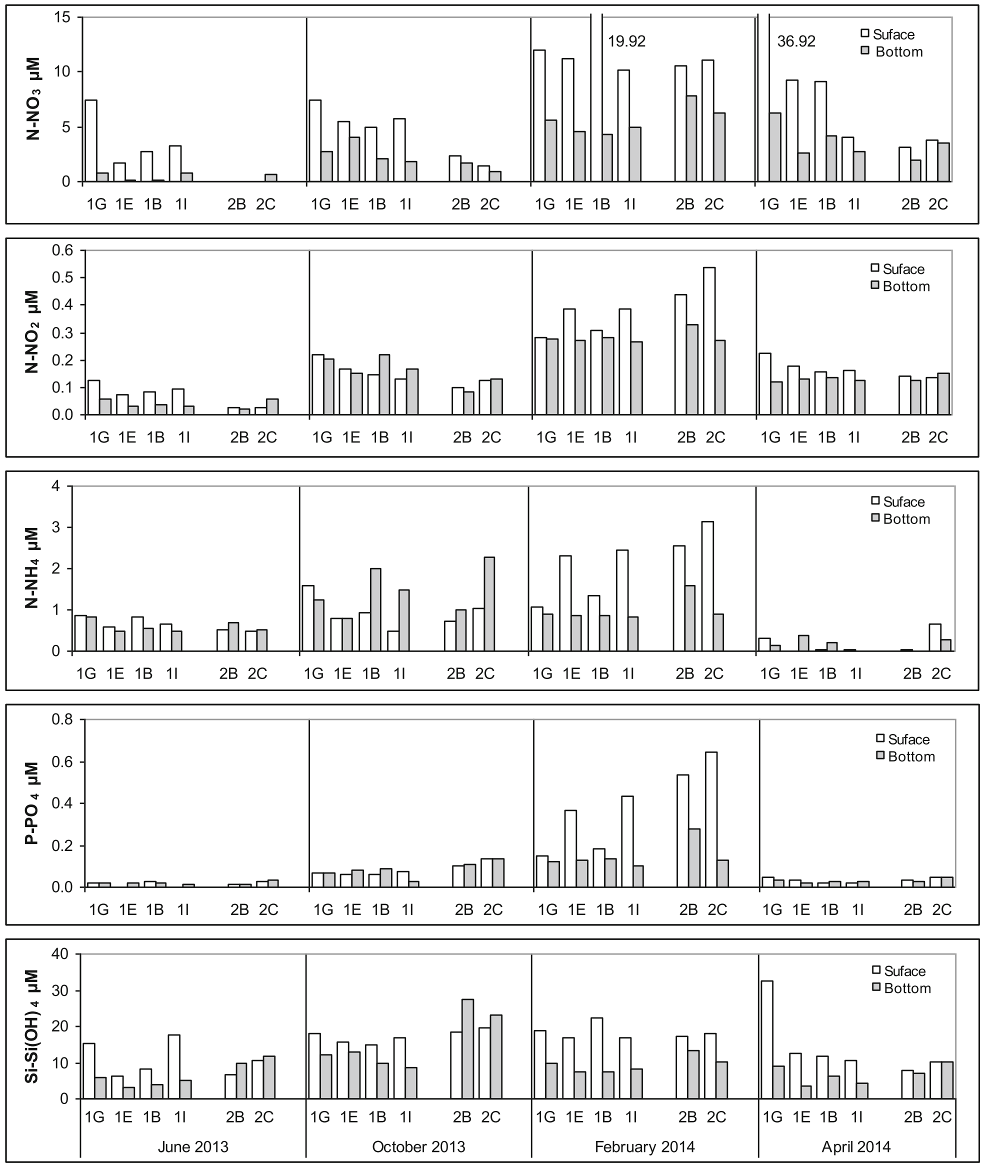


Fig. 5 Surface and bottom concentrations of N, P and Si nutrients in the Mar Piccolo of Taranto during the four sampling surveys (June and October 2013, February and April 2014)

Silicate concentration varied from 3.01 μM (minimum measured at the bottom of St. 1E, in June) and 32.53 μM (maximum reached in April at the surface of St. 1G). On average, seasonal higher concentrations were observed during October (16.50±5.41 μM) and February (13.84±5.08 μM) while lower values characterized June and April even if the absolute maximum was measured, as for N-NO_3, in April 2014 at the surface of St. 1G.

The PCA analyses on 2013–2014 biogeochemical data (Fig. 6) showed that the principal components 1 and 2 explained 71.5 % of the variance. All stations had a clear seasonal variation with DIN and phosphate concentrations characterizing February 2014 and POC, PN and DIC concentrations characterizing October. Between April and June, the distinction is not so sharp, probably due to the generally lower concentrations of ammonium and phosphate characterizing the spring/summer period. The only exceptions are the surface samples of two stations: 1G, in April, influenced by the river load supplying high nitrate and silicate concentrations, and 2C, in June, characterized by high levels of POC and PN.

The analysis of the data in the period extending from 1991 to 2000 (Fig. 7) indicates that N, P and Si show a similar behaviour with maximum values during autumn/winter and minimum values being reached during April–August. The high nutrient values, in January and February, could be ascribed to the high amount of discharges in the rainiest period as suggested by the high N-NO_2+NO_3 concentrations and low ammonia values, while in October, November and December, the remineralisation of organic matter prevailed as confirmed by the higher N-NH_4.

The depletion of silicates, which reaches values at or near the limits of detection, takes place between April and June, while nitrate minimum is observed 1–2 months later. Summer P-PO_4 minima were detected in the SI from April to June,

Table 1 Average and standard deviation values of Corg/Ntot ratios, DIN and chl-*a*/phaeo in the two inlets during the four sampling surveys (June and October 2013, February and April 2014)

		Surface				Bottom			
		FI		SI		FI		SI	
		Average	SD	Average	SD	Average	SD	Average	SD
Corg/Ntot	Jun 2013	7.19	0.20	7.20	0.11	6.77	0.58	6.68	0.47
	Oct 2013	7.28	0.87	6.38	0.07	6.86	0.47	6.61	0.50
	Feb 2014	6.13	0.29	7.89	0.86	6.92	0.70	7.22	0.69
	Apr2014	7.37	0.58	6.77	0.49	7.30	0.22	6.20	0.12
DIN (μM)	Jun 2013	4.62	2.62	0.59	0.01	1.06	0.46	0.98	0.32
	Oct 2013	7.01	1.47	2.85	0.42	4.21	0.59	3.05	0.46
	Feb 2014	15.47	4.09	14.13	0.89	5.89	0.58	8.53	1.65
	Apr2014	15.15	15.08	3.99	0.92	4.25	1.65	3.04	1.29
chl-*a*/phaeo	Jun 2013	2.70	1.42	1.01	0.84	2.91	0.76	1.85	0.07
	Oct 2013	1.15	0.10	1.04	0.10	1.04	0.13	1.00	0.07
	Feb 2014	0.55	0.10	0.61	0.03	0.40	0.11	0.39	0.14
	Apr2014	0.99	0.03	1.51	0.47	0.88	0.21	1.14	0.19

while in the FI no noticeable decrease from the high winter concentrations was evident.

The chlorophyll *a* concentrations appear to follow a classic pattern of annual succession with summer maxima and winter minima. Excluding some outliers and the months of August and September, when maxima up to 10 μg L^{-1} were registered, the concentrations generally did not exceed 5 μg L^{-1}.

Looking at the period 2001–2009, it appears that while before 2001, DIN exceeded 300 μM and phosphate and silicate peaked 15 and 1500 μM, respectively, after 2001 the DIN never reached 40 μM and P-PO_4 and Si-Si$(OH)_4$ were always lower than 0.8 and 40 μM, respectively (Fig. 7). The distribution of nutrient concentrations was in tune with the primary production cycle and the tributaries discharge. The temporal evolution of DIN concentration was characterized by a decrease throughout spring and summer and an evident increase in autumn. Less clear was the evolution of phosphate concentration during spring and summer; nevertheless, as for DIN, highest

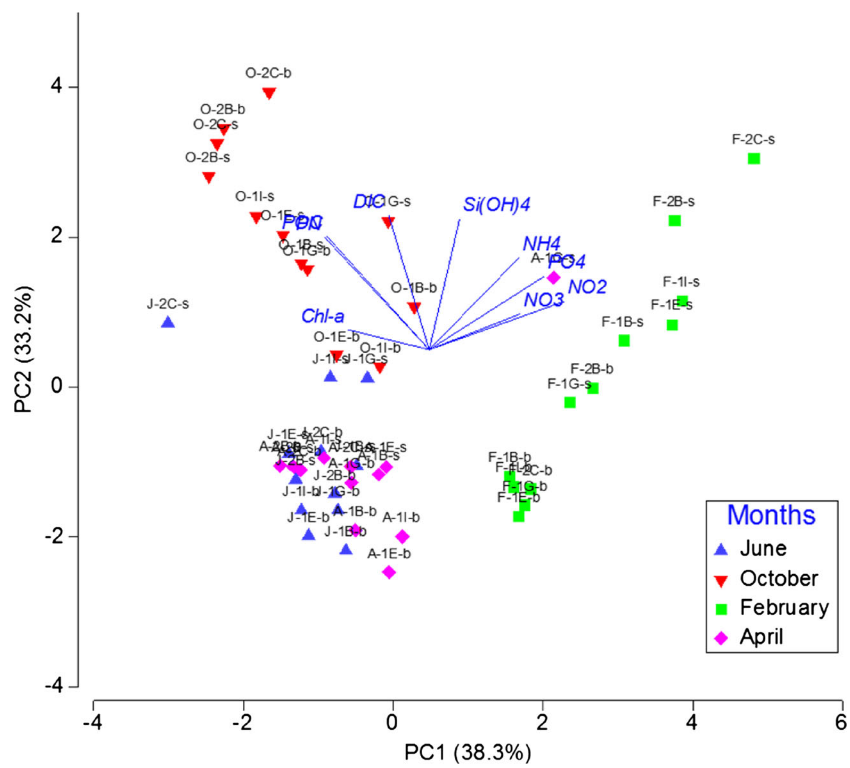


Fig. 6 Biplot of the PCA analyses on 2013–2014 biogeochemical data. Parameters and stations are plotted on the plane of the first two principal components (PC1 and PC2). The explained variance is shown on the axes

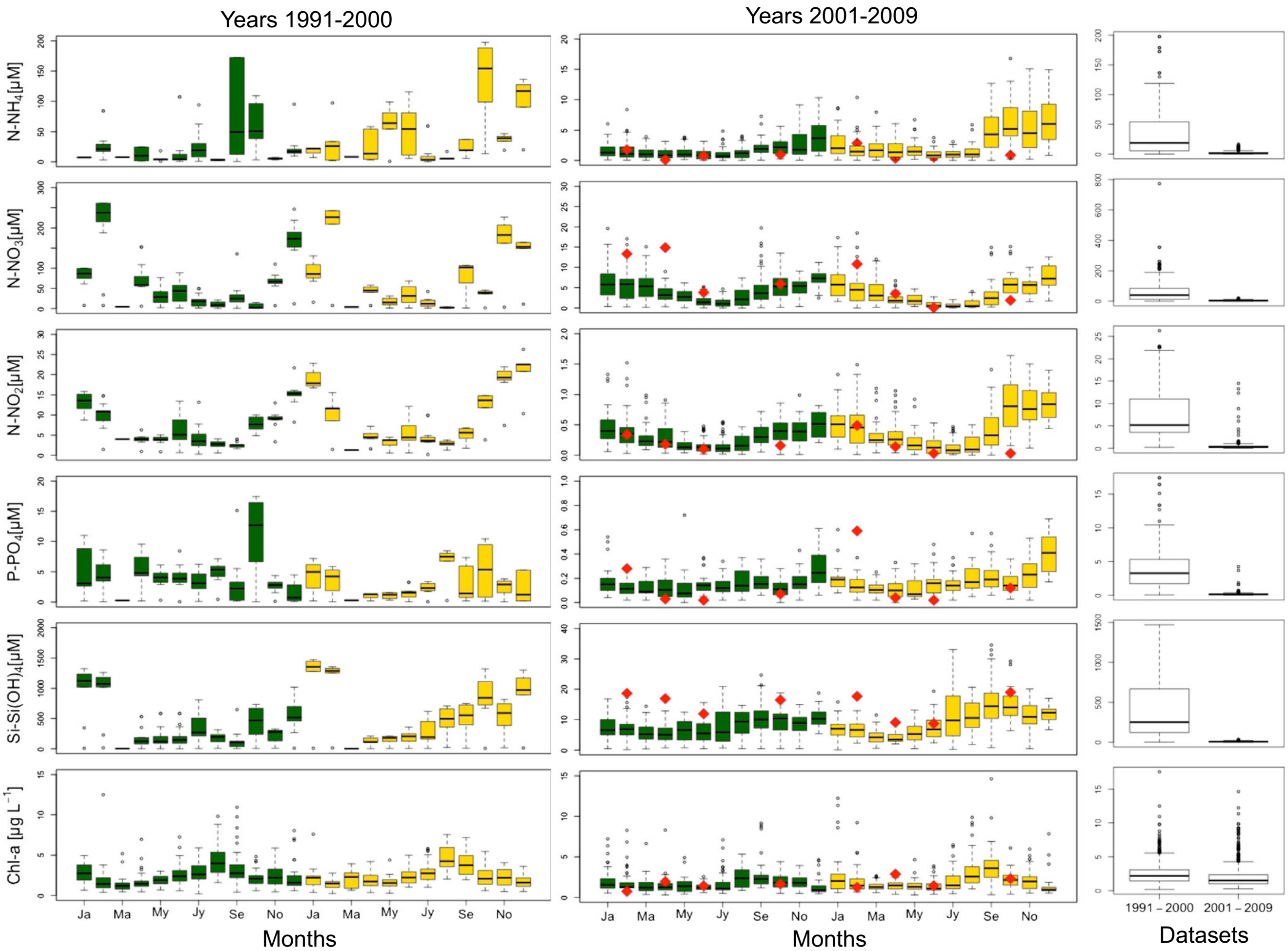


Fig. 7 Box and whiskers plots showing the variability of the monthly values of N-NH_4, N-NO_3, N-NO_2, P-PO_4, Si-Si$(OH)_4$ and chl-*a* in two different periods (1991–2000 and 2001–2009) at the surface water of the First (*green*) and Second Inlet (*yellow*). On the right, box and whiskers plots showing the variability of the two sets of historical analysed data. *Boxes* represent the interquartile range (25th to 75th percentile), the *horizontal line* is the median, the *ends of the whiskers* are the 5th and 95th percentiles and the *points* are the outliers. *Red diamonds* represent average values of 2013–2014 data. Note the different order of magnitude range

concentrations were registered in autumn. The monthly evolution of silicate showed a slight decrease in spring (March and April) and a progressive increase with maxima reached in late summer. Overall, the increase in concentrations registered from September to December was remarkably higher in the SI for N-NH_4, N-NO_2 and P-PO_4.

Chl-*a* did not show an evident seasonal trend even if a slight increase in concentrations from July to September, as before 2001, occurred.

PCA analyses (Fig. 8) performed to compare the present situation with the former datasets showed a remarkable separation between the dataset 1991–2000 and the dataset 2001–2009. Data collected during 2013–2014 were clearly included in the dataset 2001–2009. The first two principal components explained 71.5 % of the total variance. The principal component 1 explained approximately the 60 % of the variance and represents the distribution of all the nutrients, while the second principal component, which explained an additional 16.6 % of the variance, is represented by variations in the chl-*a* concentration.

Discussion

The transitional systems, like the Mar Piccolo of Taranto, are defined by a complex equilibrium of several factors, as the energy flows, the matter inputs and the biogeochemical processes inside the system. The geomorphologic characteristics of the basin act as a filter to modulate all these factors (Cloern 2001) determining space-time fluctuations in the biogeochemical heterogeneity of the system as yet encountered in other similar environments such as the Venice Lagoon (Bianchi et al. 2004; Sfriso et al. 1994; Solidoro et al. 2004), the Mar Menor (García-Pintado et al. 2007), the Arcachon Bay (Gle´ et al. 2008) and the Lesina Lagoon (Roselli et al. 2009).

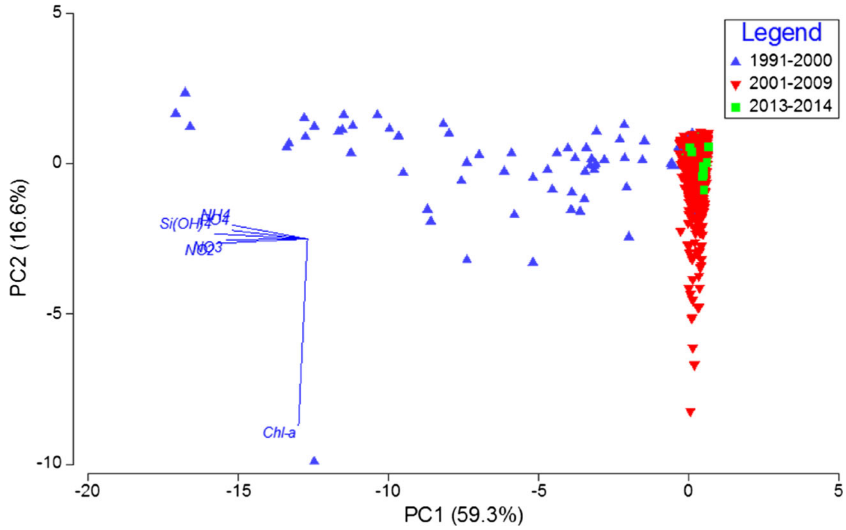


Fig. 8 PCA analyses performed to compare the present situation (2013–2014 surveys) with the former datasets (1991–2000 and 2001–2009). Parameters and data are plotted on the plane of the first two principal components (PC1 and PC2). The explained variance is shown on the axes

Spatial and temporal variability of hydrological and biogeochemical characteristics in the years 2013–2014

The data obtained during 2013–2014 show a considerable physical and biogeochemical inter-annual variability in the two inlets, as confirmed by the highly significant differences evidenced by ANOSIM analysis among the sampling periods ($p<0.001$) and by the PCA results (Fig. 6).

This can be ascribed to the concurrence of several meteorological, hydrological and biological forcing factors taking place in this basin. Irregular discharges of freshwater from its watershed intermittently provide nutrients to the water column. The differences between the two inlets were significant ($p<0.01$) even if ANOSIM demonstrated a certain degree of overlapping among variables ($R=0.27$) and can be attributed to the levels of confinement of the swallow waters, as previously reported by Alabiso et al. (2005). The shallowness of the basin, the strong influence of the freshwater and drainage discharges and the presence of extensive shellfish farming areas, acting as sinks of particulate matter and sources of nutrients for the water column (Souchu et al. 2001), make the elaboration of an annual cycle of nutrients difficult (Caroppo and Cardellicchio 1995).

Referring to the hydrological variables, the basin, despite its small extension, could be subdivided in different areas depending on sea water characteristics (Alabiso et al. 1997). The FI is clearly influenced by the freshwater discharges, derived from the inland tributaries and 'citri' in the northern part, and also from the seawater coming from the Mar Grande basin through the two connection channels, while the SI is characterized by lower water mass exchange and lower freshwater inputs (Caroppo and Cardellicchio 1995). That means that the biogeochemical characteristics of the basin are strongly dependent to the amount of discharges of tributaries. This was observed in the northern part of the FI basin during June 2013 when, both at bottom and surface waters, low salinity and an increase in nutrients, DIC and DOC concentrations were detected. Excluding this area of the FI, during this survey, the rest of the basin was characterized by the lowest DIN and marked depletion of P-PO_4, probably related to the phytoplankton uptake, as suggested by the high chlorophyll concentrations and high chl-*a*/phaeo ratio, which could be explained by a recent phytoplankton bloom mainly due to the phototrophs nanoflagellates fraction (Karuza et al. 2015).

The scarce hydrodynamism (De Serio et al. 2007) and the low water exchange with the nearby Mar Grande determine, mainly in summer, a high water stratification (Cardellicchio et al. 2007; Caroppo and Cardellicchio 1995). In 2013, this situation lasted until October, when the presence of thermocline and halocline regulated the vertical distribution of nutrients and their confinement and accumulation in the bottom waters as consequence of natural regeneration processes that occur at the water–sediment interface, determining an oxygen depletion in the deeper layer. The lower chl-*a*/phaeo ratio, compared with June, although could be related to senescent phytoplankton, suggests a higher herbivorous grazing pressure (Peña et al. 1991). This hypothesis is supported by the increase of particulate matter concentrations probably as consequence of a transfer of biomass from phytoplankton to zooplankton through grazing, as confirmed by the high concentrations of mesozooplancton observed in the same period by Karuza et al. (2015). Once a year, in fact, in late summer–early autumn, the study area is characterized by the maximum abundance of zooplankton (Belmonte et al. 2013).

The intense precipitation before the February 2014 survey (56.2 mm within 5 days, of which 33.8, 2 days before the sampling, data supplied by Servizio Protezione Civile of Puglia), produced a high discharge of freshwaters that carried riverine nutrients and lowered the surface salinity in the whole basin to the minimum registered during the study period. Freshwater transport supplied high concentrations of DIN and P-PO_4, which persisted in the water column also as consequence of the scarce uptake from the phytoplanktonic community, reaching the lowest abundances during the winter months (Caroppo and Cardellicchio 1995), as evidenced by the low chl-*a* concentrations and chl-*a*/phaeo ratios. These results have been confirmed also by Karuza et al. (2015). The concentrations of reduced nitrogen forms and of P-PO_4 were higher in the SI, probably enhanced by the wide mussel rope community that covers the 61 % of the basin, which represents a large source of DIN (La Rosa et al. 2002) and phosphorus to the water column (Nizzoli et al. 2005).

Also in April 2014, the sampling was performed 4 days after an intense rainfall event (31.4 mm within four days), but the nutrient loads resulted quite different both quantitatively and qualitatively. Evidence of the freshwater input was present particularly in the northern area of the FI characterized by extremely high concentrations of nitrate and silicate but of really low phosphate. This could be due to the concurrence of other severe forcing factors such as the onset of intense biological processes, i.e. phytoplankton bloom (Caroppo et al. 2015) which, in shallow basins, may deeply modify the concentration and the coupling among the nutrients. The high chlorophyll *a* concentration detected especially in the SI supports the hypothesis of a crucial role of phytoplankton in P-PO_4 depletion. On the whole, these observations indicate that riverine loads of nutrients are, in early spring, an important factor for the rapid trigger of early phytoplankton blooms in the basin, even when other environmental conditions such as temperature and total irradiance are still close to the winter values.

In this study, even during intense discharge of freshwater, the dissolved pool was always deficient in phosphorous relative to nitrogen, and the highest DIN:P-PO_4 ratio were encountered in April straight after one of this events. These results suggest that the variability of nutrient loads is mainly linked to the runoff and to the concomitant presence of point and diffuse sources of nutrients ascribing to different levels of anthropogenic pressure.

Comparison of the present situation with the former dataset

The anthropogenic pressures that have taken place in the Mar Piccolo basin have caused significant alterations in its hydrological and chemical states and have probably influenced the biological communities (Caroppo and Cardellicchio 1995; Caroppo et al. 2008). Uninterrupted series of monitoring in multiple points of the basin and at different depths are lacking. Keeping in mind these difficulties, we tried to make preliminary considerations, with the aim to stress or to exclude the changes in the water quality of the Mar Piccolo after the closure of some sewage channels and the installation of depuration systems for the waters coming from the inland.

For what concerns the hydrological parameters, significant differences ($p<0.05$) were observed between the two climatological datasets (1991–2000 and 2001–2009) only for salinity.

The comparison between the climatological dataset (2001–2009) and the data collected during 2013–2014 and represented with red diamonds in the Fig. 3 shows that during February 2014, the observed salinity in the FI was slightly lower than the climatological values, but always in the range of variability, while there were no substantial differences in temperature. In June 2013 and April 2014, T, DO and SAL fell within the historical dataset, while in October 2013, these parameters were slightly higher with respect to the climatology even if always comprised between the 5th to 95th percentile. The only exception was the dissolved oxygen mean concentration in the FI, which exceeds the 95th percentile indicating the presence of more oxygenated waters. It was observed that October 2013 averaged data matched more with the September climatology (Fig. 3), suggesting that the basin still maintained summer environmental characteristics.

Differently, the analysis of the available biogeochemical data demonstrated the improvement of the water quality in the Mar Piccolo of Taranto after the treatment plant installation. As shown in the Fig. 7, nutrient concentrations were highly variable between the two inlets, and drastic changes in concentrations were found between the two analysed time series. The significant ($p<0.01$) lowering of the nutrient concentrations, evidenced by the ANOSIM test and confirmed by the PCA analysis (Fig. 8), suggests that an external cause determined the changes in the input regime, that is, the installation of the treatment plants (Taylor et al. 2011). The load of nutrients associated with inputs carrying inadequately treated waste waters from the inland, in the period before 2001, lead to concentrations of 1 order of magnitude higher than after 2001.

The 1991–2000 chl-*a* dataset significantly differed ($p<0.01$) from 2001–2009 ones due to a general reduction of chlorophyll concentration after the treatment plant installation. Nevertheless, high concentration values of chl-*a* were often reached also during 2001–2009, even if a drastic reduction of the total microphytoplankton and particularly of diatom abundance was observed (Caroppo et al. 2010, 2015). This could be due to a shift of the ecosystem towards a lower trophic level (Caroppo et al. 2010) as confirmed by the observations of Karuza et al. (2015) and in other systems tending to oligotrophication (Mozetič et al. 2010). The drastic reduction of diatom could explain the less marked spring chl-*a* peak, while the mean lower chl-*a* concentrations of July–September could be due to a reduction of dinoflagellates, which generally prevailed during summer (Caroppo et al. 2010).

Data collected during 2013–2014 and represented with red diamonds in the Fig. 7 were generally in the range of variability of the 2001–2009 climatology as evidenced also by the

PCA plot (Fig. 8). Values out of the 5th–95th percentiles were observed in February 2014, for P-PO_4 and Si-$Si(OH)_4$, in the SI; during April 2014, for nitrate and silicate, in the FI (as consequence of the extremely high concentrations detected at the St. 1G) and in October for nitrate, in the SI. This data confirms the lowering of the nutrient concentrations after the treatment plant installation yet observed in the 2001–2009 dataset.

Similar abrupt decrease in nutrient, up to −65 and −66 % of DIN and DIP, respectively, and −80 % of N-NH_4, were found also in other coastal systems, such as the Boston Harbor and the Kaneohe Bay, that have experienced decreases in nutrient loadings, while lower system responses were observed in areas with higher water residence time (Taylor et al. 2011 and references therein).

Conclusions

Coastal lagoon and basins with growing population densities and activities have undergone many environmental changes. In the Mar Piccolo of Taranto, several concurrent human actions have led to the alteration of the weak equilibrium characteristic of this transitional system and the increase of nutrients is among the main consequences because this coastal system acts as a trap for rivers and streams loadings during the high runoff periods. In the basin, the biological processes (production and mineralisation) affecting the nutrient budgets are largely influenced also by the intensive mussel culture (Cardellicchio et al. 2006), which by filtration and production and deposition of faeces and pseudofaeces, increases inputs of labile organic matter to the superficial sediment. Faeces and pseudofaeces are, in fact, characterized by a large bioavailability to microbial assemblages and by rapid degradation rates, which contribute to a rapid turnover of the organic biodeposits and to the massive release of nutrients at the water–sediment interface, which, in turn, can modify the nutrient budgets (La Rosa et al. 2002).

While relationships between anthropogenic nutrient loads and eutrophication processes in Mar Piccolo of Taranto have been previously demonstrated (Caroppo and Cardellicchio 1995), this is, in our knowledge, the first study that analyses and compares long-term seasonal variation of hydrological data and nutrient concentrations before and after the remediation and environmental cleaning up planned by the Italian Government.

The 20-year dataset analysis evidenced that the reduction of nutrient inputs into the basin from 1991 to 2009 has changed the biogeochemical characteristics of the Mar Piccolo from being relatively eutrophic before 2001, to moderately oligotrophic after 2001 when treatment plants began to be operational and phosphorous appeared to be the potential limiting nutrient for phytoplankton production in spring. The comparison between the two datasets shows that since 2001, an abrupt decrease in nutrient concentrations has occurred and that the response was higher, up to −90 % in the first inlet characterized by lower hydraulic residence time.

Our results, which represent a contribution to the characterization of the waters of the Mar Piccolo and an update of its climatology, demonstrate that, even if this costal ecosystem is still severely impacted by anthropogenic activities, the control of the point sources through depuration systems has been successful for the decrease in nutrient concentrations. Conclusions obtained from this study could be useful in the perspective of the water quality management for an overall understanding of the mechanistic linkages between man-made alterations of hydrologic and nutrients regimes, in order to plan integrate short and long-term remediation actions.

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