ASSESSING THE CORRELATION BETWEEN CONTAMINATION SOURCES AND ENVIRONMENTAL QUALITY OF MARINE SEDIMENTS USING MULTIVARIATE ANALYSIS

Claudia Labianca1*, Sabino De Gisi1, Michele Notarnicola1

Department of Civil, Environmental, Land, Building Engineering and Chemistry, Polytechnic University of Bari, Via E. Orabona no. 4, 70125 Bari, Italy

Abstract

Water sea pollution is influenced mainly by anthropogenic causes due to industrial and municipal activities which affect the quality of sea water, sediments and the whole ecosystem. In this paper, the correlation between contamination sources and the environmental quality of marine sediments was analyzed through multivariate analysis, in particular Principal Components Analysis (PCA), Cluster Analysis (CA) and Correlation Analysis. Considering the case study of Mar Piccolo in Taranto (Ionian Sea, Southern Italy), it was performed first a PCA on the total matrix consisting of 1023 samples 3m deep and 20 variables (moisture content, granulometry, metals, metalloids and nutrients). Then, a PCA only for the superficial layers (0-50cm) was performed to better understand correlations with anthropogenic and natural impacts. Cluster and correlation analyses corroborated PCA results, identifying sub-clusters among the variables. The assessment showed how the type of pollution in Mar Piccolo of Taranto is widespread on superficial layers with some particular areas (hotspots) with a heavy and deeper contamination. Correlation between nutrients and metals, validated by CA analysis, showed that the excessive presence of nutrients and organic matter, in the Mar Piccolo water, acts as carrier for many contaminants that concentrate in the fine fraction of sediments with high percentage of organic matter.

Key words: chemometric techniques, environmental management, heavy metals, remediation, Total Organic Carbon

Received: March, 2018; Revised final: May, 2018; Accepted: September, 2018; Published in final edited form: October 2018

1. Introduction

The presence of polluting loads in watercourses and the concentration of industrial and production activities may result in contamination of river sediments, port and marine areas. Usually, sediments can be contaminated with metals (Aluminium, Arsenic, Cadmium, Chromium, Mercury, Nickel, Lead, Copper, Zinc, Vanadium), organic compounds (hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), aromatic solvents, polychlorinated biphenyls (PCBs)), microorganisms and other substances. In Italy, many coastal-marine areas coexist with large industrial and port settlements that have, over time, compromised the quality of the seabed in front of them. Some of these have been identified by the National Programme for Environmental Remediation and Recovery as contaminated Site of National Interest (SNI) (Ministerial Decree 468/01, 2002). As stated by Gabellini et al. (2011), recovery national activities are planned in these areas.

Contaminated sediment management strategies may consider in situ and ex situ techniques. In situ remedial alternatives normally involve Monitored Natural Recovery (MNR) (De Gisi et al., 2017a) and in situ containment and treatment (De Gisi et al., 2017b; Lofrano et al., 2016). Ex situ remedial
options include Stabilization/Solidification (S/S) (Todaro et al., 2016; Tang et al., 2015), Nano-scale Zero Valant Iron (nZVI) treatment (De Gisi et al., 2017c), landfarming (NSW EPA, 2014), composting (Mattei et al., 2017), sediment washing (Catianis et al., 2018; Stern et al., 2007), thermal desorption (Rumayor et al., 2017), vitrification (Colombo et al., 2009), biological treatment (Matturro et al., 2016) and/or their combination (Careghini et al., 2010). However, the definition of a remediation project requires a deepening of the study area. In this respect, the study of the sources of contamination is of great importance, especially for very complex contaminated sites.

Several statistical techniques and methodologies are available in literature, applied for different environmental problems. For example, Sabia et al. (2016) proposes a composite indicator-based methodology with the goal of identifying and then prioritising critical wastewater treatment plants, taking into account the territorial background issues. The alternatives were processed by analyzing the relationships between the sub-criteria and the dimensions of data coverage (i.e., collinearity, similarities/dissimilarities). The software Statistica (Statsoft) was used to evaluate the degree of correlation and the relative significance among the sub-indicators while, an explorative multivariate analysis (Factor Analysis FA) permitted to evaluate whether the alternative matrix was sufficiently supported by the statistical dimensions covered by the data. De Gisi et al. (2017d) used Multiple Correspondence Analysis (MCA) as a statistical exploratory technique to depict associations between categorical variables. The MCA was performed by using the software R-3.1.2 with the package “FactoMineR”. Furthermore, in executing the analysis the eigenvalues and rates of variance were corrected by applying the Benzécri’s method. Mali et al. (2017) combined chemometric tools for assessing hazard sources and factors acting simultaneously in contaminated areas. The study was aimed mainly at verifying the applicability of the methodologies adopted; in particular, Principal Component Analysis/Cluster Analysis (PCA/CA) and factorial Analysis of Variance (ANOVA) were exploited as complementary techniques for apprehending the impact of multi-sources and multi-factors considering the case study of Mar Piccolo in Taranto (Southern Italy).

The aim of the present study is to analyze by means of multivariate analysis (PCA, CA and correlation analysis) the correlation between contamination sources and the environmental quality of marine sediments, considering all the sub-areas of the First Seno of Mar Piccolo in Taranto, used as case study since it is one of the most industrialized and contaminated zones in the Mediterranean Sea. In particular, possible correlations between pollutant distribution and particle size characteristics, identification of areas of particular concern (hot spot) as well as areas characterized by geochemical anomalies (eventual natural presence of some substances) and/or strongly man-made areas, are identified and stressed.

2. Material and methods

2.1. Background information

Mar Piccolo is a semi-enclosed basin with a reduced water circulation, strongly influenced by human activities and with one of the most important areas in Italy for mussel farming. It is a typical polluted semi-enclosed basin characterized by scarce water circulation, which encourages organic matter sedimentation transport and accumulation of metals in sediments (Cardellicchio et al., 2006a). It has a surface area of 20.7 km² divided in two inlets, called First Seno and Second Seno, with a maximum depth of 13m and 9m, respectively. In particular, the first inlet is directly collected with the Mar Grande through two channels, one named Navigable Channel and the other one called Porta Napoli’s Channel, while, the second one is connected only to the first inlet. Mar Grande is the area for incoming ships and it is separated from the Ionian Sea by a little archipelago. A particular characteristic of Mar Piccolo is the presence of some submarine freshwater springs called “citri”, two of which are “citro Galeso” and “citro Citrello”.

From several decades this area is subjected to chemical pollution deriving from the industrial activities carried out in the surroundings, the most important of which are ILVA, Cementir, Eni station and Military Arsenal. Contaminants presence and distribution in Mar Piccolo sediments already have been identified and documented. Between 2005 and 2009, first the Commissioner-Delegate for the waste emergency in Apulia and, then, the Commissioner-Delegate for the environmental emergency in Apulia, performed environmental characterizations aimed at area safety works and remediation. Later in 2014, the local environmental Authority (ARPA Puglia) and other public institutions performed additional analyses to complete previous results. One of the main objectives was the development of a standardized methodology to apply to other marine coastal areas of Mediterranean Sea by means of: mathematical models related to hydrodynamism, evaluation of sediment contamination, carbon exchanges to sediment–water interface, pollutant mobility by studying water–sediment interactions, PCBs anaerobic degradation and ecotoxicological effects of pollutants (Cardellicchio et al., 2016).

2.2. Sampling points and data input

The data set analyzed is the one obtained from the sampling campaign in the First Seno carried out by ISPRA in 2010, since it is one of the most complete, both for information and number of variables.

The considered matrix consists of 1023 samples, 3m deep (822 samples in the area external to
mussel activities and 201 internal to it) and 20 variables (moisture percentage, granulometry, metals and metalloids Al, As, Cr, Cd, Hg, Fe, Ni, Pb, Zn, Cu, V and, lastly, nutrients concentrations, total nitrogen (N$_{tot}$), total phosphorus (P$_{tot}$) and total organic carbon (TOC)). Instead, PCBs, PAHs, organochlorine compounds and pesticides have been excluded from this analysis because their complex and different behavior needs a separate analysis.

In order to simplify the analyses, two secondary qualitative variables have been studied: the depth of surficial samples (S=Surficial = layers 0-10 cm (a), 10-30 cm (b), 30-50 cm (c); I=Intermediate = layers 100-120 cm; P=Deep = layers 180-200 cm, 280-300 cm); the different activities conducted on the specific area. The last qualitative variable has been created dividing the First Seno in the following areas: entry-exit channels; Military Arsenal area, mussels’ area, citri, ILVA water-pump area and the remaining area (Fig. 1). In particular, during the 1970s, ILVA steel factory installed a large cooling water intake system that removes 120,000 m³d⁻¹ of water from Mar Piccolo and discharges it into the Gulf of Taranto (ILVA, 2009).

In addition to the industrial impact, other anthropogenic effects are widely spread along and within the study area (Buonocore et al., 2013; Annicchiarico et al., 2011; Calace et al., 2008): several urban sewages from Taranto and nearby cities are discharged into Mar Piccolo, streams and citri are the responsible for the drainage of the surrounding agricultural soils and, lastly, there is the shipyard of the Italian Navy, located on the southern shores of the First Inlet (Cardellicchio et al., 2004; 2006b; Lerario et al., 2003). Furthermore, the Mar Piccolo sustains the largest mussel production of Italy (about 30,000 t year⁻¹) over a total legal farm area of 10 km² (Caroppo et al., 2012).

2.3. Multivariate analysis and software

A multivariate analysis with a PCA (Principal Components Analysis) and a CA (Cluster Analysis) has been used. The PCA allows to reduce data and to describe multidimensional systems by means of a smaller number of new variables, through the linear combination of the original ones (Loska et al., 2003).

Instead, the combination of CA and correlation analysis allows to identify and confirm correlations between variables, grouped in clusters. Experimental data have been elaborated by multivariate statistical analysis to evaluate the possibility of differentiating sampling areas, according to the correlation between them and the several pollution sources. Three different types of software have been used to conduct multivariate analyses on the available data: the software Unscrambler and the software SIMCA for the PCA analysis and the software Statistica10 for the CA and the Correlation analyses.

2.3.1. Software Unscrambler®X

The Unscrambler®X software was originally developed in 1986 by Harald Martens and later by CAMO Software (v. 9.7 AS, Norway). Unscrambler®X was an early adaptation of the use of partial least squares (PLS). Other supported techniques include principal component analysis (PCA), 3-way PLS, multivariate curve resolution, design of experiments, supervised classification, unsupervised classification and cluster analysis. The software is used in several fields: chromatography, spectroscopy, quality control systems in sensory analysis and pharmaceutical and chemical industries.

2.3.2. Software Simca (Soft independent modelling by class analogy)

SIMCA allows to extract valuable information, structuring and finding hidden details, using data mining, process modeling and interactive graphics.

Whether it is large amounts of data, batch data, time-series data or other data, SIMCA transforms data into visual information for easy interpretation. It can work even with just 10 samples per class and there are no restrictions for the variables number per class, important aspect in chemical studies (chemometric techniques).

![Fig. 1. First Seno sampling map with main anthropogenic and natural impacts](image-url)
2.3.3. Software Statistica10

The software Statistica10 was created by StatSoft and can be considered one of the most powerful tools available today for data analysis, data mining, quality control, process monitoring, clustering and data visualization.

3. Results and discussion

3.1. Principal Components Analysis results

The paragraph is organized to reflect the main findings of the PCA, focusing on subgroups created by correlation. Firstly, a PCA was carried out on all data sets; secondly, attention was focused on the superficial layers in order to fully understand the influence and correlation between anthropogenic impacts and sediments.

3.1.1. PCA on total dataset

The considered model consists of three principal components PC1, PC2, PC3 covering 60% of the cumulative variance, with respectively variance of 31%, 19% and 10%. The loading plot of the variables on the first two principal components plan (Fig. 2) showed that all metals and nutrients are dominant variables on the variance of surficial layer data, while the variances of intermediate and deep layers were influenced mostly by geo-physical characteristics.

In particular, the surficial samples group was composed of two sub- groups of variables because of the different concentrations in metals, one in the space characterized by positive values in PC2 and negative in PC1 (concentrations of V, Cr, Al, Ni, Fe) and one characterized by negative values both in PC1 and PC2 (concentrations of Cd, As, Hg, Zn, Cu). It is assumed that V, Cr and Ni, associated to Al and Fe, natural elements in phyllosilicate minerals and ubiquitous in all marine sediments, appeared because of natural factors, while Cd, Cu, Hg, Pb, As were certainly added on account of anthropogenic activities and they were influenced by nutrients and organic matter (TOC, Ntot and Ptot).

Fig. 2 highlighted the presence of some samples from the deep layer in the space of the ones from the surficial area. In particular, they were samples adjacent to the Military Arsenal and the ILVA water-pump areas (Fig. 1) assuming that in such samples metal concentration has reached even deeper layers. At the same time, considering the few surficial samples among the deep ones analyzed, it was found that their variance was more influenced by physical-chemical characteristics and not by metal concentration. Most probably, they are all samples from an excavation area anthropologically generated, explained by the impact of sea currents in this area on the surficial layers, mobilizing the fine fraction of sediments in suspension. Same phenomenon occurred in the "citri" area: currents induced by fresh-water springs suspended the fine fraction of sediments, to which metal contaminants are associated, triggering a desorption process of the metals in the superficial layers through leaching of metals in the water column.

3.1.2. PCA on surficial data and different areas

The results from previous analyses have led to focus attention on surficial samples because of the widespread contamination. The PCA analysis was performed on different sub-clusters (Arsenal area; Citri; Entry-exit channels; Area between First and Second Seno; ILVA water-pump area; Remaining Fist Seno area), created according to the anthropogenic activities carried out in each area.

For the Arsenal area (Fig. 3) it was possible to notice that samples at c depth (from 30 to 50 cm, grouped in a green circle) had a negative value on PC1 and a maximum variance caused by the fine fraction (silt+clay). This means that the layer c of the Arsenal area presented an average contamination, compared to the dataset analyzed. A different situation occurred for the layer b (from 10 to 30 cm, grouped in a blue circle) with a positive value on PC1 and a negative one on PC2. In this case, contaminants that influenced this sub-group were Hg, Cu, Pb, Zn, Cd, As, which changed according to the organic matter (TOC) and all the previous ones according to Ptot, as explained by M. Zhang and Zhang (2010).
Assessing the correlation between contamination sources and environmental quality of marine sediments using multivariate analysis

Fig. 3. Unscrambler output: Arsenal area

Fig. 4. Simca output: Arsenal area: a) projection of Score and Loadings plots on space PC1/PC2; b) PCs variance

It is possible to intuitively assume that TOC was the responsible mover of contaminants, since it behaves like carrier, but phosphorus has a central role too. Lastly, samples at a depth between 0-10 cm (grouped in red circle) were more influenced by Fe, Cr, V and N_{tot}. Using a 3 PCs model it was possible to reach an acceptable cumulative variance of 74%, with respectively 54% from PC1, 16% from PC2 and 4% from PC3. SIMCA was used to compare and confirm the previous results from Unscrambler software, considering all the geo-physical parameters. Maintaining the separation between levels (a, b, c), the outputs are shown in Fig 4. Also in this case layer b was the one more affected by pollution from Hg, As, Cu, and Cd.

The surficial layer appeared to be affected by high concentrations of TOC which drive Cr, V and Ni into the fine fraction of sediments, while the layer c does not appear polluted. It is important to underline that pollution from As and Hg in this area was related to deeper layers (150-200 cm), in line with the previous results (paragraph 3.1.1).
Consequently, the area adjacent to the Arsenal was affected by: (i) Pollution in the layer 10-30 cm from Hg, As, Cd and Cu and in some spots even from Pb and Zn; (ii) Widespread pollution from Hg and As in the deeper layers (150-200 cm) driven by high-concentrated TOC and P_{tot}; (iii) High concentration of Cr and V, supposedly naturally present in surficial layers. The impact of industrial activities on Mar Piccolo occurred even indirectly by means of “citri”, fresh-water springs spreading groundwater. As said, in the First Seno there are two “citri” called “Galeso” and “Citrello”. From the PCA analysis of this area, results showed how most of samples c (at depth 30-50 cm) had the biggest influence on the variance only from the fine fraction (Table 1).

However, it was observed the presence in this group of some samples from the layer b. The remaining samples (all samples from layer a and two samples from layer c) were characterized by a high influence on the variance from the heavy metals group, divided in two sub-groups: (i) Hg, Pb, As, Zn, Cd, Cu; (ii) Cr, V, Fe, Ni. Therefore, the analysis of “citro Citrello” has shown widespread pollution that affects even the deepest layers, with particular peaks of Hg, Pb and As (found in all the layers considered).

For the entry-exit channels (Porta Napoli’s natural channel, close to the commercial port, and Navigable channel) and the channel between First and Second Seno (Fig. 1), SIMCA application results emphasized how the Porta Napoli’s channel and the surficial layer of the Swing Bridge area were influenced on the variance only by physical parameters. Instead, the layers b and c belonging to the Swing Bridge were part of the area characterized by a high variability with respect to all types of contaminants. Mali et al. (2017) pointed out that Pb and Hg can also result from oil spilling and ship-fuel losses. The area between First and Second Seno was characterized by a particular distribution since it is located between two deeply polluted areas, Arsenal and “citro Citrello”.

More specifically, both Unscrambler and Simca results showed how the layer c and part of b were in the area characterized by high variance from geo-physical parameters, while the layer a and the remaining part of b were more influenced on the variance by all nutrients and heavy metals. ILVA water-pump, on First Seno northwest coast, totally changed Mar Piccolo currents and increased the salinity level bringing a large amount of saltwater from Mar Grande. The Unscrambler outputs highlighted an irregular and widespread distribution of contaminants (in all the layers), reaching the layer c in some spots.

Table 1. Main results from PCA analysis on the different sub-areas

<table>
<thead>
<tr>
<th>N.</th>
<th>Sub-area</th>
<th>PCA Model (Unscrambler/Simca)</th>
<th>Main influence on the variance (PCA analysis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Arsenal</td>
<td>PC1 54%, PC2 16%, PC3 4%</td>
<td>• layer c ONLY by geo-physical parameters,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• layer b by P_{tot} → TOC → Hg, Cu, Pb, Zn, Cd, As (HEAVY METALS TRANSPORT EFFECT),</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• layer a by Fe, Cr, V and N_{tot}.</td>
</tr>
<tr>
<td>2</td>
<td>Citro “Citrello”</td>
<td>PC1 52%, PC2 20%, PC3 18%</td>
<td>• most of samples from layer c and few from layer b ONLY by Geo-physical parameters,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• layer a totally, layer b partially and two spots from layer c by ALL the contaminants (two sub-groups Hg, Pb, As, Cd, Cu and Fe, Cr, Ni, V) D POLLUTION with HOT SPOTS).</td>
</tr>
<tr>
<td>3</td>
<td>Entry-Exit Channels (Porta Napoli’s Channel, Swing bridge - Navigable Channel)</td>
<td>PC1 56%, PC2 14%, PC3 7%</td>
<td>• layers a, b and c of the Porta Napoli’s Channel and the layer a of the Swing Bridge Channel ONLY by physical parameters,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• layer b and c of the Swing Bridge Channel by ALL the contaminants (two sub-groups Hg, Pb, As, Cd, Cu and Fe, Cr, Ni, V) (POLLUTION IN DEEP LAYERS).</td>
</tr>
<tr>
<td>4</td>
<td>Channel I-II Seno</td>
<td>PC1 40%, PC2 27%, PC3 11%</td>
<td>• layer c and part of b ONLY by geo-physical parameters,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• layer a and remaining part of b by ALL nutrients and heavy metals.</td>
</tr>
<tr>
<td>5</td>
<td>Ilva water-pump</td>
<td>PC1 50%, PC2 19%, PC3 13%</td>
<td>• some samples from layers a, b and c by geo-physical parameters,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• some samples from layers a, b and c by ALL the contaminants (IRREGULAR POLLUTION IN ALL THE LAYERS)</td>
</tr>
<tr>
<td>6</td>
<td>Other areas</td>
<td>PC1 43%, PC2 19%, PC3 15%, PC4 7%, PC5 4%</td>
<td>• layer c and part of b ONLY by geo-physical parameters,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• layer a and remaining part of b by a contamination pattern As, Pb, Cd, Cu, Zn, P_{tot}, N_{tot} and TOC, in particular layer a by Cu, Cd, Hg, V, Fe and Cr, while layer b more by Pb, As and Zn (information from space PC1/PC5)</td>
</tr>
</tbody>
</table>
For what concerns the samples in the remaining First Seno area, a new PCA analysis was performed. Results showed that all samples from layer c and some from layer b were not influenced on the variance by the concentration of contaminants, unlike the layer a and the remaining samples from layer b, associated to a contamination pattern composed of As, Pb, Cd, Cu, Zn, Ptot, Ntot and TOC.

The projection on space PC5/PC1 made it possible to understand the contamination pattern specifically for each layer. In particular, layer a was influenced on the variance more by Cu, Cd, Hg, V, Fe and Cr, while layer b more by Pb, As and Zn.

3.2. Cluster Analysis and Correlation Analysis results

In order to deepen and confirm PCA results, a CA was performed on the dataset. The software Statistica10, used for this type of analysis, allowed to identify sub-groups among the variables according to the correlation patterns (Table 2). The obtained dendrogram is shown in Fig. 5.

Table 2. Statistica output: correlation Table

<table>
<thead>
<tr>
<th>1° Cluster</th>
<th>TOC</th>
<th>As</th>
<th>Cd</th>
<th>Zn</th>
<th>Hg</th>
<th>Pb</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOC</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>0.30</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>0.43</td>
<td>0.63</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>0.44</td>
<td>0.67</td>
<td>0.87</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hg</td>
<td>0.43</td>
<td>0.53</td>
<td>0.54</td>
<td>0.53</td>
<td>1.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>0.40</td>
<td>0.70</td>
<td>0.68</td>
<td>0.76</td>
<td>0.49</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0.35</td>
<td>0.53</td>
<td>0.58</td>
<td>0.68</td>
<td>0.34</td>
<td>0.62</td>
<td>1.00</td>
</tr>
<tr>
<td>2° Cluster</td>
<td>Ptot</td>
<td>Ntot</td>
<td>Al</td>
<td>Cr</td>
<td>Fe</td>
<td>Ni</td>
<td>V</td>
</tr>
<tr>
<td>Ptot</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ntot</td>
<td>0.50</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>0.11</td>
<td>0.21</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>0.28</td>
<td>0.39</td>
<td>0.62</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>0.28</td>
<td>0.53</td>
<td>0.78</td>
<td>0.60</td>
<td>1.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>0.17</td>
<td>0.22</td>
<td>0.41</td>
<td>0.85</td>
<td>0.37</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>0.37</td>
<td>0.56</td>
<td>0.61</td>
<td>0.92</td>
<td>0.64</td>
<td>0.74</td>
<td>1.00</td>
</tr>
</tbody>
</table>

It was possible to identify two macro clusters: (i) TOC, As, Cd, Zn, Hg, Pb, Cu, clay and gravel; (ii) Ptot, Ntot, Cr, Fe, Al, V and Ni. In the first cluster it was possible to intuit that the responsible correlating element was TOC, while in the second cluster the responsible ones were both the nutrients. One of the three correlation outputs from the software Statistica10 is shown in Fig. 6.

4. Conclusions

The chemometric techniques, used jointly with software Unscrbumbler, Simca and Statistica10, allowed to clearly understand the correlation between contamination sources and the environmental quality of marine sediments as well as the existence and identification of hot spots within the study area. The analysis of the case study allowed to focus on the following main aspects:

• The strong correlation of TOC, Ptot and Ntot with As, Cd, Hg, Pb, Cu and Zn, suggested that the excessive presence of nutrients and organic matter in the water, acted as carrier for many contaminants that concentrate in the fine fraction of sediments with high percentage of organic matter. This situation was observed for some area of particular interest such as the Arsenal area, the “citri” area and the entry-exit one (with a peculiar distribution pattern due to hydrodynamic effects);
• All the surficial layer, the so-called fresh sediments, had a spread contamination; it suggested that the primary sources of contamination are still active;
• The presence of contamination even in the deeper layers (hot spots) led to hypothesize that those spots could become “secondary sources of contamination” where appropriate containment measures will not be taken;
• Areas with particular interest (entry-exit channels) suggested to investigate more on the influence of currents on the sediment quality.

Lastly, in methodological terms, the framework adopted could certainly be a powerful tool for the preliminary study of heavy metal pollution in coastal marine areas, because it is allowed to (i) identify the accumulation sites, (ii) evaluate the possible pollution sources and (iii) hypothesize one or more remediation techniques to use for the environmental restoration.

References

Cardellicchio N., Annichiarico C., Di Leo A., Giandomenico S., (2004), Mercury in Marine Sediments and Mussel from Taranto Gulf (Ionian Sea, Southern Italy), Proc. 7th Int. Conf. on Mercury as a Global Pollutant, Ljubljana.
Fig. 5. Statistica output: dendrogram

Fig. 6. STATISTICA10 output: 1st cluster correlation (TOC, As, Cd, Hg, Pb, Cu, Zn)
Assessing the correlation between contamination sources and environmental quality of marine sediments using multivariate analysis


De Gisi S., Minetto D., Lofrano G., Libralato G., Conte B., Todaro F., Notarnicola M., (2017c), Nano-scale zero valent iron (nZVI) treatment of marine sediments slightly polluted by heavy metals, *Chemical Engineering Transactions*, 60, 139-144.


