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WATER QUALITY IN THE PORT OF VIAREGGIO: A GEOCHEMICAL AND BIOLOGICAL CHARACTERIZATION

Jacopo Cabassi[1], Claudia Rossano[2], Simone Gambineri[2], Fabiola Fani[2], Orlando Vaselli[1], Franco Tassi[1], Luciano Giannini[1], Luigi Lazzara[2], Caterina Nuccio[2], Antonella Buccianti[1], Francesco Capecchiacci[1], Mannuccio Mannucci[2], Luca Massi[2], Chiara Melillo[2], Giovanna Mori[2], Felicita Scapini[2]

[1]Dipartimento di Scienze della Terra, Università degli Studi di Firenze e CNR-IGG – Istituto di Geoscienze e Georisorse, Via La Pira, 4 - 50121 Firenze, Tel. +39 055 2757507, Fax. +39 055 284571, e-mail: jacopo.cabassi@unifi.it

[2]Dipartimento di Biologia, Università degli Studi di Firenze – Laboratori di Zoologia ed Ecologia, Via Romana, 17 - 50125, Via Micheli, 1 - 50121 Firenze

Abstract – Port areas are generally affected by anthropogenic impacts, which favor pollution and spoil water quality and aquatic ecosystems. In July 2015, a geochemical and biological transect was carried out in the Port of Viareggio (Tuscany, central Italy) from the main channel (Burlamacca), predominantly fed by the waters of the adjacent Massaciuccoli Lake, to the main docks and the open sea. Nine stations were studied for physical, chemical, bio-optical and biological parameters investigating, for each site, the vertical profile of the water column. The main aim was to provide a preliminary water quality assessment of the port area. The inorganic chemical composition highlighted the presence of mixing processes between seawater and low-salinity waters, causing a gradient of transitional waters and a vertical stratification of the water chemistry with increasing Na^+-Cl^- concentration in the deep waters and moving toward the sea while dissolved O_2 was decreasing with depth and towards inland. Relatively high concentrations of Hg and Ni were localized in seven samples in the docks area and the Burlamacca Channel, possibly related to: 1) industrial punctual pollution; 2) input of domestic wastewaters; 3) input from agricultural practices. A sharp decreasing trend from the innermost waters to the open sea characterized most of the analyzed parameters. Trophic indicators (chlorophyll-*a*, total nitrogen-N and total phosphorus-P) and CDOM (chromophoric dissolved organic matter) concentrations decreased from the highest values in the inner docks to the site located outside the port. The highly eutrophic conditions of the waters were summarized using TRIX index (Chl*a*, oxygen saturation, N and P), which assigned a "poor" ecological status to all the port sampled stations and "moderate" to the marine site. The light attenuation coefficient was well correlated with the concentrations of the optical components (total suspended matter-TSM, CDOM, Chl*a*), with a prevailing role of CDOM and Chl*a*, confirming the eutrophic conditions and the key role of phytoplankton, which was present in relatively high abundances with a typical composition of transitional waters. An inside-outside gradient of zooplankton diversity was also observed, along which the more confined waters showed the lowest biodiversity index values, with the presence of a few dominant species. The multivariate models showed water temperature, conductivity and CDOM as significant variables to explain the observed variations. Impact of shipyards, low hydrodynamics and nutrient inflow from the Burlamacca Channel appeared as the main elements affecting the port, posing serious risks to the natural balances.

Introduction

Aquatic systems, more than terrestrial ones, are mutable in space and time. A port area is subjected to strong anthropogenic impacts and is characterized by many variables that interact to produce more or less stable equilibrium. Organic and inorganic pollution is commonly buffered by physical and chemical processes, such as currents, dispersion, dilution, or chemical reactions, as well as by biological ones, e.g. transformation of substances by microorganisms, phytoplankton and zooplankton. In coastal waters and, in particular, in port areas, the impairment of such equilibrium, generated by spills of excessive amounts of harmful substances and/or huge intake of nutrients, lead to unpleasant side effects, including: odour, presence of floating debris and foam on the water surface, possibility of abnormal algal blooming resulting in water quality degenerative processes as anoxia, accumulation of harmful substances in the water and sediment, diffusion of allergenic substances along the coast, die-off of organisms contributing to maintain low concentrations of organic matter and negative effects on fish species of commercial interest. Anthropogenic impacts acting on the port area can be amplified due to specific features of each site, such as low hydrodynamics and natural intake of nutrient load through input channels, or potentially polluting substances such as heavy metals.

In order to have a detailed snapshot of the ecological situation in the Port of Viareggio, known for its importance for both shipbuilding and tourism activities, a set of geochemical and biological parameters, potential indicators of water quality useful for a quick overall assessment of the harbour environmental state, were selected and studied. These parameters were:

1) Dissolved oxygen (O_2), highlighting the water oxygenation, a fundamental parameter affecting the sustainability of the port ecosystem. An O_2 concentration close to zero may result in a water anoxia state, leading to the disappearance of aerobic organisms.
2) Trace elements (As, B, Ba, Be, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se, Sn, V and Zn), which may cause harmful effects on human health if assimilated even in small doses for a long period. They are diffused in water depending on their own geochemical mobility (regulated by redox potential, pH and concentration of complexing substances) and are useful to search out potential sources of pollution, e.g. industrial or domestic wastewater or discharge of nutrients and fertilizers used in agriculture [11].
3) Phytoplankton, unicellular microalgae constituting the main primary producers suspended in the water column. It is strongly influenced by light, inorganic nutrients (nitrogen, phosphorus and silicon) and physical conditions of the water column. It may be characterized by concentration of Chlorophyll-*a* (Chl*a*), cell abundance, taxonomic composition and species diversity and responds quickly to environmental changes, acting as one of the Biological Quality Elements that define the ecological status of the aquatic ecosystems (Water Framework Directive, WFD 2000/60 and Marine Strategy Directive, MSFD 2008/56, [3]). Furthermore, Chl*a*, together with total suspended matter (TSM) and chromophoric dissolved organic matter (CDOM), is the main Light Absorbing Substances (LAS), and this analysis was processed to attempt a classification of the port waters based on their bio-optical properties.
4) Zooplankton, small animals feeding on phytoplankton and bacteria or smaller zooplankton organisms. Ports can provide protected areas rich in nutrients, where these

planktonic organisms make their entire life cycle, but anthropogenic pollution can also cause their rapid die-off. Zooplankton represents a well-known organism group for its ecology and is considered a potential biomarker within the WFD [3].

This work was focused on the assessment of the water quality inside the Port of Viareggio, by also checking the possible existence of water gradients affecting the selected geochemical and biological parameters.

Materials and Methods

Water sampling was performed on July 8-9, 2015 in the area immediately outside of the port, in the docks and along the Burlamacca Channel at a total of nine stations (Fig. 1), located in points that, according to a first cartographic examination, were considered of particular interest. The surveys involved: physical-chemical parameters of the water column, heavy metals bio-available and not bio-available in water, nutrients and organisms in the water column (phytoplankton and zooplankton).

The water physical-chemical parameters along the vertical profile were measured using a multi-parametric probe (Hydrolab Idroprob), to provide a correct estimation of depth (m), temperature (°C), Eh and pH, dissolved oxygen (O_2 in mg L^{-1}) and electric conductivity (mS cm^{-1}). Water aliquots for nutrient analysis and phytoplankton samples were also taken. The collection of zooplankton samples was performed with an Apstein net. Water aliquots for chemical analyses were sampled at the surface and near the bottom for each station (with the exception of ST7 that was only collected at the surface).

For each sample, specific aliquots were collected, as follows: 1) a 125 mL sample for the determination of the main anions; 2) a 50 mL sample, filtered at 0.45 μm and acidified with 0.5 mL of HCl Suprapur, for the determination of the main cations; 3) a 50 mL sample, filtered at 0.45 μm and acidified with 0.5 mL of HNO_3 Suprapur, for the determination of trace elements. The geochemical analyses were carried out in the laboratories of the Department of Earth Sciences of Florence, CNR-IGG (Institute of Geosciences and Earth Resources, Unit of Florence) and CSA of Rimini (Accredia laboratories). Water samples were analyzed with the following analytical techniques: automatic titration (HCO_3^-), anionic and cationic chromatography (F^-, Cl^-, Br^-, NO_3^-, SO_4^{2-} and Ca^{2+}, Mg^{2+}, Na^+, K^+) and ICP-MS (trace elements).

At each station 5 L of water were sampled under the surface (about 50 cm) for Chl*a* and diagnostic pigments, nutrients, TSM, CDOM and phytoplankton analysis. An aliquot of 1.5 L was filtered (Whatman GF/F, ø 47 mm) for Chl*a* and pigments analysis with HPLC (Shimadzu Class VP), following [9, 1]. Another aliquot of 1.5 L was filtered for gravimetric determination of TSM [7, 8]. An aliquot of the filtered water (fixed with $HgCl_2$ 1 %) was used for the determination of inorganic dissolved nutrients (phosphates, nitrites, nitrates, silicates) following standard methods [6] with Autoanalyzer3 (Bran Lubbe). Absorbance measurements of CDOM were carried out on filtered water using a Shimadzu UV 2501 PC spectrophotometer and the resulting values were converted in absorption according to [2]. An unfiltered aliquot of the samples was used for the determination of total Nitrogenous (Ntot) and Phosphorus (Ptot) [6]. Water filtering and the following analyses were performed at the Ecology Laboratory of the Biology Department. Samples of 250 mL were collected from the ST 7 site and three stations representative of the different docks (ST 6, ST 3) and Burlamacca Channel (ST 8) and were fixed with neutralized formaldehyde (final concentration 0.8 %) for phytoplankton analysis. Microscopic analyses were performed on an inverted microscope (Zeiss IM35, 40x, ph.c.) following standard methods [6].

Figure 1 – The studied area in the Port of Viareggio and location of the sampling stations: ST1, Darsena Lucca; ST2, Darsena Toscana; ST3, Darsena Italia; ST4, Darsena Europa; ST5, Nuova Darsena; ST6, Avamporto; ST7 outside the port; ST8, Burlamacca Channel Madonnina; ST9, Burlamacca Channel railroad bridges.

Optical measurements were made at site: PAR attenuation coefficient (Kd PAR) was calculated from downwelling irradiance (Ed) measured at 30 and 80 cm (LiCor Li-195) and spectral reflectance (R%) and attenuation (K λ) were obtained from downwelling and upwelling (Eu) measurements at 30 cm, with the portable radiometric system PUMS [4]. TRIX index [10] was calculated using Chl*a*, inorganic N and Ptot concentrations, and oxygen saturation.

An Apstein net for zooplankton with a 40 cm diameter mouth, net length 1 m and 200 µm mesh was used to perform three vertical tows from bottom to surface at each station. The samples were fixed with a neutralized formalin solution in seawater (8 %), stored and further analyzed at the Biology Department, Laboratory of Zoology. Individuals were counted and taxa identified to the lowest possible level, including also larval stages.

Results

The values of depth, temperature, pH, O_2, concentrations of the water major elements and the Total Dissolved Solids (TDS) values for each sample are shown in Table 1. The concentrations of the water trace elements are listed in Table 2.

Table 1 – Depth (in m), temperature (in °C), pH, O_2 (in μmol L^{-1}), concentrations of the water major elements (in mg L^{-1}) and TDS values (in mg L^{-1}) of the sampled water. S and P stand for samples taken at the surface and near the bottom, respectively.

Name	Depth	Temp.	pH	O_2	HCO_3^-	F^-	Cl^-	Br^-	NO_3^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Na^+	K^+	TDS
ST1 S	/	28.66	7.79	1.12	292	1.4	10380	35	1.2	1639	247	607	6135	204	19542
ST1 P	1.61	27.47	7.80	0.00	260	0.8	16114	45	0.8	2440	354	1029	9487	330	30060
ST2 S	/	27.89	7.80	2.15	255	0.9	16092	52	1.0	2371	347	992	9258	323	29692
ST2 P	3.33	26.01	7.82	0.00	209	1.5	20312	76	0.4	3326	435	1341	11504	430	37635
ST3 S	/	27.63	7.80	2.99	226	1.0	18120	60	1.6	2690	370	1090	9550	352	32461
ST3 P	4.58	25.44	7.85	0.29	216	1.5	22685	81	0.2	3520	438	1342	14578	431	43293
ST4 S	/	28.34	7.95	2.80	209	1.6	21780	70	1.2	3098	419	1269	11630	410	38888
ST4 P	5.54	24.92	7.85	1.39	211	1.2	23391	79	0.5	3463	442	1353	14667	432	44040
ST5 S	/	28.50	8.15	2.82	209	1.1	22713	77	0.8	3373	444	1370	13684	440	42312
ST5 P	5.55	24.89	7.98	2.32	207	1.6	23625	76	0.1	3330	443	1383	13944	443	43453
ST6 S	/	27.72	8.11	2.81	220	1.1	22339	75	0.4	3303	435	1333	13294	427	41428
ST6 P	3.33	25.23	8.14	2.63	210	1.2	23262	76	0.1	3324	449	1391	13698	446	42857
ST7 S	/	27.48	8.20	3.38	204	2.4	23219	78	0.3	3412	445	1368	13318	436	42483
ST8 S	/	27.87	7.85	2.25	235	1.1	17760	58	0.9	2619	356	1028	9542	333	31933
ST8 P	1.96	26.44	8.07	2.91	207	1.1	24132	76	0.3	3339	449	1385	13697	441	43727
ST9 S	/	28.14	7.82	0.32	312	2.2	6848	22	1.5	1067	251	456	3644	158	12761
ST9 P	1.48	27.42	7.90	0.00	217	2.4	23104	68	0.6	3003	408	1244	14231	394	42672

Table 2 – Trace elements contents in the sampled water (in μg L^{-1}). S and P as in Table 1.

Sample	As	B	Ba	Be	Cd	Co	Cr	Cu	Hg	Mo	Ni	Pb	Sb	Se	Sn	V	Zn
ST1 S	3.9	1961	23.7	< 0.1	< 0.1	1.3	0.2	9	< 0.1	4.8	1	1.1	0.7	0.5	< 0.5	2.1	< 5
ST1 P	2.9	3153	16.8	< 0.1	0.1	1.7	0.1	7.8	< 0.1	8.3	0.9	0.6	0.7	< 0.5	< 0.5	2.1	< 5
ST2 S	2.9	2771	24.9	< 0.1	0.1	1.7	0.1	13.1	6.4	7.6	0.6	0.3	0.6	< 0.5	< 0.5	2.1	7
ST2 P	1.8	3512	9	< 0.1	0.1	2.1	0.1	4.4	< 0.1	11.1	< 0.5	0.1	0.6	< 0.5	< 0.5	2.2	< 5
ST3 S	2.8	3264	25.4	< 0.1	0.1	1.8	0.1	19.1	1.1	9.3	< 0.5	0.1	0.6	< 0.5	< 0.5	2.3	16
ST3 P	2.7	3586	24.3	< 0.1	0.1	2.2	0.1	5.9	5.9	10.9	< 0.5	< 0.1	0.4	< 0.5	< 0.5	2.4	11
ST4 S	3.4	3326	11	< 0.1	0.1	1.9	0.1	22.7	< 0.1	13.1	0.5	0.2	0.6	1.7	< 0.5	2.2	21
ST4 P	2.8	3630	9.4	< 0.1	0.1	2.2	< 0.1	4	2.7	12.2	< 0.5	< 0.1	0.4	< 0.5	< 0.5	2.3	< 5
ST5 S	2.2	3559	17.7	< 0.1	0.1	2.2	0.1	10.4	< 0.1	11.9	< 0.5	< 0.1	0.4	< 0.5	< 0.5	2.3	< 5
ST5 P	2.2	3655	18.7	< 0.1	0.1	2.3	0.2	4.9	31.4	11.7	< 0.5	< 0.1	0.3	< 0.5	< 0.5	2.5	< 5
ST6 S	2.3	3543	9.9	< 0.1	0.1	2.1	0.1	12.1	< 0.1	12.0	< 0.5	< 0.1	0.3	< 0.5	< 0.5	2.4	< 5
ST6 P	1.6	3610	8.2	< 0.1	0.1	2.2	< 0,1	5.3	< 0.1	11.8	< 0.5	< 0.1	0.3	< 0.5	< 0.5	2.7	< 5
ST7 S	1.7	3637	8.9	< 0.1	0.1	2.2	0.2	2.5	< 0.1	12	< 0.5	< 0.1	0.2	< 0.5	< 0.5	2.7	< 5
ST8 S	2.8	3100	14.5	< 0.1	0.1	1.8	0.1	8.5	< 0.1	8.9	0.9	0.1	0.3	< 0.5	< 0.5	1.9	< 5
ST8 P	2	3620	10.9	< 0.1	0.1	2.2	0.1	4.5	6.1	10.3	< 0.5	< 0.1	0.2	< 0.5	< 0.5	2.3	< 5
ST9 S	3.5	1518	27	< 0.1	0.3	1.1	0.2	17.2	5	4.5	20.4	0.6	0.4	< 0.5	< 0.5	1.6	51
ST9 P	2.7	3337	13.6	< 0.1	0.1	2.1	< 0.1	3.9	< 0.1	10.1	< 0,5	< 0.1	0.3	< 0.5	< 0.5	1.9	< 5

The water temperature and pH values ranged between 24.9 and 28.7 °C and between 7.79 and 8.2, respectively. The O_2 concentration, between 0 and 3.4 μmol L^{-1}, decreased with depth (P, Table 1) and moving landward (ST9). The TDS was between 12.8 and 44 g L^{-1}. The water composition was dominated by Na^+ and Cl^-, typical components of seawater, whose concentration increased in the deeper samples and moving offshore (ST7). Concentrations of other elements, e.g. Br^- and SO_4^{2-}, also indicated a strong marine input.

Among the trace elements, referring to the current regulations concerning their content in natural waters (Italian Legislative Decree 152/1999 and subsequent Legislative Decree 31/2001 and 152/2006), it should be noted that:

- The high contents of B, exceeded in all samples the limits provided by the regulations on water quality relating to human consumption (1000 µg L^{-1}). The concentrations varied between 1.5 (ST9 S) and 3.7 (ST5 P) mg L^{-1}, therefore was lower than the limit for emissions into sewer (≤ 4 mg L^{-1}).
- The concentration of Hg exceeded the limits for human consumption (1 µg L^{-1}), in seven samples (i.e. ST2 S, ST3 S, ST3 P, ST4 P, ST5 P, ST8 P, ST9 S) with a maximum of 31.4 µg L^{-1} (ST5 P). Five of the above samples (i.e. ST2 S, ST3 P, ST4 P, ST5 P and ST8 P) also exceeded the limit for mercury emissions into sewer (≤ 5 µg L^{-1}).
- The Ni concentration of ST9 S (20.4 µg L^{-1}) exceeded the limits for human consumption (20 µg L^{-1}), but was lower than the limit for emissions into sewer (≤ 4 mg L^{-1}).

All the other trace elements did not exceed the Italian law concentration limits.

A sharp decreasing trend in the concentrations of nutrients (Fig. 2a) and Chl*a* (Fig. 2b), both indicators of the trophic status of the waters, was noticeable from highest values in the innermost docks (ST1 and 9) of the port, up to 1.2 mg L^{-1} of P_{tot}, around 10 mg L^{-1} of N_{tot} and 15.7 mg m^{-3} of Chl*a*, to the lowest abundances in the marine station (ST7). Generally, P_{tot} concentrations were mainly inorganic (PO_4) whereas N_{tot} was principally organic (Fig. 2a). The highly eutrophic conditions were confirmed by the values of TRIX (Fig. 2a) that established the "moderate" state of quality for the marine waters (ST7) and "poor" for all the other stations in the port and Burlamacca Channel (ST9 and ST8).

The PAR attenuation coefficient (Kd) was well correlated with the LAS ($r=0.95$; $p<0.05$) and also for these parameters (Fig. 2b) it was evident a decreasing gradient of concentrations and Kd from the inner waters of the port and Burlamacca Channel towards the sea, with CDOM and Chl*a* playing the major role in light attenuation process.

In the selected samples phytoplankton abundances were in the order of magnitude of 10^6 cell L^{-1}, with lower densities in ST7 and 8 (around 1.5 10^6 cell L^{-1}) and higher in ST6 and 3 (up to 4.6 10^6 cell L^{-1}) and taxonomic composition shifts from diatoms dominance in ST7 and 6 (bloom of *Skeletonema costatum* sensu lato) to a co-occurrence of more classes, typical of transitional waters, as Cryptophytes, Chlorophytes and Cyanobacteria. The PC analysis (OriginPro) well synthesizes the main forces driving the biological variability (Fig. 3). Conductivity was inversely correlated with PC1 (61 % of variance), on the contrary Chl*a*, phosphates, inorganic Nitrogen, CDOM, TSM, Kd showed a direct correlation. Consequently, PC1 can be interpreted as distance from the sea, where the most eutrophic conditions were found towards the innermost stations (ST1, 9), which were also characterized by the increase in Cyanobacteria (zeaxanthin). Temperature is inversely correlated with PC2 (27 % of variance), which can be related to the hydrodynamic features explaining the opposite position of Fuco (diatoms) in more dynamic conditions (ST7, 8) and Chl*b* (Chlorophytes) in more still waters (ST4, 3, 2).

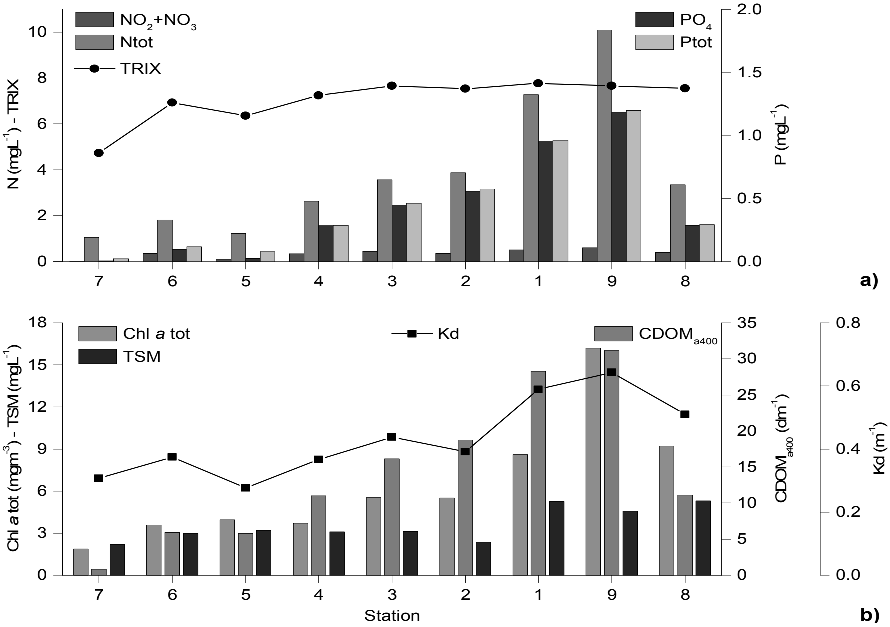

Figure 2 – a) Concentrations (mg L^{-1}) of Ntot, inorganic N (nitrites + nitrates), Ptot and inorganic P (phosphates) and calculated TRIX for every station (line); b) concentrations of Chl*a*, TSM and absorbance of CDOM (m^{-1}) as estimated concentration, PAR attenuation coefficient Kd (m^{-1}) (line).

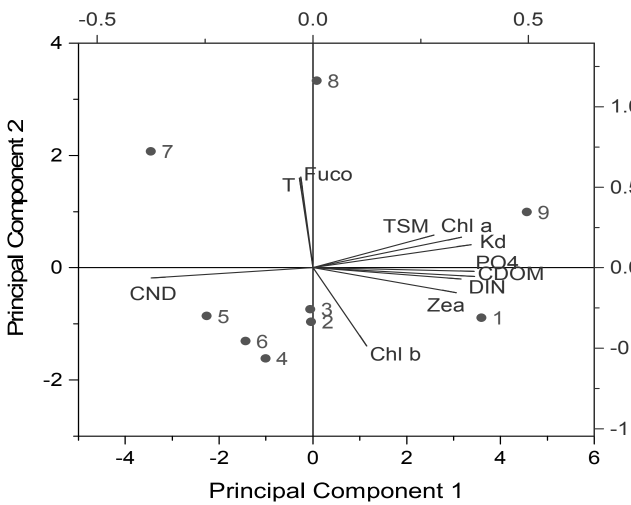

Figure 3 – PC Analysis with variables (blue) T(°C), conductivity (CND), TSM, Kd, phosphates (PO4), inorganic N (DIN), Chl*a*, Chl*b*, Zea (zeaxanthin), Fuco (fucoxanthin), and case projections (stations, red).

As far as zooplankton is concerned, a gradient was observed for all the considered parameters (density, number of taxa and community diversity) from inside the port to the outer stations. The inner stations (ST1 and ST9) showed the highest zooplankton densities (300-450 individuals m^{-3}) and the lowest number of taxa, compared to the other stations. Here, the dominant taxa were Cirripedia nauplii, Polychaeta larvae and Copepoda, confirming the data from [5]. At ST7, in the sea outside the port, the mean density was around 150 individuals m^{-3} and the number of taxa was comparable to that of stations ST3 to ST6. The community in the outer stations was mainly consisting of Copepoda, Hydromedusae and Appendicularia; all the stations spatially located between ST7 and ST1 (channel stations ST8 and ST9 included) showed communities with intermediate composition.

DistLM analysis (PRIMER 6) was used to produce models that associated the community structure to the environmental variables (Selection criterion AICc, selection procedure: Best). The best model highlighted water temperature, conductivity and CDOM as variables explaining a good percentage of the data variability, as represented by the dbRDA plot (Fig. 4). The TSM was a further variable explaining the data aggregation.

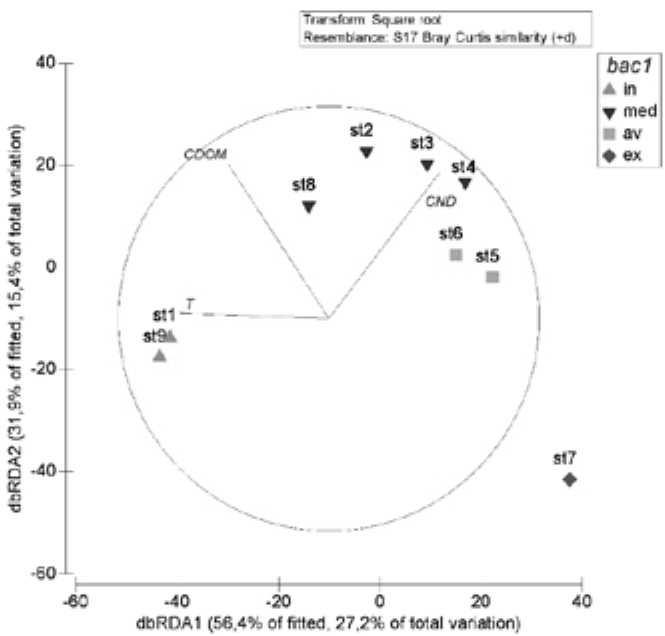

Figure 4 – dbRDA plot linking community structure and environmental variables at each station. Stations are categorized as: in, internal; med, intermediate; av, avamporto (outer harbor, i.e. port entrance); ex, external (sea). From left to right the three variables vectors, T (temperature), CDOM (chromophoric dissolved organic matter) and CND (conductivity).

Discussion

The analytical results revealed the geochemical processes acting within the study area, with particular reference to the state and quality of water. The inorganic chemical composition of the water samples can be attributed to a strong marine contribution, mixed or superimposed by a component with lower salt load, from inland areas. Such a particular condition, causing a clear gradient and a vertical stratification of the water, has a direct effect on the concentration of Na^+ and Cl^-, which increases in the deeper samples and moving offshore, and also on the concentration of O_2, which, on the contrary, tends to decrease at depth and moving landward. This yields the lack of oxygenation of ST1 P, ST2 P and ST9 P samples, resulting in a poor water quality.

The presence of high concentrations of B can be attributed to the normal amounts in seawater. On the contrary, the concentrations of Hg and Ni in some samples can be related to human activities. The possible causes are, as follows:

- punctual pollution, due to the interaction between water and industrial material;
- non-punctual emission from boats and ships;
- inputs of industrial or municipal and domestic waste waters;
- inputs of nutrients and fertilizers used in agriculture.

The noticeable input of inland waters produces an inside-outside gradient of trophic parameters, bio-optical components, phytoplankton composition and zooplankton diversity, along which the more confined waters show the highest phytoplankton biomass and the lowest zooplankton biodiversity, with the presence of a few dominant species.

The multivariate models showed conductivity, water temperature and CDOM as significant variables to explain the observed variations in zooplankton and phytoplankton communities. Salinity changes from inland to the sea cause a shift in communities, which are very different inside and outside the port. The observed dependence of community structure on water temperature and quantity of dissolved organic matter was expected, as both these factors may influence growth and reproduction of heterotrophic organisms. The observed scarcity in zooplankton could act as a reduced natural control in the case of eutrophic phytoplankton blooms.

Conclusion

The performed geochemical reconstruction, coupled with the assessment of the trophic conditions and phyto and zooplankton communities, proved to be suitable to estimate the ecological water status within the Port of Viareggio.

The obtained data can be used to program future sampling campaigns and analyses, in order to increase the compositional database and the knowledge of the water quality. The combined investigation of the geochemical and biological analyses highlighted some criticalities; consequently, further studies are required to evaluate the seasonal variation of the selected parameters in one of the most important ports of Tuscany.

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