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Ecosystem functioning approach applied to a large contaminated coastal site: the study case of the Mar Piccolo of Taranto (Ionian Sea)

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Response to Reviewers:	I have uploaded the Response to Reviewers as supplementary material.

Ecosystem functioning approach applied to a large contaminated coastal site: the study case of the Mar Piccolo of Taranto (Ionian Sea)

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Abstract

Knowledge on ecosystem functioning can largely contribute to promote ecosystem-based management and its application. The Mar Piccolo of Taranto is a densely populated area at a high risk of environmental crisis. Here planktonic primary production (PP) and heterotrophic prokaryotic production (HPP) were measured as proxies of functioning in three sampling sites located in two inlets at different levels of industrial contamination, during three sampling surveys (June 2013, February and April 2014). To have a better overall view and provide some insights into the benthic-

pelagic coupling, we integrated PP and HPP in the water column with those in the sediments and then discussed this with the origin of the organic matter pools based on analysis of stable isotopes. Heavy metals and Polychlorobiphenyls (PCBs) were also analysed in the surface (1 cm) sediment layer and related to the overall ecosystem functioning. MDS analysis, based on the main data, clearly separated the 2nd Inlet from the 1st one, more severely impacted by anthropogenic activities. The stable isotope mixing model suggested the prevalent terrestrial/ riverine origin of the particulate organic matter pools (mean 45.5%) in all sampling periods, whereas phytoplankton contributed only up to 29% in February. Planktonic PP rates peaked in June, reaching up to 10.14 ± 1.45 µg C l^{-1} h^{-1} in the 1st Inlet, and up to 20.07 ± 3.12 µg C l^{-1} h^{-1} in the centre of the 2nd Inlet of the Mar Piccolo. HPP rates were about one order of magnitude lower than the PP rates but they followed the same pattern. On the contrary, in the surface sediments microphytobenthic PP rates were almost negligible over the study period while in June 2013 HPP rates in the sediments were comparable to those in the water column. These results indicate that although the Mar Piccolo is very shallow, the water column is much more productive than the surface sediments. The sediment resuspension is likely responsible for a pulsed input of contaminants into the water column. However, their interference with the proper functioning of the pelagic ecosystem seems to be limited to the bottom layers.

Keywords: Ecosystem functioning; Primary production; Heterotrophic prokaryotic production; C and N stable isotopes, Benthic-pelagic coupling; Contamination; Satellite imagery mapping

Introduction

Shallow coastal photic systems are among the most productive on the planet (Odum 1983). In these environments, light penetration to the bottom fuels multiple primary producers, including phytoplankton, benthic microalgae, macroalgae and seagrasses.

The coupling between planktonic primary production (PP) and prokaryotic utilization of the labile, i.e. rapidly decomposable, phytoplankton extracellular release has been demonstrated to be a key process in organic carbon cycling influencing the ecosystem functioning in aquatic ecosystems (Cole et al. 1988). Heterotrophic prokaryotes mainly consume and respire organic matter produced by photosynthesis, therefore heterotrophic prokaryotic production (HPP) is typically dependent on this organic matter supply. However, the coupling between PP and HPP may vary according to the ecosystem characteristics. For example, in estuarine and coastal systems the prokaryotic C demand could be supported not only by the degradation of phytoplankton exudates but also by local non-phytoplanktonic material and allochthonous organic matter supplies (Lee et al. 2001). This can be reflected in a loose coupling between PP and HPP and a shift to net heterotrophy of the planktonic system (Pugnetti et al. 2005; 2010).

Aside from light, temperature and nutrients, that are key parameters regulating system production, coastal processes are largely influenced by physical factors such as horizontal transport, sediment composition and resuspension. Rapid sinking of phytoplankton blooms, efficient filtration of the water column by benthic fauna and a tidal energy subsidy can determine a tight benthic pelagic coupling that leads to a high local benthic production (Kennish et al. 2014). Moreover, microbial mediated processes in sediments can enhance nutrient availability for primary production in benthic and pelagic habitats and become important in regulating the relative magnitude of benthic versus pelagic primary production (Kennish et al. 2014). Apart from phytoplankton and local benthic production, terrestrial matter carried by coastal rivers represents a non-negligible contributor to coastal organic matter pools.

The understanding of the nature and origin of the organic matter pools may provide interesting insights about the occurrence of natural processes and anthropogenic pressures in coastal environments (Hedges and Stern 1984). At this regard, analyses of stable isotopes of organic matter are useful tools to characterise nitrogen and carbon transport and transformation processes in continental margins (Vidal et al. 2009).

Shallow coastal photic systems rank among the most heavily impacted aquatic ecosystems, being affected by a wide range of anthropogenic activities. Multiple anthropogenic disturbances create both acute and insidious problems for many estuarine biotic communities and habitats that can compromise the stability and resiliency of these systems and their long-term integrity. Among other stressors, chemical contaminants can cause severe changes in ecosystem structure and function (Kennish et al. 2014).

Regarding organic pollutants and particularly polychlorinated biphenyls (PCBs), current sources of these compounds are landfills, open burning of products containing PCBs, waste incineration, accidental fires, and revolatilization from formerly exposed soils. Organic pollutants enter the sea and estuary via atmospheric deposition, river input and point source along the coast. Once delivered to the water column, the primary removal processes are sedimentation of atmospheric particles and partitioning of the gaseous/dissolved phase contaminants into organic carbon-rich particles with subsequent settling and accumulation in surface sediments (Di Leo et al. 2014).

The main process determining the distribution and concentration of contaminants in shallow systems is the exchange between the water column and the uppermost sediment layer that is repeatedly resuspended and settled again. In this way, contaminants are transferred to the water column, diluted and redistributed over the entire basin through water circulation. Usually, for monitoring purposes, analysis of contaminants is performed on a sediment layer up to 5 cm (Cardellicchio et al. 2007). However, focusing on the benthic-pelagic coupling, it is important to

estimate the contaminants concentrations in the uppermost few millimetres of sediments that are often resuspended.

The Mar Piccolo is a shallow coastal basin located near the city of Taranto (southern Italy). Since 1960s Taranto and its coastline have been subjected to the industrialization process that has caused profound environmental changes. This industrial zone is characterized mainly by the presence of the largest steelworks in Europe and navy arsenal in Italy (Military area in Figure 1), a major oil refinery, shipbuilding and other industrial activities that are responsible for severe environmental contamination, mainly due to heavy metals, asbestos, polycyclic aromatic hydrocarbons (PAHs), organic solvents, PCBs and dioxin. Previously collected data on organic and inorganic pollutants in the Mar Piccolo have shown high levels of contamination and stress conditions on different communities (Cardellicchio et al. 2007; Spada et al. 2012). In 1998, this area has been declared Site of National Interest (SIN) i.e. a very large contaminated area, classified as the most dangerous by the Italian State and in need of remediation. According to the current legislation, the characterization plan of such polluted areas is based solely on the quantification of contaminants. In contrast, other pivotal ecological aspects, such as those focused on the C cycling through the production processes, have been completely neglected.

The principle behind “the ecosystem approach to management” is that the management of human activities is based on the limits within which ecosystem structure, functioning, productivity and biological diversity can be maintained (Ottersen et al. 2011). There are still major science and knowledge gaps in applying the ecosystem approach to management, related to our limited understanding of the dynamics and resilience of ecosystems, the cumulative impacts of human uses on the marine environment and the effectiveness of management and governance systems (Katsanevakis et al. 2011). To study the ecosystem functioning of a particular environment, as much information as possible have to be gathered on that area. The simultaneous investigation of structural and functional parameters and their subsequent integration is needed in order to represent an overview of the C flow through the system. In the Mar Piccolo of Taranto there are no data

available on either PP or HPP that are considered important proxies of ecosystem functioning. In this study, we have focused on the pelagic processes of carbon production. To gain more insights into the ecosystem functioning and the influence of pelagic-benthic and import/export processes we have: i) integrated the PP and HPP in the water column with those in the benthic domain; and ii) linked such information with the nature and origin of suspended and sedimentary organic matter (OM) pools based on analyses of stable isotopes ($\delta^{13}C$ and $\delta^{15}N$). Moreover, we discussed the high contamination levels in the very uppermost sediments layer, their transfer to the water column through bottom resuspension and the consequent potential effects on the overall ecosystem functioning of this basin.

Materials and methods

Study area

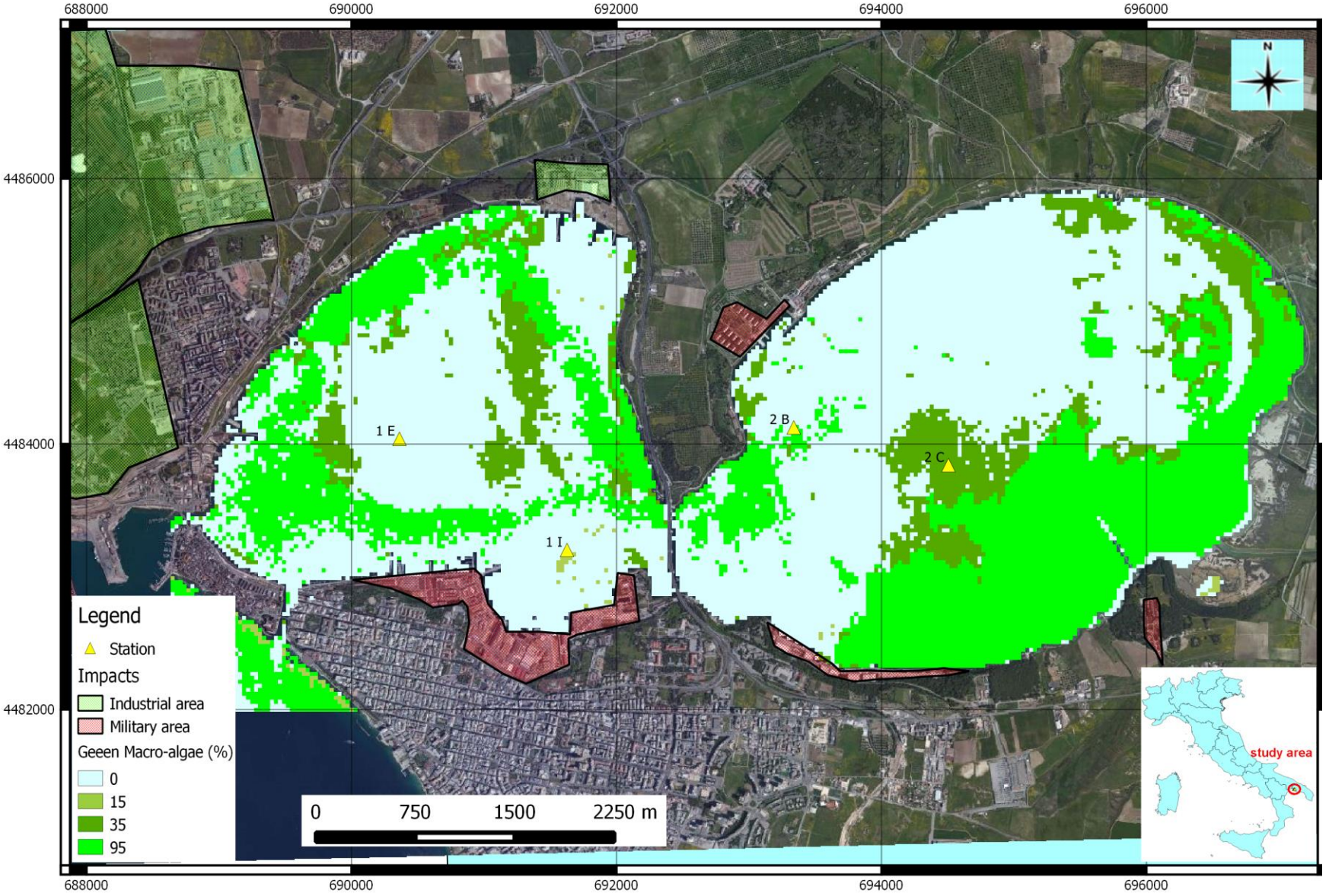
The Mar Piccolo is a shallow, nearly enclosed basin connected through two narrow canals with the Mar Grande and widely with the Gulf of Taranto. It consists of two naturally divided basins, the 1st and 2nd Inlet, with maximum depths of 13 and 10 m and a surface area of 8.28 km^2 and 12.43 km^2, respectively. The sedimentation in this area is mainly influenced by land runoff, numerous submarine springs, small streams, sewage outfalls and industrial discharges rather than by marine currents. The sediment composition in both Inlets is clayey silt. The features of the Mar Piccolo in the Gulf of Taranto have been exhaustively described by Cardellicchio et al. (2015 this issue).

Sampling

Sampling in the water column was carried out during 11th-17th June 2013, 3rd-5th February and 1st-8th April 2014 at three stations: St. 1E (depth = 11.2 m) was located in the middle of the 1st Inlet (40° 29' 46"N, 17° 14' 10"E), St. 1I (depth = 11.0 m) was located nearby the military arsenal

(40° 28' 37"N, 17° 15' 35"E) and St. 2C (depth = 8.0 m) was positioned in the innermost part of the 2nd Inlet (40° 28' 41"N, 17° 17' 57"E) (Fig. 1).

Figure 1. Location of the four sampling stations in the Mar Piccolo of Taranto (yellow triangles): 1I and 1E in the 1st Inlet and 2B and 2C in the 2nd Inlet. Superimposed are the industrial area and the military area (i.e. the navy arsenal in the 1st Inlet) and the green macro-algal coverage (%). Its distribution was assessed by means of atmospherically corrected Landsat 8 OLI multispectral data acquired on 13th June 2013 and suitably calibrated using *in situ* point measurements at the sampling stations.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Military area
Geeen Macro-algae (%)
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95
0
750
1500
2250 m
study area

165

Seawater temperature, dissolved oxygen and salinity were measured along the water column using a Seabird 19 Plus Seacat probe (June 2013 and April 2014) whereas in February 2014 seawater temperature was measured by a PNF-300 Profiling Natural Fluorometer and salinity by a CDM83 conductivity meter (Radiometer Copenhagen).

During each sampling, the Photosynthetic Available Radiation (PAR) was registered by a PNF-300 Profiling Natural Fluorometer (Biospherical Instruments Inc.). The PAR value at the sampling depth was expressed as the percentage of measured irradiance with respect to the surface irradiance (%PAR).

Water samples were collected at the surface layer (1 m below water surface) and bottom layer (1 m above bottom) by Niskin bottles. For isotopic analyses of suspended particulate organic matter (POM), water samples were collected from the bottom layer of the three stations listed above and at the additional St. 2B (depth = 7.0 m; 40° 28' 42"N, 17° 16' 57"E) located nearby the strait between the two Inlets. Replicated water samples (1-1.2 L) were filtered through precombusted (450°C for 4h) Whatman GF/F and stored at -20°C until analyses.

Sediment sampling was carried out in June 2013 and April 2014 at the four stations sampled for water analyses. At each station, at least three virtually undisturbed sediment cores were collected by scuba divers using polycarbonate sample tubes (12.7 cm I.D. with a sample area of 127 cm^2). The oxic sediment layer (0-1 cm ca.) of each core was collected, homogenised and used for the analysis of heavy metals and PCBs (see below) as well as primary and heterotrophic productions (as reported in Rubino et al. (2015 this issue) and Franzo et al. (2015 this issue), respectively).

Additional sediment samples (0-3 cm layer) were used to analyse the stable isotopic signatures of sedimentary organic matter (SOM) as described in Bongiorni et al. (2015 this issue). For this analysis, an additional sampling was carried out in February 2015. In order to characterize the contribution of different primary sources to POM and SOM pools, most common macroalgal

species were also collected during June 2013 and April 2014 by hand or a van Veen grab (as reported in Bongiorni et al. (2015 this issue)).

Chlorophyll a

Water sub-samples for Chlorophyll *a* (chl *a*) analysis were collected on-board, stored in the dark and kept at 4°C until the filtration. In the laboratory the water was filtered immediately on 47 Ø mm Whatman GF/F filters and the filters were stored at -20 °C. Chlorophyll *a*, corrected for phaeopigments, was measured fluorometrically after extraction (90% acetone) and centrifugation of samples kept in the dark, according to Lorenzen and Jeffrey (1980), on a Perkin Elmer LS50B fluorometer.

Primary production (PP)

PP was estimated *in situ* by the ^{14}C technique (Steemann-Nielsen 1952). Water samples were poured into 75 ml translucent and dark polycarbonate carboys (Nalgene) and kept in the darkness for 30 minutes to stop the residual photosynthetic activity. Subsequently, 6 µCi (0.22 MBq) of $NaH^{14}CO_3$ (DHI, Denmark) was added per bottle. Three light and one dark samples per depth were fixed on a rosette, lowered at the corresponding depth and incubated for 2 h around noon. At the end of the incubation, samples were transferred to 100-ml bottles and supplemented with 320 µl of 5 N HCl (Cibic and Virgilio 2011) to stop the photosynthetic activity and remove the residual labelled bicarbonate, not assimilated by the phototrophic plankton. From each sample 25 ml were filtered through polycarbonate 0.2 µm filters (Nuclepore) applying a low vacuum pressure (5 mmHg) in order to avoid cell damage. Filters were placed into 6 ml plastic scintillation vials (Perkin Elmer) and 5 ml of Filter Count scintillation cocktail (Perkin Elmer) was added. Disintegrations per minute (DPM) were measured by a QuantaSmart TRI-CARB 2900 TR Liquid Scintillation Analyzer (Packard BioScience, USA) including quenching correction, obtained using internal standards. Assimilation of carbon was calculated as described by Gargas (1975), assuming

5% isotope discrimination. Activity of the added $NaH^{14}CO_3$ and inorganic carbon concentration (tCO_2) were calculated on the basis of total alkalinity measured in the same samples.

Similarly to the water column, benthic PP was estimated using ^{14}C as radiotracer. ^{14}C-incubation of sediment slurries was performed *in situ*, then samples were treated and analysed as described in detail by Cibic et al. (2008).

Heterotrophic prokaryotic production (HPP)

HPP was measured by the incorporation of ^{3}H-leucine (Leu) (Kirchman et al. 1985). Triplicate seawater aliquots (1.7 ml) and two controls killed by the addition of 90 µl 100% trichloracetic acid (TCA), were amended with a 20-nM radiotracer and incubated *in situ* in the dark. Incubations were stopped with TCA (5% final concentration) after 2 h. The extraction with 5% TCA and 80% ethanol was carried out using the microcentrifugation method (Smith and Azam 1992). Activity in the samples was determined by a QuantaSmart TRI-CARB 2900 TR Liquid Scintillation Analyzer (Packard BioScience, USA) after the addition of 1 ml scintillation cocktail (Ultima Gold MV; Perkin Elmer).

Benthic heterotrophic production was measured by the incorporation of ^{3}H-leucine following the method by Manini et al. (2004). ^{3}H-incubation of sediment slurries was performed *in situ*, and then samples were treated and analysed as exhaustively described by Cibic et al. (2012).

Stable isotope analysis

Analyses of C and N stable isotopes ($\delta^{13}C$ and $\delta^{15}N$) of POM and SOM, and primary producers were conducted as detailed in Bongiorni et al. (2015 this issue). Briefly, from each sample, a sub-sample was analysed without any prior treatment for $\delta^{15}N$ determination. A second subsample was used for $\delta^{13}C$ analysis, after acidification with HCl (1 N) to remove carbonates which present a higher $\delta^{13}C$ than organic carbon, and oven-dried at 40°C for 24 h (Hedges and Stern 1984). The $\delta^{13}C$ and $\delta^{15}N$ ratios in the samples were determined using a Delta Plus XP isotope ratio

mass spectrometer (ThermoFinnigan) equipped with a Flash EA 1112 elemental analyser (ThermoFinnigan). Isotope ratios were expressed as parts per thousands (‰) differences from a standard reference material VPDB (Vienna Pee Dee Belemnite) for $\delta^{13}C$ and AIR for $\delta^{15}N$. The Uncertainty of methods was 0.3 ‰ for $\delta^{13}C$ and $\delta^{15}N$.

In order to evaluate the contribution of different primary sources to the POM and SOM mix pools we applied a Bayeasian mixing model by using the package SIAR V4 (Stable Isotope Analysis in R, (Parnell et al. 2010)). The greatest advantage of this procedure is the incorporation of uncertainty linked to sources, consumers and trophic enrichment factors within the model (Dubois et al. 2012; Parnell et al. 2010; Phillips et al. 2014). The model was run for POM and SOM separately and for each of the four sampling stations/seasons assuming a zero fractionation factor for each isotopes. Both models included two variables ($\delta^{15}N$ and $\delta^{13}C$) and up to five end-members (macroalgae, terrestrial/ riverine POM, phytoplankton, treated sewage for POM and SOM models and autochthonous POM for SOM model). Since different macroalgae displayed similar isotopic signature for the model we consider an average value. The isotopic values of the end-members that were not directly measured during our surveys, were extracted from the literature: phytoplankton (Harmelin-Vivien et al. 2008), riverine/terrestrial POM (Berto et al. 2012 and Carlier et al. 2007), and treated sewage (Berto et al. 2012 and Berto unpubl. data).

Satellite imagery mapping of the seabottom and primary productivity of green algae

The Green macroalgae distribution in the Mar Piccolo of Taranto was assessed by means of the high resolution multispectral satellite remote sensing technique based on the data acquired on 13 June 2013 by new NASA polar Landsat 8 OLI (Operational Land Imager) sensor. The OLI multispectral data were previously corrected for atmospheric noise (Borfecchia et al. 2013a) (scattering/attenuation from image derived AOD and adjacency effects) and then they were classified into three classes using a supervised ML (Maximum Likelihood) parametric algorithm. Different *in situ* cover values (%) of the dominant green algae *Caulerpa* sp., recorded at the four

stations in the same period, allowed us to properly calibrate the remotely sensed data. The improved spectral and radiometric features of the OLI multispectral sensor (five acquisition bands in the VIS and NIR ranges including the new deep blue coastal one, at 30 m resolution with increased SNR) allowed us to obtain these preliminary results in terms of green algae effective mapping (Borfecchia et al. 2013b) in the optically complex shallow waters of the Mar Piccolo. The primary productivity of green macro-algae (such as *Caulerpa prolifera*, *Caulerpa* sp.) in the Mar Piccolo was evaluated through an integrated method including satellite remote sensing technique and *in situ* observations. In order to obtain an estimate of the overall primary productivity of the Mar Piccolo, a maximum hourly rate of productivity (Pmax) of *Caulerpa* sp., in relation to depth and seasonal variation, was used according to Terrados and Ros (1992) and Bernardeau-Esteller et al. (2011) and converted from oxygen to carbon to allow an integration with primary production data in the water column.

Analysis of polychlorobiphenyls (PCBs) and heavy metals

For PCBs one g of lyophilized samples was extracted with n- exane/acetone (1:1 v/v) by Microwave Extraction (EPA Method 3546) concentrated and then purified with Florisil (EPA Method 3620C) to remove the co-extracted polar compounds. In order to eliminate sulphur, 5 g of copper powder, activated with HCl (2 N), was added to the sample before clean up. Finally, PCBs were eluted with n-hexane concentrated to small volume prior to analysis that were carried out using a gas chromatograph (model 7890, Agilent Technology) coupled to a mass detector (5975C Agilent Technology). The calibration standard mixtures consisted of 28 individual PCB congeners (IUPAC No PCB 18, 31, 28 (Tri-CBs), 44, 52 (Tetra-CBs), 95, 101, 99, 110, 123, 118, 114, 105 (Penta- CBs) 151, 149, 146, 153, 138, 128, 167, 156, 157 (Hexa-CBs) and 187, 183, 177, 180, 170, 189 (Hepta-CBs) (Ultra Scientific, Co.). PCB 209 was used as internal standard solution and PCB 112 and tetrachloro-m-xylene (TCMX) was added to all samples as a surrogate standard before extraction (EPA method 8082A).

The reproducibility and recovery of the analytical procedure were determined by using certified marine sediment (NIST SRM 1941b Chemical Research). For triplicate analysis, the mean recovery percentage was >85%, whereas standard deviation ranged from 8–15%. The detection limit ranged from 0.1µg/kg to 0.5 µg/kg on dry basis (d.w.).

For metal determinations (As, Cd, Cr, Cu, Fe, Ni, Zn, Pb, Al, V, Mn, Sn, Hg), aliquots of 0.25 g of dried sediment were digested with 9 mL of nitric acid, 2 mL of hydrochloric acid, and 3 mL of hydrofluoric acid (SW-846 EPA Method 3052, 1995) using a MARSX microwave oven (CEM Corporation, Matthews, NC). For each digestion program, a blank sample was prepared with the same amount of acids. After digestion, 20 mL of boric acid was added to samples in order to delete excess of hydrofluoric acid. Each sample was diluted to 50 mL with ultra pure water and analyzed. The accuracy and precision of the analytical procedures have been checked with a certified reference marine sediment IAEA-356. Metal concentrations were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS), using a Perkin Elmer model Elan 6100 DRC Plus (Perkin Elmer, Norwalk, CT, USA). Sediment samples were analyzed in triplicate. For a more detailed explanation of the protocols for PCBs and metals analyses see Di Leo et al. (2015 this issue).

Statistical analysis

Data normality was checked by Shapiro-Wilk's test. Mean HPP and PP data and values of surface and bottom layers were compared by Mann-Whitney U-test. In order to highlight differences in PP, HPP and stable isotopes among sampling months and stations One-way and Two-way ANOVA were applied. Prior to analyses, the heterogeneity of variance was tested using Cochran's C test, and when the assumption was not reached, data were appropriately transformed. When significant differences were observed, means were compared using a Tukey's HSD test. To highlight interactions between structural and functional variables the non parametric Spearman's rank correlation analysis (R) was applied. All analyses including the Bayesian Stable Isotope

mixing model (SIAR V 4 package), were performed using the R software (R Development Core Team 2005).

Multidimensional Scaling Analysis (MDS) was performed using PRIMER software v.5 on bottom and surface data separately. The two data matrices were constructed with three replicate samples of PP and HPP rates, and were implemented with structural biological parameters such as the abundances of picoplankton (both heterotrophic and autotrophic fractions) and nanophytoplankton (data from Karuza et al. 2015 this issue). Stable isotopes data ($\delta^{15}N$ and $\delta^{13}C$ signature of POM) were included only in the bottom layer dataset. Normalized Euclidean distance was applied. Variation in trends among sampling periods, inlets and stations was subsequently tested for significance with an analysis of similarity (ANOSIM) using the same software. ANOSIM tests *a priori*-defined groups (subgroupings based on the above mentioned factors) against random groups in ordinate space. A zero (0) indicates that there is no difference among groups, while a one (1) indicates that all samples within groups are more similar to one another than any samples from different groups. Only statistically significant data are presented.

Results

Physical-chemical parameters in the water column

At the three sampling stations temperature varied between 20.9 and 23.5°C in June and between 15.5 and 17.0 °C in April, whereas no thermocline was registered in February (Table 1). The water column displayed oxygen saturation conditions both in June and April, reaching 124.6% at the bottom layer of the 2nd Inlet in April. A strong halocline was observed in all sampling periods, with differences of up to 3.7 between the surface and the bottom layers (measured in the center of the 1st Inlet during February), probably due to surface freshwater inputs. During all sampling periods, PAR irradiance was never a limiting factor for the phototrophic organisms; the lowest values did not drop below 22.6 $\mu Em^{-2}s^{-1}$ at the bottom layer in February, representing 4.9% of the surface PAR. Phaeo /chl *a* ratio showed low values in June (with the exception of the surface layer

at St. 2C) and in April indicating the presence of fresh produced organic matter of phytoplankton origin.

Sampling date	Station	Depth m	Temp °C	%O2	Salinity	E0 $\mu Em^{-2}s^{-1}$	Eref $\mu Em^{-2}s^{-1}$	%PAR	phaeo/chl *a*
		1	22.8	114.8	36.1	1477.3	2486.4	59.4	0.72
11/06/2013	**St. 1E**	10	20.9	101.0	38.4	206.6	2486.4	8.3	0.31
		1	21.4	102.0	36.3	1451.3	2443.3	59.4	0.49
13/06/2013	**St. 1I**	10	20.9	105.1	38.3	218.6	2453.7	8.9	0.44
		1	23.5	113.6	36.2	1734.7	2343.8	74.0	2.44
15/06/2013	**St. 2C**	7	21.3	115.6	37.7	368.6	2347.2	15.7	0.56
		1	12.0	NA	34.3	126.7	716.4	17.7	1.94
05/02/2014	**St. 1E**	10	13.2	NA	38.0	38.5	797.4	4.8	2.12
		1	12.1	NA	36.3	134.3	466.1	28.8	1.48
04/02/2014	**St. 1I**	10	13.2	NA	38.3	22.6	460.1	4.9	3.71
		1	12.2	NA	34.9	112.6	407.6	27.6	1.58
03/02/2014	**St. 2C**	7	12.8	NA	37.4	26.9	406.5	6.6	3.45
		1	16.5	106.4	35.6	755.8	2108.9	35.8	1.04
01/04/2014	**St. 1E**	10	15.5	105.7	37.4	161.8	1971.1	8.2	1.19
		1	17.0	105.3	35.6	396.4	2006.6	19.8	1.01
03/04/2014	**St. 1I**	10	15.7	110.4	37.5	146.9	1906.2	15.3	1.02
		1	16.6	111.9	35.7	301.9	1576.6	19.2	0.54
07/04/2014	**St. 2C**	7	16.6	124.6	36.8	91.3	1318.0	6.9	0.99

Table 1. Physical-chemical parameters measured in the water column at the three stations and three sampling periods: temperature (Temp), oxygen saturation (%O2), salinity, PAR irradiance measured in the water column (E0), surface PAR irradiance measured in the air (Eref), the percentage of measured PAR irradiance in the water column with respect to surface PAR irradiance (%PAR), ratio between pheopigments and chlorophyll *a* (phaeo/chl *a*).

Primary (PP) and heterotrophic prokaryotic production (HPP)

Planktonic PP was always significantly higher at the surface than at the bottom water layer (Mann-Whitney U test, $U = 587$, $p < 0.001$). The only exception occurred in April in the 2nd Inlet, where not significant differences between the two layers were found. The Two-way ANOVA

highlighted differences in PP of the surface layer between seasons and sampling stations ($F_{2,18}$=200.70 and $F_{2,18}$=20.3, $p< 0.001$, respectively). Similar results were obtained for PP at the bottom layer ($F_{2,18}$=841.83 and $F_{2,18}$=141.47, $p< 0.001$). At both surface and bottom layers, with the only exception of February, higher values were consistently recorded at St. 2C (Tukey's HSD, $p< 0.01$). The highest PP values were obtained in June, when hourly rates varied between 2.82 ± 0.10 µgC L^{-1} h^{-1} at the bottom of St. 1I and 20.07 ± 3.12 µg C L^{-1} h^{-1} at the surface of St. 2C (Fig. 2).

The Mar Piccolo was productive also in February, i.e. in lower light conditions, with values up to 3.22 ± 0.14 µg C L^{-1} h^{-1} at the surface layer of the 1st Inlet. Intermediate rates were estimated in April, varying between 1.20 ± 0.14 µg C L^{-1} h^{-1} at the surface of St. 1I and 6.71 ± 0.91 µg C L^{-1} h^{-1} at the bottom of the 2nd Inlet. In June and April, chl *a* – normalized photosynthetic rates displayed quite a different pattern compared to the not normalized rates. At the bottom layers of the three stations the two rates were rather comparable, whereas at the surface layers PP chl^{-1} values were about half of the not normalized rates (Table 2).

In February, except for the surface layer of St. 1I, where a higher PP chl^{-1} rate was calculated, comparable PP normalized and not normalized rates were obtained. Mean PP values were calculated from data collected at the two depths along the water column to obtain the areal phytoplankton production (PPa). At the shallowest St. 2C, PPa rates displayed the highest variability, ranging from 1.20 mg C m^{-2} h^{-1} in February to 12.62 mg C m^{-2} h^{-1} in June and representing the absolute minimum and maximum of the study period. With the exception of February, higher PP areal rates were obtained in the 2nd Inlet.

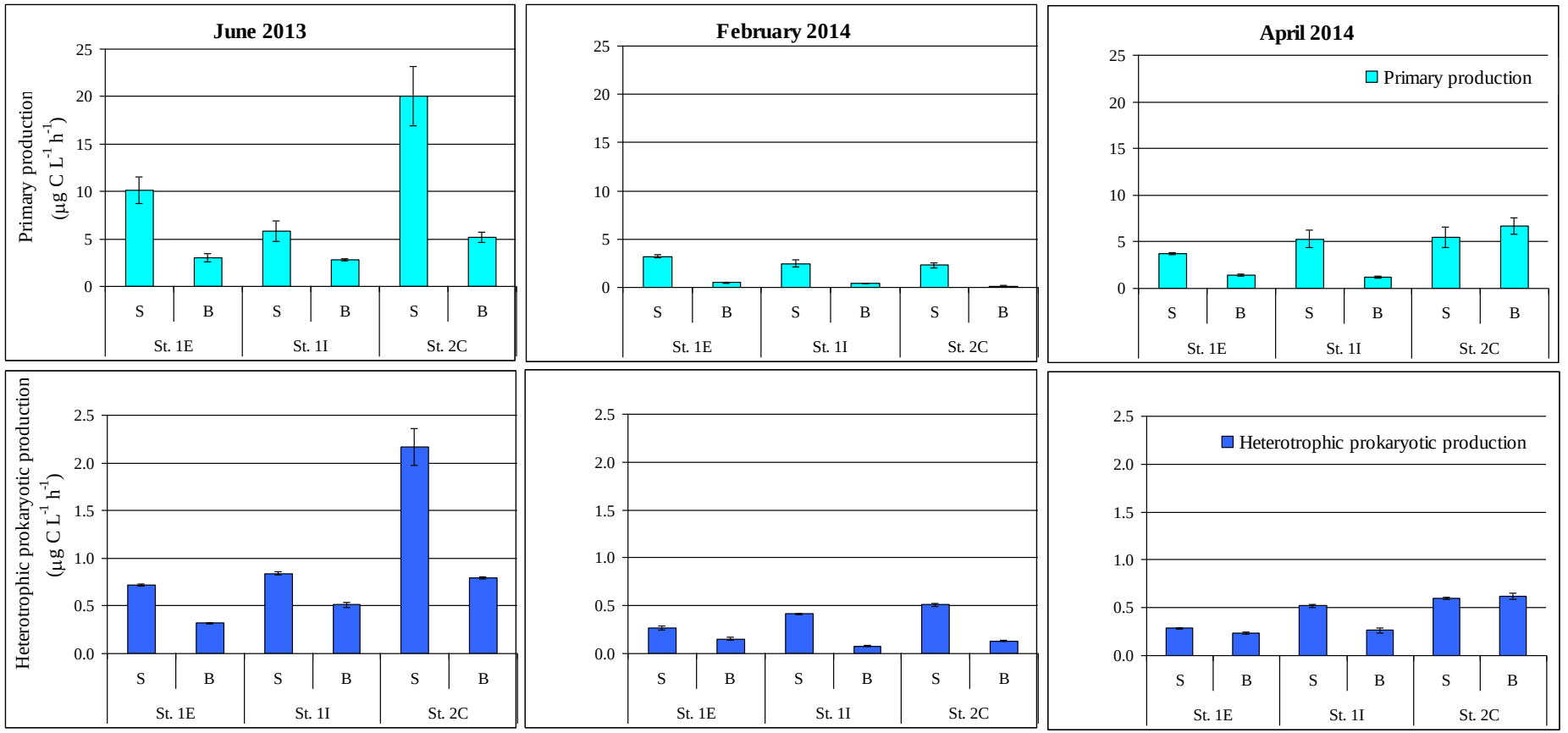

Figure 2. Primary production (PP) and heterotrophic prokaryotic production (HPP) at the three sampling stations in the three study periods.

Sampling date	Station	Depth	PP chl^{-1} µg C µg chl *a*$^{-1}$ h^{-1}	PPa mg C m^{-2} h^{-1}
		1	5.65	
11/06/2013	**St. 1E**	10	2.03	6.59
		1	4.27	
13/06/2013	**St. 1I**	10	1.95	4.32
		1	10.92	
15/06/2013	**St. 2C**	7	4.93	12.62
		1	3.50	
05/02/2014	**St. 1E**	10	0.82	1.87
		1	2.86	
04/02/2014	**St. 1I**	10	1.15	1.44
		1	2.05	
03/02/2014	**St. 2C**	7	0.24	1.20
		1	2.13	
01/04/2014	**St. 2E**	10	1.11	2.58
		1	2.46	
03/04/2014	**St. 2I**	10	0.98	3.24
		1	2.21	
07/04/2014	**St. 2C**	7	1.81	6.09

Table 2. Primary production measured at the sampling stations in the three study periods. PP chl^{-1} = chl *a* – normalized photosynthetic rates; PPa = phytoplankton production areal rates.

PP was always higher than HPP (U = 324, p< 0.001). The HPP rates in the water column displayed quite similar patterns to those observed for the PP (Fig. 2). HPP rates resulted regularly higher at the surface than at the bottom depth (U = 554, p < 0.01); only at St. 2C in April no difference was observed between the sampling depths. The Two-way ANOVA highlighted differences in the HPP rates of the surface and bottom layers between seasons and sampling stations ($F_{2,18}$=491.46 and $F_{2,18}$=252.91, p< 0.001 for surface layers and $F_{2,18}$=695.02 and $F_{2,18}$=131.14 p< 0.001 for bottom layers, respectively). The highest HPP rates were detected in June (Tukey's HSD, p< 0.01), always exceeding 0.72 ± 0.01 µgC L^{-1} h^{-1} at the surface and 0.32 ± 0.01 µgC L^{-1} h^{-1} at the

bottom. At St. 2C the HPP rates were always higher than at the other sampling stations (Tukey's HSD, $p < 0.01$), and reached the maximum value (2.17 ± 0.19 µgC L^{-1} h^{-1}) in June.

Particulate and sedimentary C and N stable isotopic ratios and contribution of organic matter sources to POM and SOM

The $\delta^{13}C$ signature of POM ranged between -26.49‰ (St. 2C, April) and -21.75‰ (St. 1I, June, Fig. 3a, Table S1) and values were distinct among sampling seasons and stations (Two–ways ANOVA, $F_{2,24}=17.58$, $p < 0.001$; $F_{3,24}=3.30$, $p < 0.05$, respectively). $\delta^{13}C_{POM}$ was higher in June compared to April (Tukey's HSD test, $p<0.01$) and at St. 1I than at St. 2C ($p < 0.05$). In the whole basin, $\delta^{15}N_{POM}$ ranged between 4.92‰ (St. 1E, June) and 9.81‰ (St. 2B, June) and values changed among seasons ($F_{2,24}=7.16$, $p < 0.005$) and stations ($F_{3,24}=12.64$, $p < 0.001$, Fig. 3b, Table S1). $\delta^{15}N$ data were higher in June and April compared to February (Tukey's HSD test, $p < 0.01$) and higher at St. 2B than at the other stations ($p<0.01$, Fig. 3b, Table S1). The average C:N ratio of POM was 6.90 ± 0.41 and did not change among seasons and stations (Table S1). $\delta^{13}C$ values in POM were generally lower than in SOM (t-test, $t=4.58$, $df=11$, $p < 0.001$) while no differences were observed for $\delta^{15}N$ (Figs. 3 and 4 and Table S1).

The $\delta^{13}C$ isotopic ratio of SOM ranged between -22.98‰ (April, St. 1I) and -20.09‰ (April, St. 2B) and did not show appreciable seasonal variations (Fig. 3a, Table S1). However, differences were observed among stations (One-way ANOVA, $F_{3,8}= 14.47$; $p < 0.01$). $\delta^{13}C_{SOM}$ at St. 2B, was higher than at the other stations (Tukey's HSD test, $p < 0.01$). The $\delta^{15}N$ values of SOM ranged between 6.12‰ (St. 1E, February) and 9.00‰ (St. 2B, June, Fig. 3b). $\delta^{15}N$ isotopic ratio did not show a seasonal trend but changed among stations ($F_{3,8}=23.67$, $p < 0.001$). St. 2B and 2C displayed higher values than St. 1E and St. 1I (Tukey's HSD test, $p < 0.01$, Fig. 3b and Table S1).

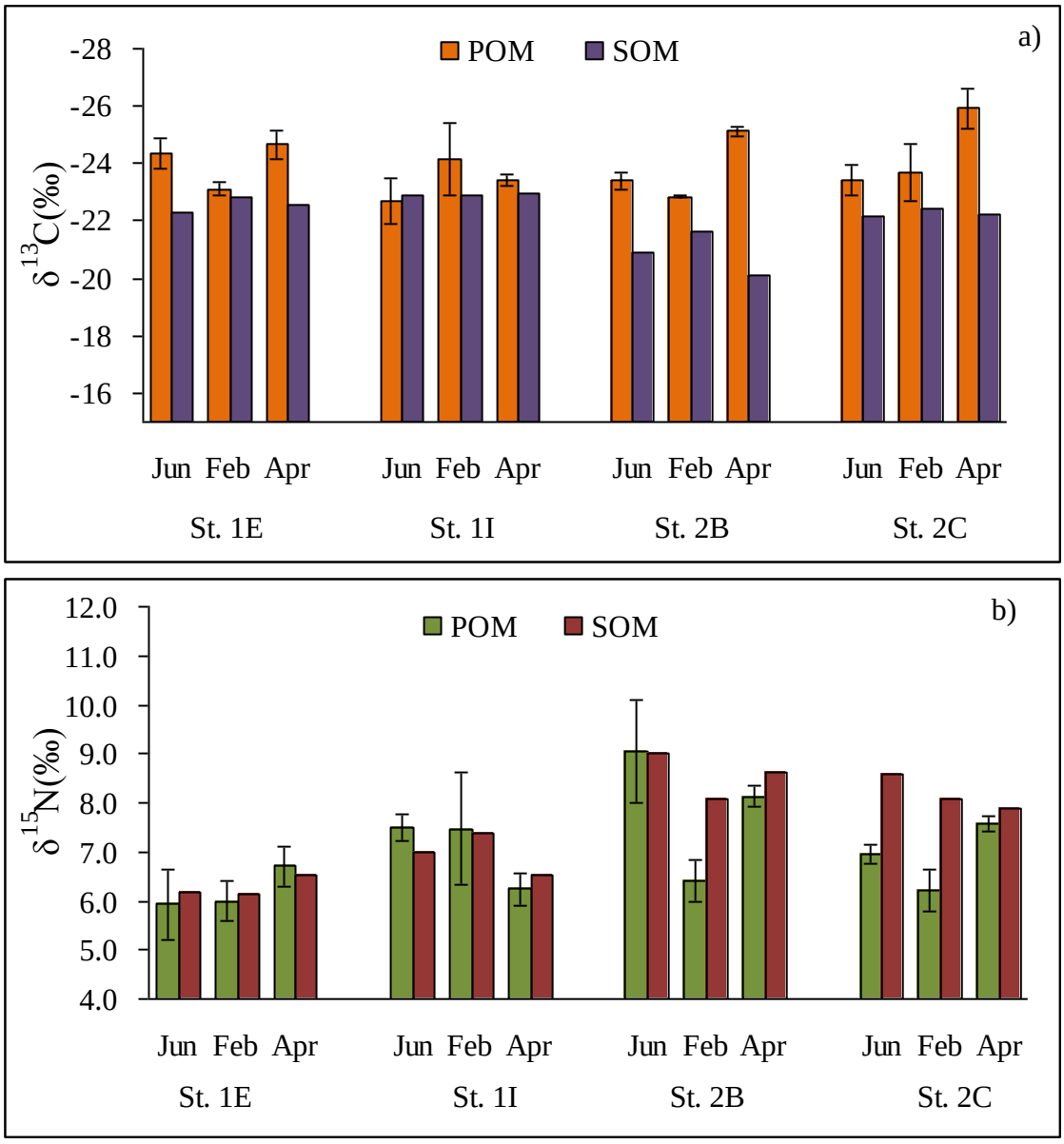

Figure 3. Average values of $\delta^{13}C$ (a) and $\delta^{15}N$ (b) of POM and SOM at each sampling station and season. The y-axis begins with a value of -16 in a) and 4 in b) to better highlight variations among stations and months. Values are shown in Table S1, supplementary material.

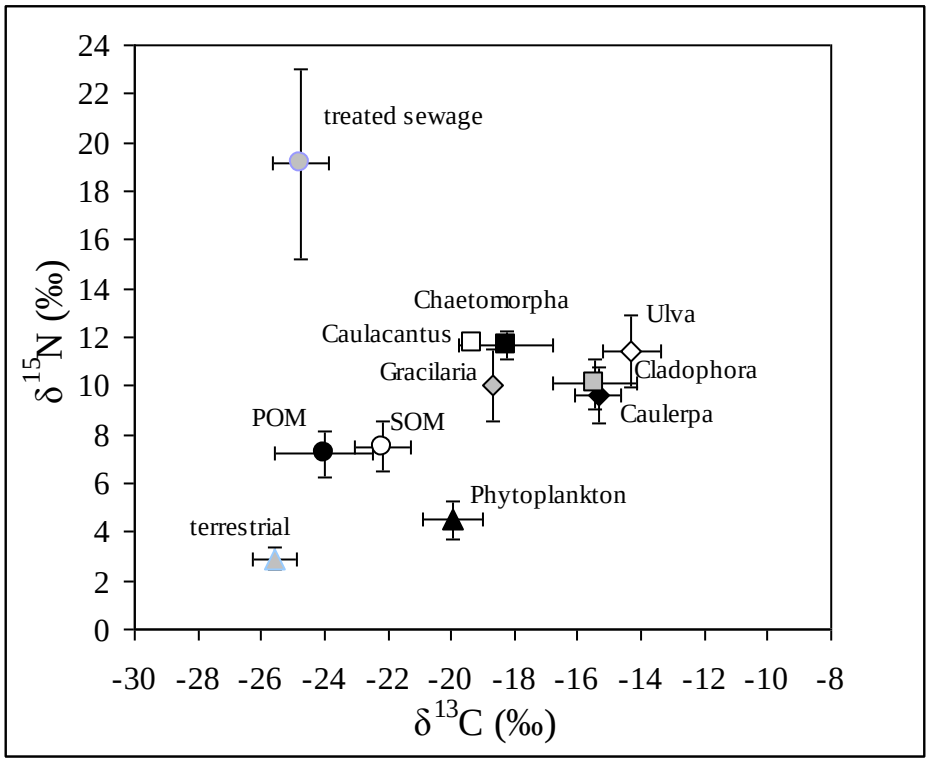

Figure 4. Stable isotope $\delta^{13}C$ and $\delta^{15}N$ bi-plots of POM (Particulate Organic Matter), SOM (Sediment Organic Matter), and potential end-members (different macroalgae, marine phytoplankton, terrestrial /riverine POM, treated sewage). Values are reported as average stable isotope and error bars represents standard deviations.

The C:N ratio in SOM ranged between 6.55 (St. 1E, February) and 17.13 (St. 1E, April) and did not change among seasons and stations (Table S1). The C:N ratio of SOM (12.14 ± 2.85) was higher than $C:N_{POM}$ ($t=2.43$, $df = 10$, $p < 0.05$, Table S1).

Average values of POM and SOM and end-members (sources) used for the model are plotted in Figure 4. Due to similar signature of different macroalgal species (Fig. 4), only the average isotopic value was used in the model (-16.83 ± 2.49 and 10.45 ± 1.27 for $\delta^{13}C$ and $\delta^{15}N$, respectively). Results of the stable isotope mixing model (SIAR) suggested that terrestrial/ riverine POM mainly contributed (45.5%) to POM pools at all sampling stations and months (Fig. 5a, Table S2). Such contribution was slightly higher during April and reached its maximum at St. 1E (mean contribution 54%). Phytoplankton only contributed up to 29% at St. 2B in February. Contribution

from sewage sources peaked at St. 2B in June and April (Fig. 5a, Table S2). As expected, SOM resulted a more homogeneous mix of organic inputs (Fig. 5b). Comparatively a higher contribution of terrestrial/riverine POM was evident in the sediments the 1st Inlet while the influence of sewage matter was higher in the 2nd one. Notably the contribution of macroalgae to the sediment pool increased up to 30-35% in June and April at St. 2B.

Macroalgal coverage

According to the map obtained by high resolution multispectral satellite remote sensing, the south-eastern area of the 2nd Inlet was the most densely colonised by macroalgae, while in the 1st Inlet a much lower areal coverage was observed. Different green macroalgae were observed by divers in the 2nd Inlet, mostly *Caulerpa prolifera* and *Caulerpa racemosa* but also *Chaetomorpha* sp. that were occasionally trapped in a van Veen grab or occurred in our sediment cores. Coverage percentages resulted to be 0% at St. 1E; 10-15% at St. 1I; 30-40% at St. 2C and 90-100% at St. 2B with a very patchy distribution at this latter station (Fig. 1). Pmax of *Caulerpa* sp. was 0.22 mg C $m^{-2}\,h^{-1}$ at St. 1I, 0.52 mg C $m^{-2}\,h^{-1}$ at St. 2C, whereas reached 1.42 mg C $m^{-2}\,h^{-1}$ at the patchy colonized St. 2B.

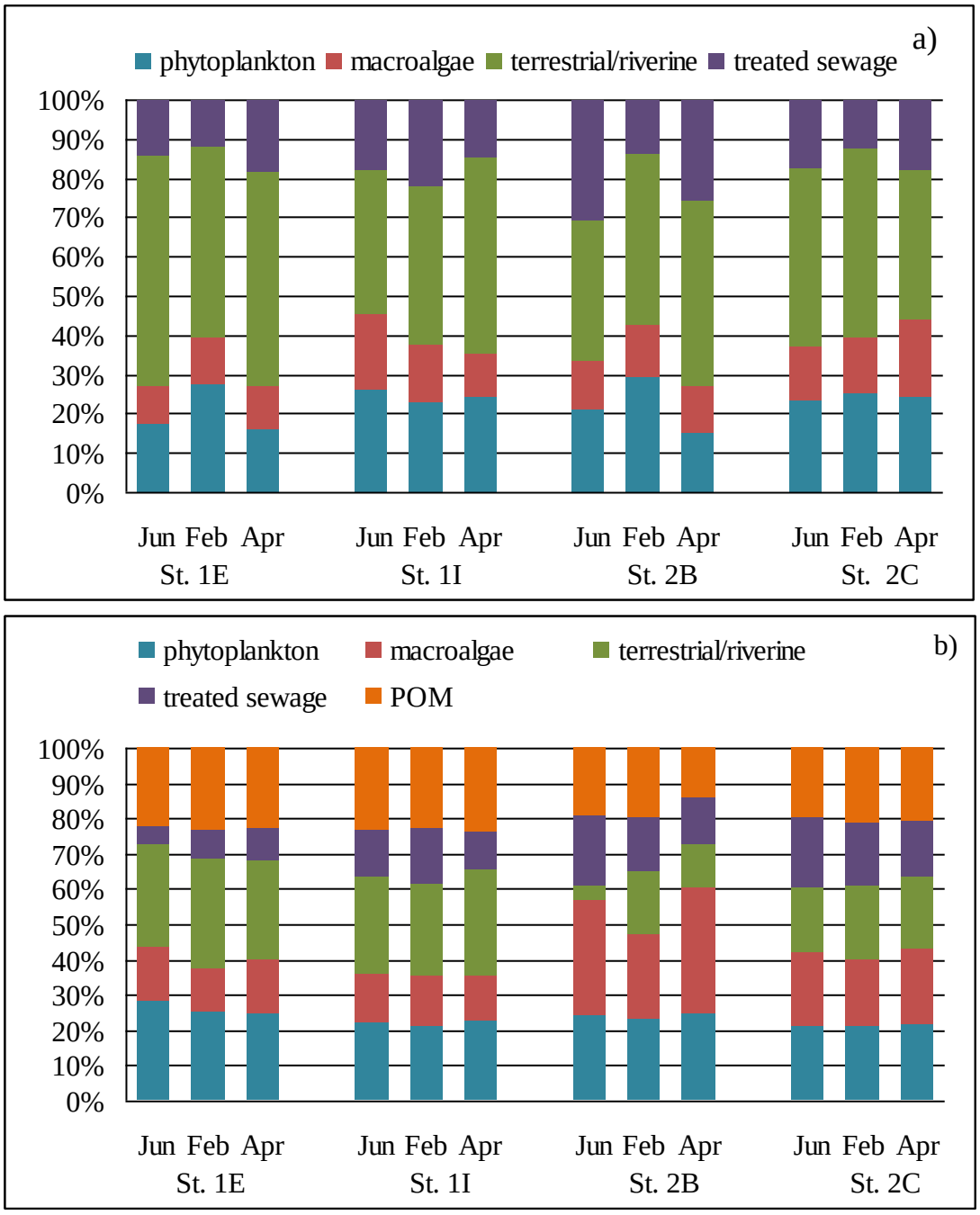

Figure 5. Output of the mixing model (SIAR) showing a) the mean percentage of contribution of potential organic matter sources to the particulate organic matter (POM) pool and b) to the sediment organic matter (SOM) pool. Values (mean, and 95% confidence intervals) for each source are shown in Table S2 in the supplementary material.

Contaminants in surface sediments

In June total PCBs concentrations ranged from about 46.0 ng g^{-1} d.w. (St. 2B and 2C) to 1159.7 ng g^{-1} d.w. (St. 1I) and in April from 39.0 ng g^{-1} d.w. (St. 2C) to 1067.6 ng g^{-1} d.w. (St. 1I) (Table 3). PCB 153 resulted the most abundant congener that accounted for approximately 15-30% of the total concentration (Table 3). PCB patterns were always dominated by hexa- penta and eptachlorinated biphenyls in both surveys, while the lower chlorinated congeners (tri- and tetrachlorobiphenyl) generally represented a small (<5%) contribution to the total loading (Fig. 6a and b).

PCBs (ng g^{-1} d.w.)	Sampling date	Stations			
		St. 1E	St. 1I	St. 2B	St. 2C
PCB ∑28	**June 2013**	551.8	1159.7	45.3	46.0
PCB ∑7target		280	590.7	24.3	22.5
PCB 153		84.1	167.3	9.0	8.5
PCB ∑28	**April 2014**	164.9	1067.6	164.8	39.0
PCB ∑7target		89.1	521.1	82.7	19.1
PCB 153		50.9	189.3	32.4	7.9

Table 3. PCBs concentrations analysed at the four stations in June 2013 and April 2014, expressed as the sum of 28 PCB congeners, the sum of 7 target PCBs (∑PCB 28-52-101-118-153-138 and 180) and of the congener PCB153 that is commonly used as a proxy of the PCB concentration.

Overall, metal concentrations measured in surface sediments were higher in April than in June, except for Fe, Al and Cr (Table 4). Higher concentrations were obtained in sediments from the 1st Inlet than those from the 2nd one. In particular, As, Cu, Zn. Pb, Mn, Sn and Hg, consistently displayed higher concentrations at St. 1E and St. 1I compared to those at St. 2B and St. 2C.

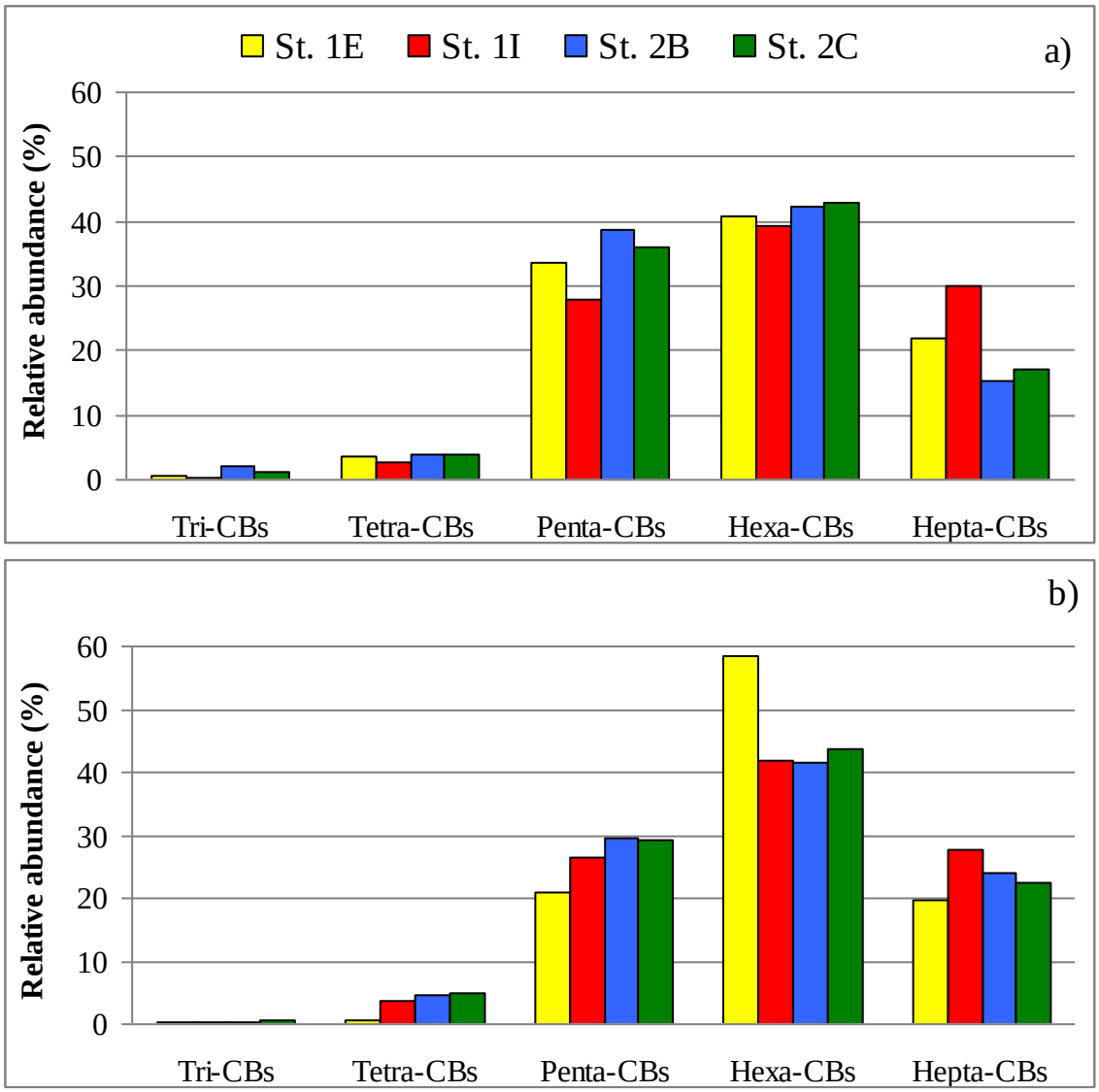

Figure 6. PCB homolog distribution in sediments at the four stations in June 2013 (a) and April 2014 (b).

Multidimensional scaling (MDS) and Analysis of Similarity (ANOSIM)

A good spatial separation of samples was obtained in the MDS both for surface (stress = 0.05) and bottom data (stress = 0.07) (Fig. 7a, b). According to ANOSIM, significant differences were obtained among sampling periods both for surface (R_{ANOSIM} = 0.658, p = 0.1%) and bottom samples (R_{ANOSIM} = 0.456, p = 0.1%), between the two Inlets (R_{ANOSIM} = 0.195, p = 2.6% and R_{ANOSIM} = 0.408, p = 0.5% for surface and bottom data, respectively) as well as among stations (R_{ANOSIM} = 0.118, p = 3.3% and R_{ANOSIM} = 0.173, p = 0.9% for surface and bottom data,

respectively). The pairwise ANOSIM test performed on stations did not result significantly different for surface data, whereas the bottom of St. 2C was significantly different from both St. 1E (R_{ANOSIM} = 0.224, p = 2.1%) and St. 1I (R_{ANOSIM} = 0.181, p = 3.8%).

Stations	Sampling date	As	Cd	Cr	Cu	Fe	Ni	Zn	Pb	Al	V	Mn	Sn	Hg
		mg kg^{-1} d.w.												
St. 1E	**June 2013**	15.05	0.87	35.50	34.86	16590	26.90	135	50	27774	47	189.08	6.91	0.90
St. 1I		17.16	0.90	26.44	56.69	22570	27.40	189	100	21499	51	163.39	7.86	1.62
St. 2B		11.90	0.90	26.76	25.80	17894	25.67	99	23	26923	49	136.36	2.48	0.60
St. 2C		11.03	0.99	32.09	25.66	21800	27.02	108	21	32942	55	125.89	1.99	0.30
St. 1E	**April 2014**	19.66	1.06	13.03	180.35	16136	43.59	231	80	18231	74	382.55	10.57	1.34
St. 1I		26.45	1.40	25.99	100.48	33840	59.28	319	152	16838	109	375.74	14.84	5.74
St. 2B		17.40	1.60	59.70	64.91	40760	63.22	222	74	25705	128	320.66	6.36	0.49
St. 2C		17.44	2.64	48.52	55.19	26944	63.94	180	51	25168	122	335.65	4.02	0.10

Table 4. Concentrations of the 13 heavy metals analysed at the four stations in June 2013 and April 2014.

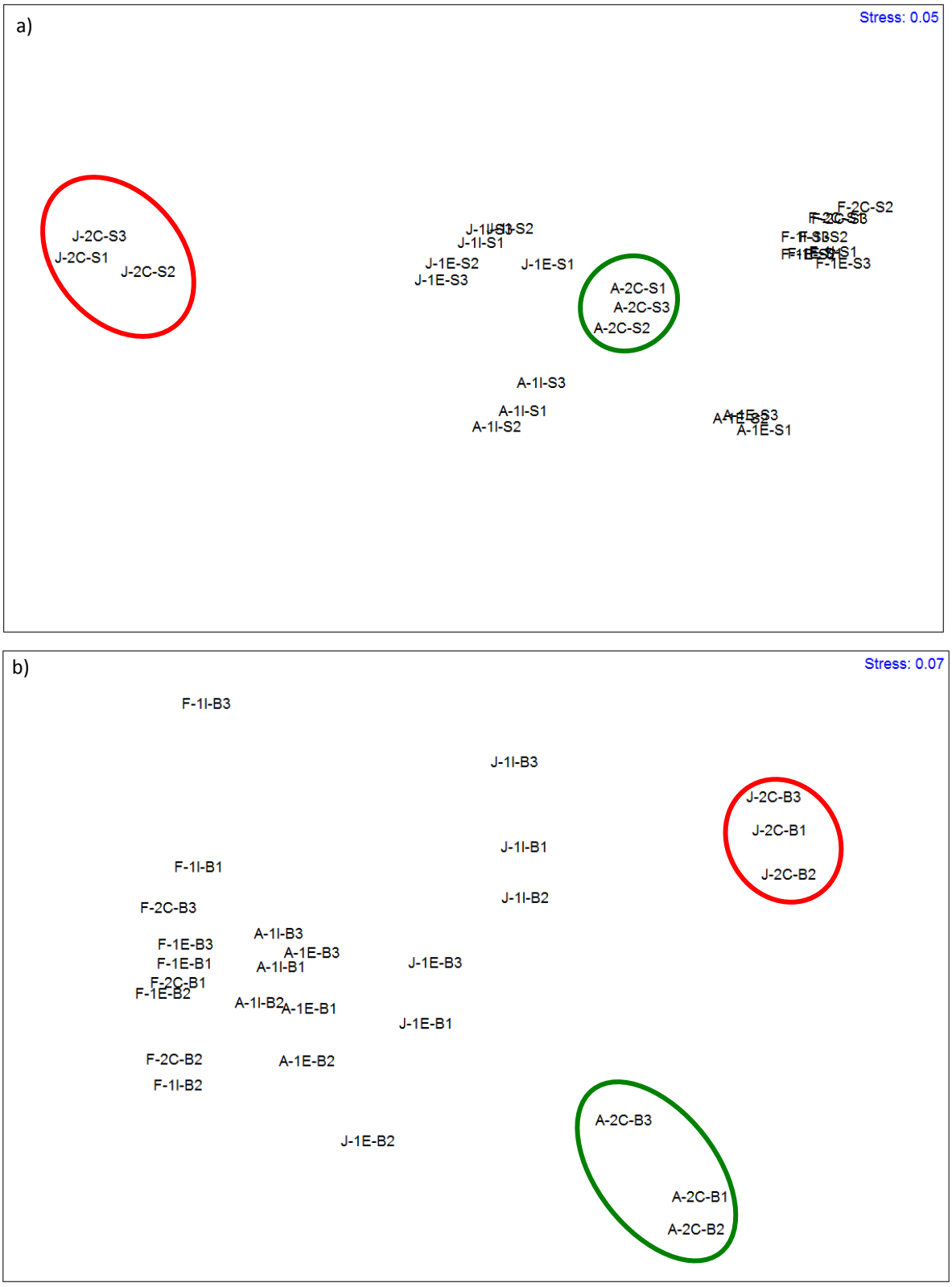

Figure 7. Multidimensional scaling analysis (MDS) based on PP and HPP, abundances of autotrophic and heterotrophic picoplankton and nanophytoplankton (a) at the surface (S) and (b) at the bottom layer (B). In b) also the $\delta^{15}N$ and $\delta^{13}C$ signatures of POM are included in the analysis. Replicated (n = 3) samples are indicated per Station (St. 1E, 1I and 2C) and samplings month (F-

February, A-April, J-June). Green and red circles enclose April and June samples from the 2nd Inlet, respectively. February data are not clearly separated between Inlets and thus are not enclosed in circles.

Discussion

Primary production and heterotrophic prokaryotic production in the Mar Piccolo

In this study, for the first time, we measured primary production (PP) and heterotrophic prokaryotic production (HPP) in the Mar Piccolo of Taranto. PP values were well above 2 µg C L^{-1} h^{-1} also during winter indicating that the Mar Piccolo is a quite productive basin. Values were strongly influenced by light availability in the water column, as demonstrated by the highly significant correlation with the PAR irradiance (R = 0.76, p<0.001, Table 1). Due to the high phytoplankton production, the basin was oversaturated in oxygen, as confirmed by the oxygen profiles registered in the water column in two sampling periods (Table 1).

PP rates were highly correlated with chl *a* concentrations (R = 0.80, p<0.001). The relatively high phaeo/chl *a* ratios (1.5 at the surface layer and up to 3.7 at the bottom) observed in February suggested that in that month the phytoplankton assemblage was in the senescent phase. Interestingly, the phytoplankton assemblage responsible for the highest PP rate estimated in June in the 2nd Inlet was presumably also in a senescent phase, as indicated by a phaeo/chl *a* ratio of 2.44.

Hourly PP rates in the Mar Piccolo resulted much lower than those reported for the highly eutrophic Berre Lagoon in France (PP rates up to 1600 µg C L^{-1} d^{-1}, Gouze et al. 2008), but comparable with those estimated in the Thau lagoon (up to 20 µg C L^{-1} h^{-1}, Bec et al. 2005). Conversely, our PP chl^{-1} values were lower compared to those estimated in a highly dynamic system, off the Po River delta (Mangoni et al. 2008).

Overall, HPP rates in the Mar Piccolo were comparable or slightly higher than the integrated values reported by Karuza et al. (2012) for the Gulf of Trieste as monthly means calculated over a 10-year period (<0.5 µg C L^{-1} h^{-1} in June, ~0.2 µg C L^{-1} h^{-1} in February and ~0.25 µg C L^{-1} h^{-1} in

April). The HPP rates estimated in February were proximal to the mean value of 487.2 ± 638.1 ng C L^{-1} h^{-1} measured in surface waters at large-spatial scale in the Adriatic Sea in the same season by Gallina et al. (2011).

HPP was highly correlated with the abundance of heterotrophic picoplancton (R = 0.88, $p<0.001$) and in June was highly coupled with the prokaryotic biomass (63.27 ± 3.10 μg C L^{-1}) (Karuza et al. 2015 this issue). HPP matched also the maximum PP rate (20.07 ± 3.12 μg C L^{-1} h^{-1}) likely due to a major abundance of small diatoms in June (Karuza et al. 2015 this issue) that are known to produce labile exudates (Hoagland et al. 1993), easily available for prokaryotic growth. Moreover, the high phaeo/chl *a* ratio also indicated the presence of sinking degraded phytoplankton that could represent highly palatable substrata for heterotrophic prokaryotes.

HPP rates were further tightly related to the concentrations of both the Particulate and Dissolved Organic matter (POC and DOC) in the water column (R = 0.81, $p<0.001$ with POC, and R = 0.73, $p<0.01$ with DOC). In particular, in June 2013 DOC varied between 1.273 mg L^{-1} and 1.587 mg L^{-1} at the bottom of St. 2C and of St. 1E, respectively. On the other hand, in April 2014 it ranged from 0.902 mg L^{-1} at the bottom of St. 1E to 1.963 mg L^{-1} at the surface of St. 2C (Kralj et al. 2015 this issue). The extracellular release of recently fixed photosynthate contributes to the production of DOC in marine ecosystems and is particularly important for the trophic ecology of the plankton. The released compounds are susceptible to rapid uptake by heterotrophic bacteria, giving way to a linkage between primary and bacterial production that is essential for the cycling of matter through the microbial loop and the microbial food web (Marañón et al. 2004). Indeed, considering the entire study period, our PP and HPP hourly rates exhibited exactly the same pattern (Fig. 2) and their correlation was highly significant (R = 0.90, $p<0.001$). Our mean PP/HPP ratio was 20.96 and, excluding one outlier, it varied between 7.09 and 29.89. Previously, Puddu et al. (1998) demonstrated that in the northern Adriatic the bacterial mediated processes are tightly coupled with the phytoplankton production. They reported that a very high percentage (40-80%) of the carbon fixed by the phytoplankton has been requested for bacterial metabolism. Data of PP and

HPP in the Mar Piccolo suggested that, especially in June, these two processes were clearly in phase. Therefore, in this basin the phototrophic plankton appear to be a main driving force in C-cycling, independently from their dimensional range and seasonal succession. The flow of C through the system seemed clearly shaped by two essential steps, i.e. the processes of primary production and OM degradation, quite active and efficient in the water column.

Higher PP and HPP rates in the 2nd Inlet are likely due to a major biomass of both autotrophic and heterotrophic organisms observed in the 2nd Inlet during our surveys (Karuza et al. 2015 this issue). Indeed, from 2002 onwards, higher plankton biomass in the 2nd Inlet has been well documented (Caroppo et al. 2012), mostly ascribable to its more lagoonal features. This Inlet is shallower and characterised by a higher freshwater input and lower salinity compared to the 1st one (Cardellicchio et al. 2015 this issue) favouring the development of the phototrophic organisms in the water column. Although mussels that cover 2/3 of the 2nd Inlet sequestrate a good part of the available biomass (Caroppo et al. 2012), the remaining fraction is still higher compared to that of the 1st Inlet. We infer that a possible co-factor responsible for both the overall lower phytoplankton biomass and PP and HPP rates in the 1st Inlet may be the higher concentration of contaminants in its surface sediments. Through resuspension these contaminants could be temporarily transferred to the water column, entering the pelagic trophic web and interfering with the proper functioning of the pelagic ecosystem. Several studies have reported detrimental effects of contaminants on phytoplankton (Caroppo et al. 2006, Lafabrie et al. 2013a, Tiano et al. 2014) and photosynthesis (Pérez et al. 2006) in association with increased respiration rates (Lafabrie et al. 2013b).

In order to have an overview of the PP and HPP in the entire basin, the rates measured in the water column were integrated to those obtained in surface sediments (Table 5) (Franzo et al. 2015 this issue; Rubino et al. 2015 this issue). Since we estimated benthic processes only in June 2013 and April 2014, an integration was possible only in these two sampling periods. Primary and heterotrophic prokaryotic production rates obtained in the water column (PPw, HPPw) were

converted from µg C L^{-1} h^{-1} to mg C m^{-2} h^{-1} and added to those estimated in surface sediments (PPs, HPPs) to have an evaluation of the total rates (PPi, HPPi) at the three sampled stations in the Mar Piccolo (Table 5).

	June 2013							
	PPw	PPs	PPi	PPs/PPw	HPPw	HPPs	HPPi	HPPs/HPPw
	mg C m^{-2} h^{-1}				mg C m^{-2} h^{-1}			
St. 1E	6.59	0.69	7.29	0.11	0.52	0.57	1.09	1.10
St. 1I	4.32	0.06	4.38	0.01	0.68	0.33	1.01	0.49
St. 2C	12.62	0.25	12.86	0.02	1.48	0.55	2.03	0.37
	April 2014							
	PPw	PPs	PPi	PPs/PPw	HPPw	HPPs	HPPi	HPPs/HPPw
	mg C m^{-2} h^{-1}				mg C m^{-2} h^{-1}			
St. 1E	2.58	0.27	2.85	0.10	0.26	0.10	0.36	0.41
St. 1I	3.24	0.13	3.37	0.04	0.39	0.05	0.44	0.14
St. 2C	6.09	0.50	6.59	0.08	0.61	0.16	0.77	0.27

Table 5. Primary and heterotrophic prokaryotic production rates in the water column (PPw, HPPw), in surface sediments (PPs, HPPs) and as integrated rates (PPi, HPPi) at the three sampled stations and during the two sampling periods.

PPw values were always much higher than PPs ones. The highest contribution of PPs to PPi was around 10.5% and was calculated in the center of the 1st Inlet in both sampling months. Lower PPs contribution was found at St. 1I close to the navy base. These total primary production rates (up to 12.86 mg C m^{-2} h^{-1}) are quite low for an enclosed shallow basin, such as the Mar Piccolo. In fact, considering the PP both in the water column and in the sediment, the microphytobenthos alone may contribute up to 50% of the total PP in shallow coastal systems (Perissinotto et al. 2002; Montani et al. 2003). We suggest that low PPs rates in the Mar Piccolo, especially at St. 1I, are likely ascribable to the high concentration of PCBs, heavy metals (Tables 3, 4) and other contaminants accumulated in the sediments that can inhibit benthic PP and therefore interfere with the proper functioning of this ecosystem.

Yet, these estimates do not consider the contribution of macroalgae. At St. 1E the bottom was unvegetated, as confirmed by the satellite map (Figure 1), and therefore no additional contribution had to be considered. At St. 1I, *Caulerpa* sp. with a P_{max} of 0.22 mg C m^{-2} h^{-1} could lead to an integrated value up to 4.60 mg C m^{-2} h^{-1} in June. At St. 2C, with a macroalgal contribution of about 0.52 mg C m^{-2} h^{-1}, the estimated total production of the system could reach 12.91 mg C $m^{-2}h^{-1}$. Overall, at the investigated stations the phytoplankton is confirmed to be by far the most important primary producer in the Mar Piccolo.

The contribution of HPPs to HPPi was much higher in June than in April (Table 5). In June, the calculated rates in the water column and in the surface sediments were comparable, particularly at St. 1E, whereas HPPs contributed approximately for one third to HPPi at the other two stations. The low phaeo/chl *a* ratios observed in June at St. 1E re-enforce the idea that the higher rates could be boosted by the input of fresh organic matter from the water column. Conversely, an overall lower HPPs contribution to HPPi was obtained in April, especially at St. 1I (ca. 12%).

Isotopic signature of POM and SOM and contribution of organic matter sources

Mean $\delta^{13}C$ (-23.90‰) of particulate organic matter (POM) in the Mar Piccolo resulted comparable to values reported in the Lapalme and Venice lagoons (Berto et al. 2013; Carlier et al. 2007) and in the bay of Marseille (Cresson et al. 2012) and lower than those reported for other Mediterranean coastal surface waters and lagoons (Mazzola et al. 1999; Vizzini and Mazzola 2003). POM was highly ^{13}C depleted when compared to the typical signature of marine phytoplankton indicating the predominance of allochthonous sources of terrestrial origin (Cresson et al. 2012; Harmelin-Vivien et al. 2008). This result was confirmed by the SIAR model which showed a contribution (up to 54%) of terrestrial/riverine POM to the entire pool. The ^{13}C depleted signal was more pronounced during April and could reflect high late-winter land runoff or freshwater intrusion which is one of the main features of this Inlet (Cardellicchio et al. 2015 this issue). $\delta^{15}N_{POM}$ values in the Mar Piccolo were comparable to those reported by Cresson et al. (2012) in the bay of

Marseille. Both $\delta^{15}N$ values and the SIAR model clearly reflected a major nutrient enrichment of the 2nd Inlet (higher $\delta^{15}N$ values detected during June and April at St. 2B for POM and at St. 2B and 2C for SOM) compared to the 1st Inlet. This enrichment could be due, as suggested by the mixing model, to the input of wastewater nutrients or alternatively to the organic matter derived from animal waste from the nearby mussel farming area (Owens 1985; Vander Zanden and Rasmussen 2001; Vizzini and Mazzola 2004) which covers 2/3 of the surface of the 2nd Inlet. The measurement of specific end-members for the mussel farm activities (faecal material, biodeposits) will help to resolve this issue.

Impact of contaminated-sediment resuspension on the ecosystem functioning

At the four investigated sites, PCBs displayed dissimilar seasonal patterns. Particularly in April, PCBs concentrations increased at St. 2B while they decreased at St. 1E. This could be attributed to natural and anthropogenic disturbance events that cause episodic sediment resuspension present in these areas of the basins and that lead to changes in the chemical properties of sediments. High levels of PCBs measured in the sediments of St. 1I obtained in this study are in agreement with previous reports in which this area is described as a major source of PCBs for the Mar Piccolo of Taranto (Cardellicchio et al. 2007). The general uniformity in the PCB pattern found in the surface sediments of the Mar Piccolo suggests that the contamination source was probably the same in all the investigated sites, likely related to the navy arsenal activities. In particular, considering the sum of the 7 target PCBs, PCB 153 alone accounted for 57 % of their concentration, followed by PCB 138 and PCB 180, a pattern that is in agreement with previously reported data (Gómez-Lavín et al. 2011; Okay et al. 2009; Secco et al. 2005). Their high concentration is consequent to the major amount of these compounds in the commercial PCB mixtures, such as Aroclor 1260. Moreover, the predominance of highly chlorinated compounds is mostly due to their relative stability and persistence (Naso et al. 2005) whereas lowly chlorinated compounds are degraded more quickly.

We obtained higher concentrations of most of the analysed metals in sediments from the 1st Inlet compared to those from the 2nd one. Our findings are in agreement with the results of Calace et al. (2005) and Cardellicchio et al. (2009), who reported that the 1st Inlet of the Mar Piccolo is more contaminated by metals than the 2nd one. These derive partially from the seawater coming from the Mar Grande through the two channels (in turn influenced by industrial wastewaters) but, to a much greater extent, from the presence of shipbuilding activities of the main Italian navy base, located in the 1st Inlet. The frequent passage of navy ships and submarines in the centre of the 1st Inlet, where the maximum depth reaches 13 m, might resuspend the first centimetres of sediments that from the deeper layers reach the surface. In these subsurface layers, due to anoxic conditions and the presence of hydrogen sulphide, metals are present in the form of insoluble sulphurs, tightly linked to the organic matter (Caroppo and Cardellicchio 1995). Once at the surface, under oxic conditions a fraction of metals could change the oxidation state becoming more bioavailable and facilitating, therefore, their entry into the pelagic food web.

Overall, higher concentrations of As, Cu, Zn, Pb, Mn, Sn and Hg were observed in April compared to June data. Also considering a certain degree of spatial variability that may have occurred during sampling, metal concentrations were consistently higher at the four stations in April. These great differences between the two sampling periods (up to more than twice) may be attributable to phytoplankton dynamics (Heimbürger et al. 2010). According to these authors, higher metal concentrations in the water column coincide with blooms of nano- and picophytoplankton because they accumulate more efficiently particle-reactive trace metals, especially Hg, due to their greater surface/volume ratio compared to microphytoplankton. Therefore, we can infer that our lower metal concentrations in surface sediments in June may be attributed to a partial sequestration of these compounds by nanophytoplankton that reached up to $1.3\times10^{7} \pm 5.9 \times10^{5}$ cells L^{-1} in that month (Karuza et al. 2015 this issue).

To date, the effects of resuspension of contaminated sediments on pelagic organisms and ecosystem functioning remain underresearched (Lafabrie et al. 2013a). For instance, the processes

of PCBs transfer at the lowest trophic levels are poorly understood and the mechanisms of PCBs uptake by plankton are still a matter of scientific discussion (Tiano et al. 2014). Our results provide new insights into these open questions as summarised in the MDS outputs. The pelagic system functioning seems to be variably influenced by resuspension events according to the season and the depth. In Figure 7b, in June St. 2C was clearly separated from the other sites suggesting a different environmental situation from the 1st Inlet. The stratification of the water column that began in early summer slowed down the water exchange between the two Inlets and enhanced the confinement characteristics of the 2nd one. In contrast, February samples were not well separated, probably following the winter mixing of the water column while the intermediate position of April samples seems to corroborate the hypothesis of the gradual decrease of naturally-induced sediment resuspension from winter towards early summer. On the other hand, the MDS performed on surface data (Figure 7a) suggests that the effects of resuspended contaminants on the pelagic system could vary according to the distance from their main source, i.e. the sediments. Surface samples, in fact, did not show a clear separation among stations and/or inlets suggesting that, at the surface, even the most impacted site was comparable to the others. This hypothesis is also confirmed by the pairwise ANOSIM test performed on stations separating surface from bottom samples. While at the surface the stations did not result significantly different among each other, the bottom of St. 2C was significantly different from both St. 1E (R_{ANOSIM} = 0.224, p = 2.1%) and St. 1I (R_{ANOSIM} = 0.181, p = 3.8%).

Conclusion

In this study, for the first time, phytoplankton primary production (PP) and heterotrophic prokaryotic production (HPP) were measured in the Mar Piccolo of Taranto and used as proxies of the ecosystem functioning. This semi-enclosed basin resulted quite productive over the study period. Considering the three major primary producers (phytoplankton, microphytobenthos and macroalgae), the phytoplankton resulted by far the most important primary producer at the

investigated sites. This was also confirmed by the SIAR model that, although indicating an overall major contribution of allochthonous material of terrestrial origin to the POM pool, pointed to a more pronounced contribution of phytoplankton compared to that of macroalgae. The contribution of macroalgae to the sediment pool was higher in one site of the 2nd Inlet densely colonized by macroalgae, as confirmed by the satellite map of the seabottom.

Over the study period, PP and HPP data exhibited exactly the same pattern, indicating that the heterotrophic prokaryotes were boosted by the extracellular release of recently fixed photosynthates and degrading phytoplankton cells. In spring and early summer, significantly lower PP and HPP rates were found in the 1st Inlet compared to the 2nd one, suggesting a detrimental effect of contaminants which could be resuspended from the heavily polluted sediments of the navy arsenal and spread over the whole 1st Inlet. However, their interference with the proper functioning of the pelagic ecosystem seems to be limited to the bottom layers.

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