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MULTIVARIATE TOOLS TO INVESTIGATE THE OCCURRENCE OF POLLUTANTS IN A HIGHLY ANTHROPISED AREA

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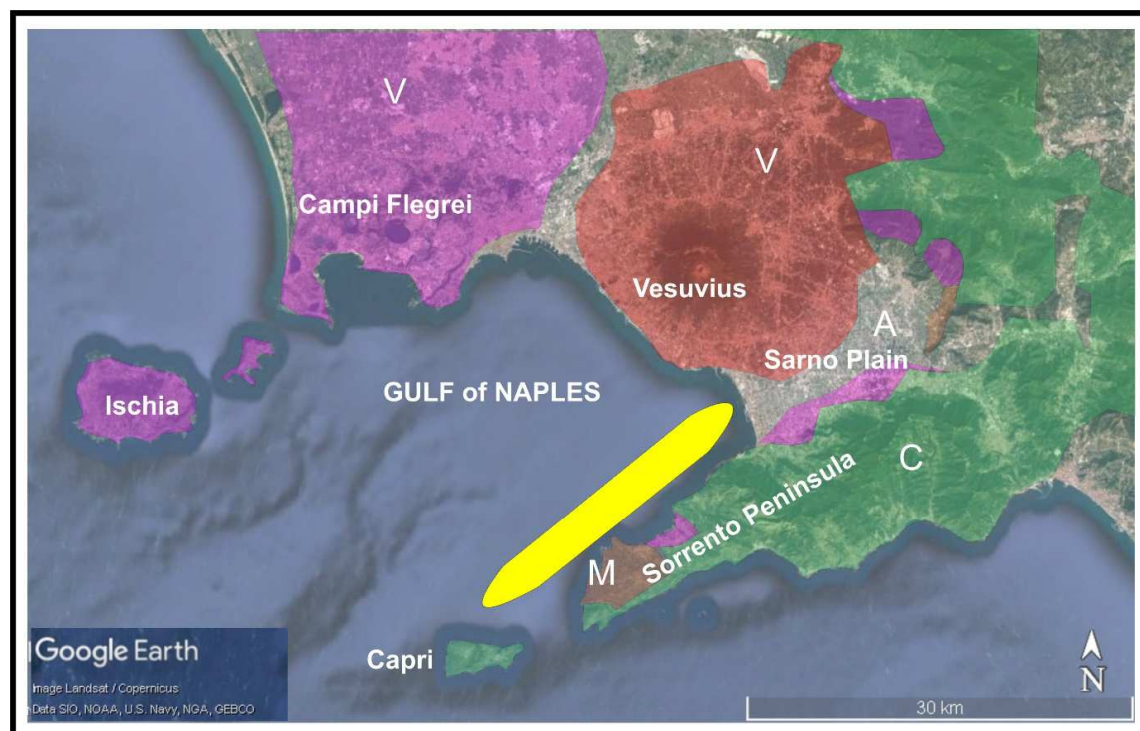
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C – calcareous rock, M – terrigenous deposits, A – alluvial deposits, V – volcanic zone.

The study area is highlighted in yellow.

This work represents a preliminary study from the Sarno river delta to the Capri island, to investigate a possible variability in the submarine environmental pollution. The Multivariate Analyses are performed to get insight the occurrence of organic and inorganic pollutants within this highly populated area.

The Gulf of Naples is characterized by a complex lithologic frame typified by calcareous rocks outcropping in the Sorrento Peninsula and pyroclastic rocks originated by several quaternary volcanoes (Vesuvius, Campania Volcanic Zone, Campi Flegrei). The adjacent Campania Plain has high density population.

The Sarno Plain is one of the most polluted area in Europe due to widespread industrialization and intensive agriculture. In particular, water from the Sarno River is heavily contaminated by the discharge of human and industrial wastes. The Gulf of Naples is the receiving environment for persistent toxic substances from the Campania Plain (Albanese et al., 2010; Arienzo et al., 2017). Montuori and Triassi (2012) reported that the discharges of PAHs from the Sarno River to the Gulf of Naples is approximately 8530 g/d. On the contrary the Sorrento Peninsula and Capri are mainly touristic areas.

158 sediments samples collected between Sarno River and Capri Island, were analyzed for:

- TOC (Total Organic Carbon)
- Grain size
- Metals
- PAHs (Polycyclic Aromatic Hydrocarbons)
- C>12
- C<12
- PCBs (Polychlorinated Biphenyls)
- Pesticides
- Ots (Organotin compounds).

Environmental monitoring of highly anthropized areas demands for deep survey of different environmental compartments and determination of numerous bio-geo-chemical parameters, due to the huge impact of natural and anthropogenic organic substances constantly released into these environments.

The interpretation of the large amount of data is not straightforward task due to their complexity that require a very tricky elaboration especially for the decision making processes.

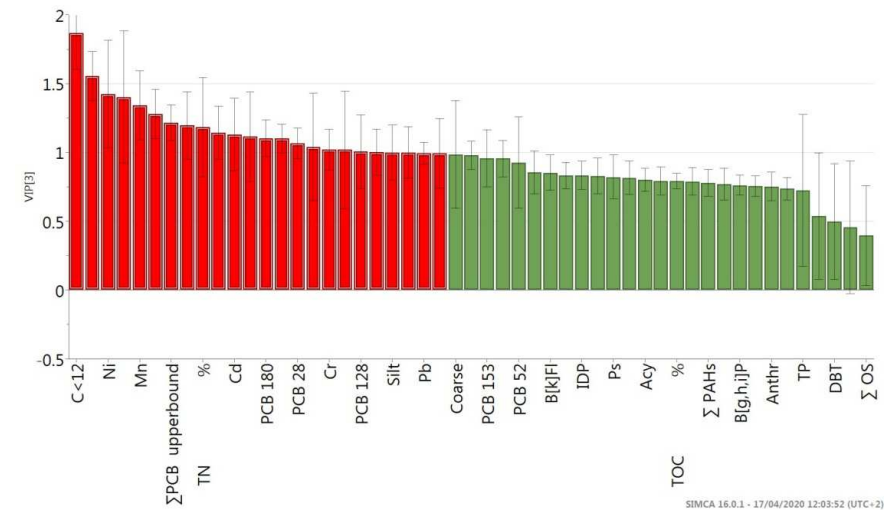
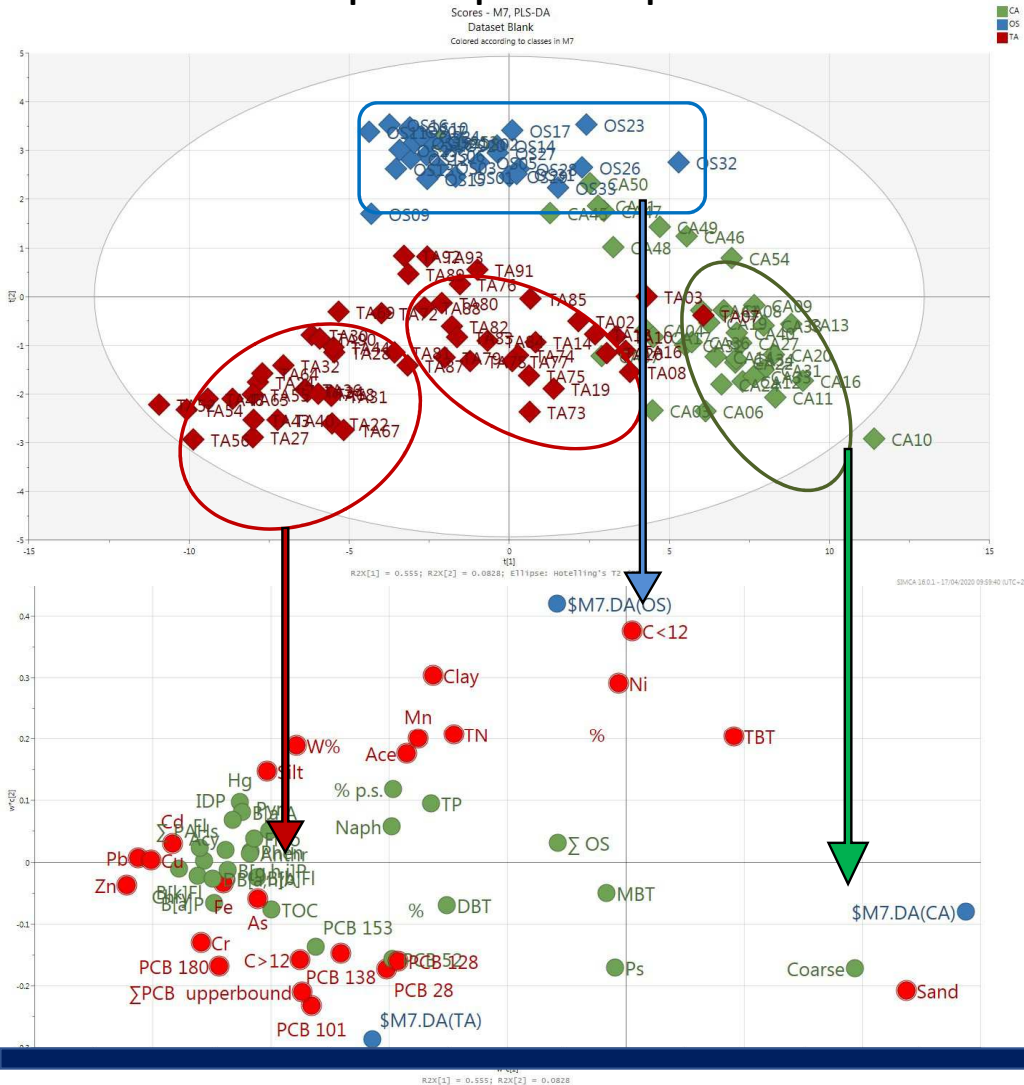
Chemometrics tools based on the multivariate statistical data analysis seems to be a powerful tool in addressing such complexity (Mali et al., 2017). In particular **Principal Component Analyses (PCA)** method is a powerful tool for analyzing complex data!!

The main benefits are:

- identifying patterns of sites with similar pollution features
- highlight their similarities:-
- To identify the most discriminant contaminants, within site clusters

Thus, passing from punctual **Univariate** analyses to **Multivariate** analyses **allows** to get insight to the complexity of ecosystem.

A model with 3 Principal Components explained 72% of the total variance was selected to describe the study area (PC1 56%, PC2 8%, PC3 8%)

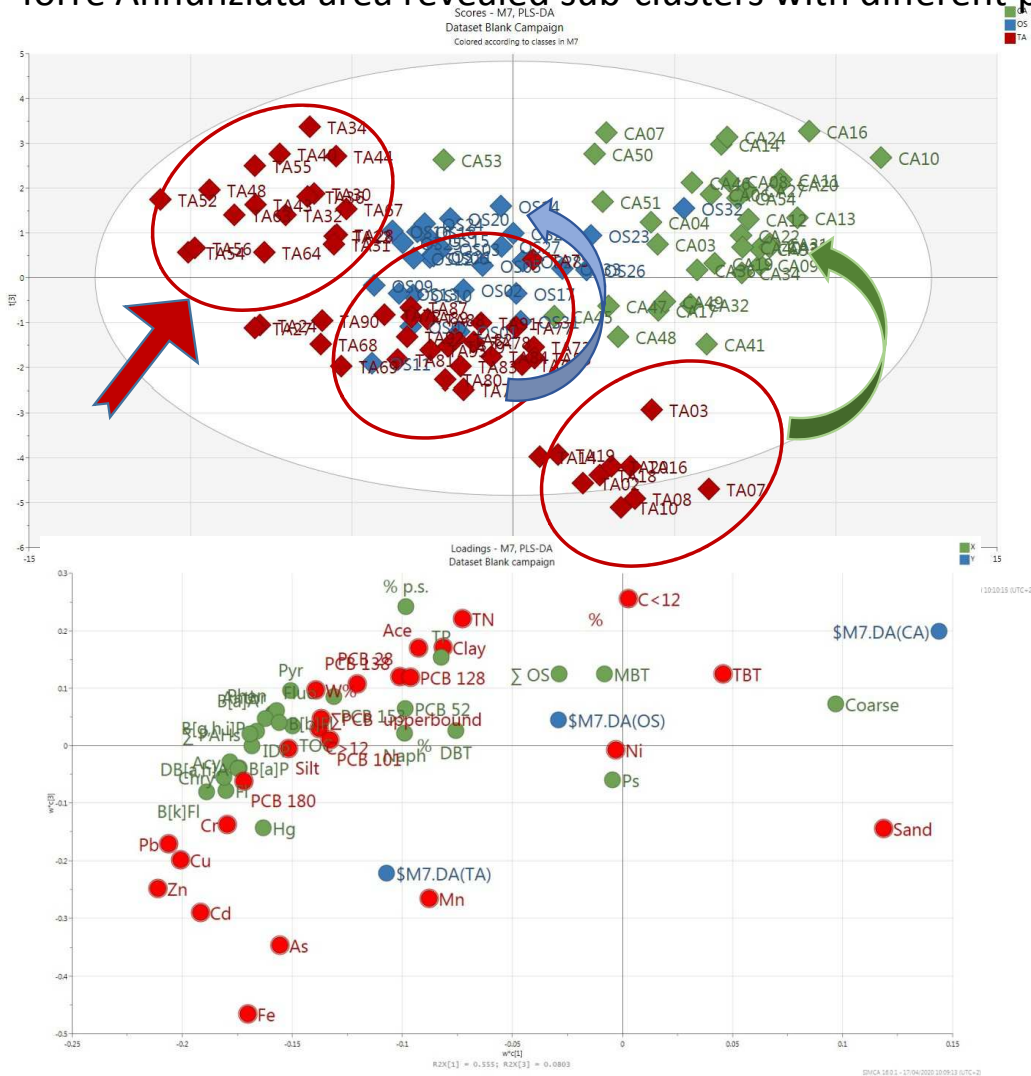


Main Findings:

The variables that control the three determined patterns are expressed in this graph, ordered for their weight (key-variables are those having Weight >1):

- The cluster of CA - seem to be controlled mainly by granulometric/textural features of sediments (Sand)
- The cluster of OS - seems to be controlled mainly by content of C<12, Clay, Ni and Mn (to a less extend from TBT, TN, ACY and W%)
- The cluster of TA - Seems to be of most concern: a high organic pollution pattern (mainly C>12, Σ PCB (including some specific congeners) and Cu, Pb, Cr, Zn) controlled mainly organic matter content and silt content

Torre Annunziata area revealed sub-clusters with different pollution pattern, displayed clearly on the projection of PC1 on PC3



Main Findings:

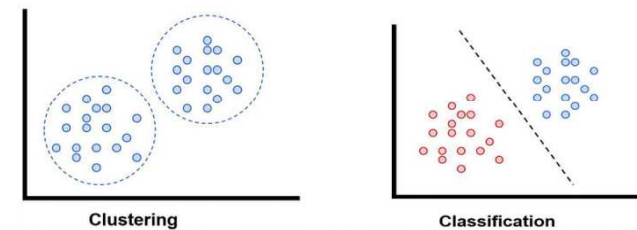
The TA sites are grouped in three sub-clusters:

- One cluster similar with CA area in term of granulometric features (percentage of sand and percentage of TBT)
- A second cluster having sites similar with OS area in terms of Clay content, Ni and Mn
- A third more specific cluster having high concentration of contaminants (metals, organic pollutant, nutrients and TOC) associated only with some sites from CA (CA53, CA07, CA50)

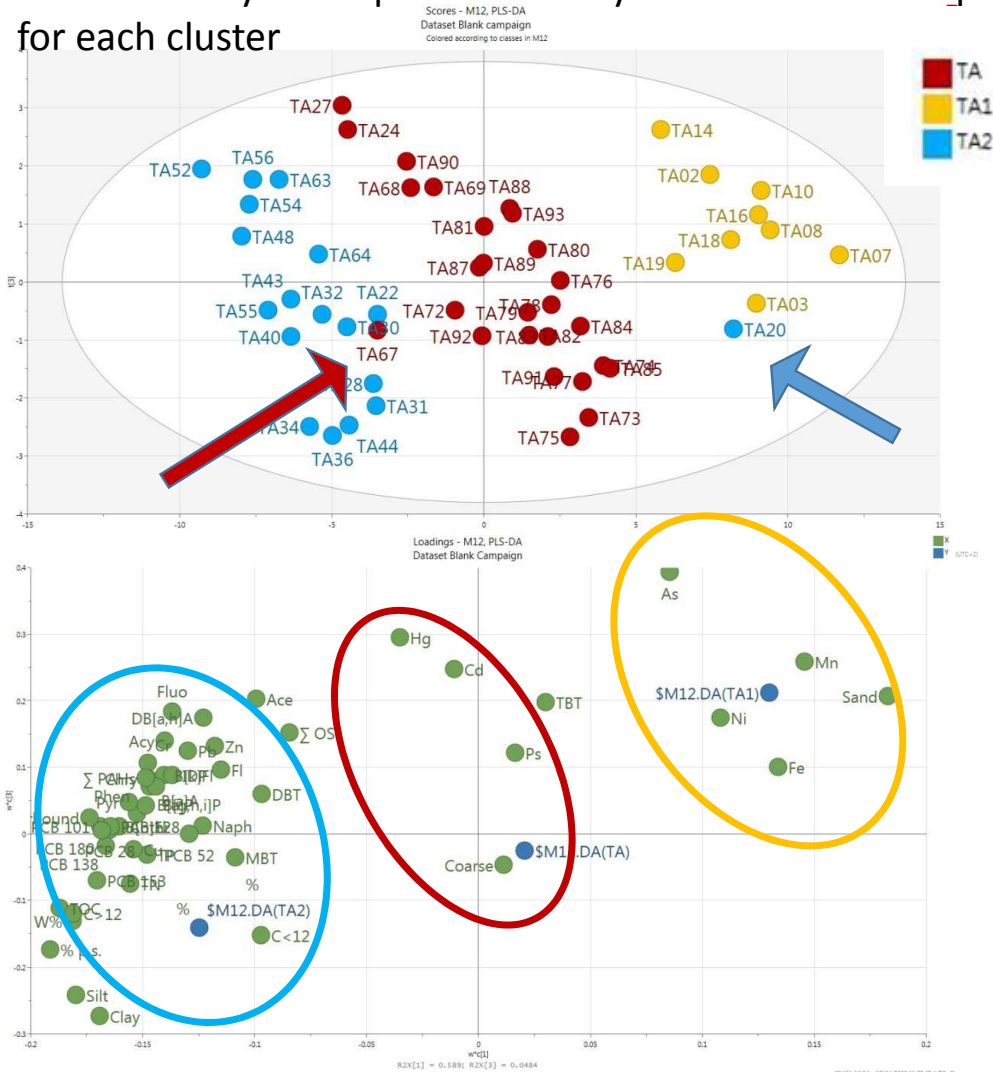


Further Analysis?:

PCA - unsupervised pattern recognition in order to define sub-clusters and subsequent **PLS supervised** pattern recognition techniques in order to get insights each patterns recognized

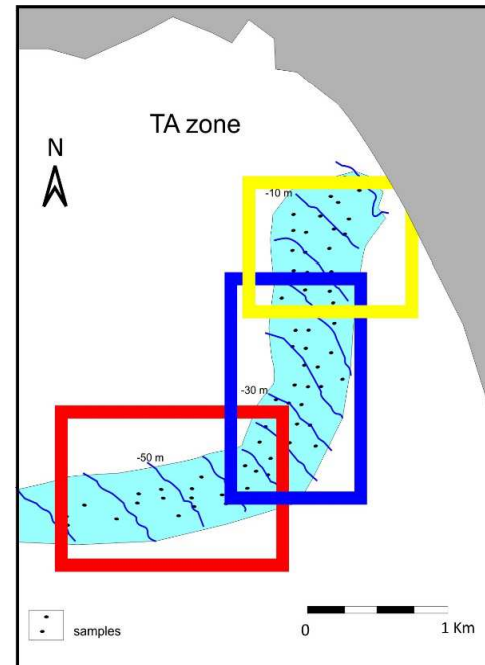


PCA-PLS analyses help us to identify sub-clusters with specific pollution pattern and to identify the most discriminated variables for each cluster



Findings from PCA-PLS: Identification of three clusters

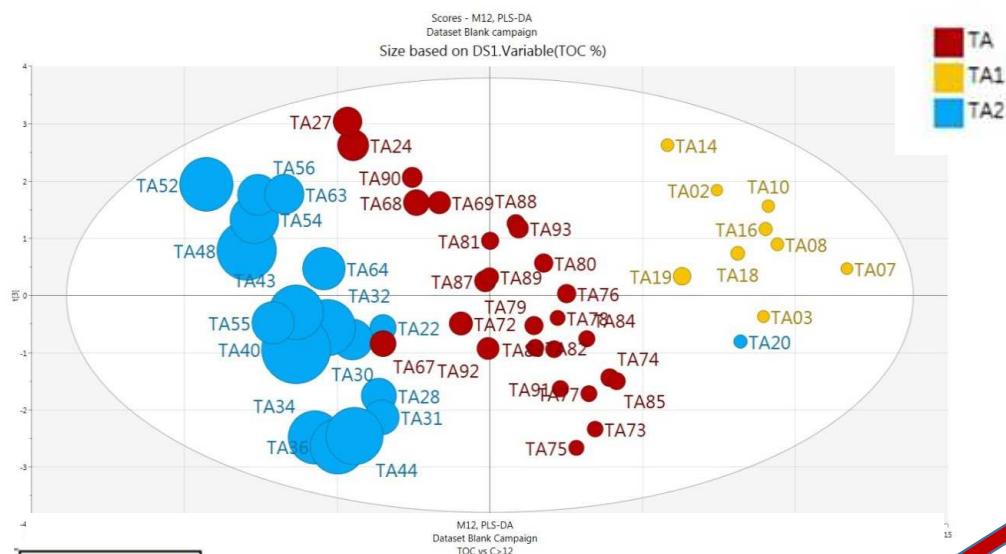
TA1 (yellow) TA01-TA20): samples near coast of TA, characterized by sandy texture granulometry have a pollution pattern dominated by Fe, Mn, As and Ni:



TA2 (blue) TA22 to TA67: are characterized by silty texture granulometry and have a high severe pollution pattern dominated C>12 and persistent organic pollutants (PCB and PAHs) as well as by Cu, Pb, Cr. These sites are controlled by high level of TOC.

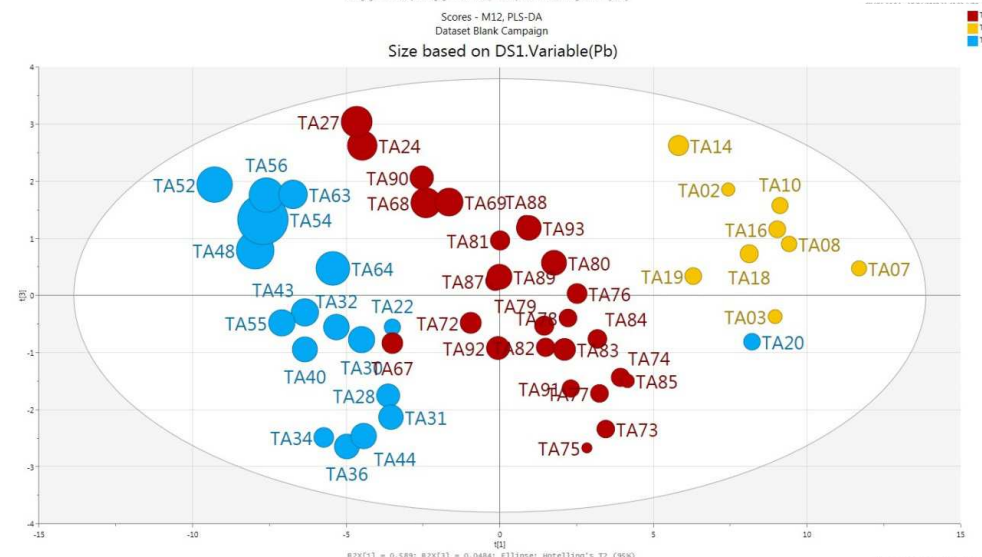
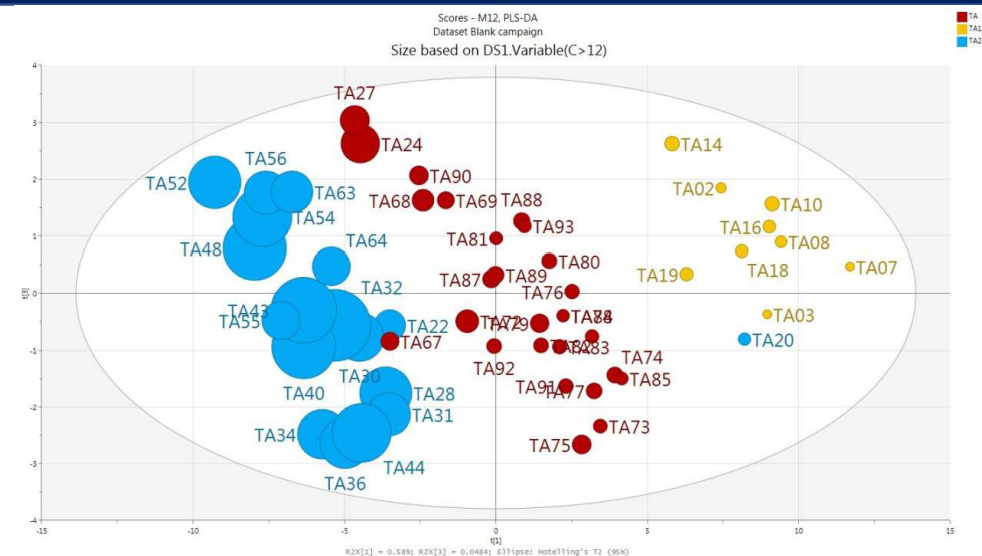
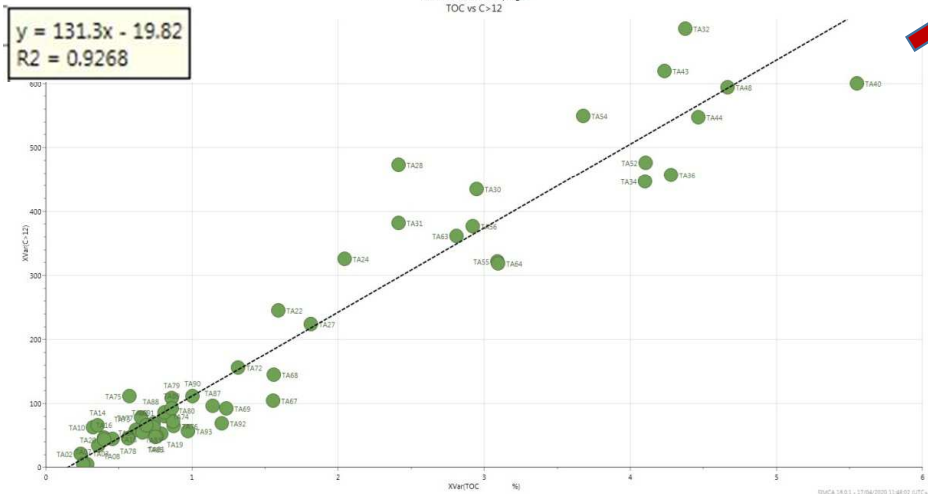
TA (red) TA68 to TA93: these sites are characterized by coarse texture granulometry and a pollution patterns dominated Cd, Hg and TBT

Distribution of TOC vs C>12 and TOC vs Pb within TA Clusters

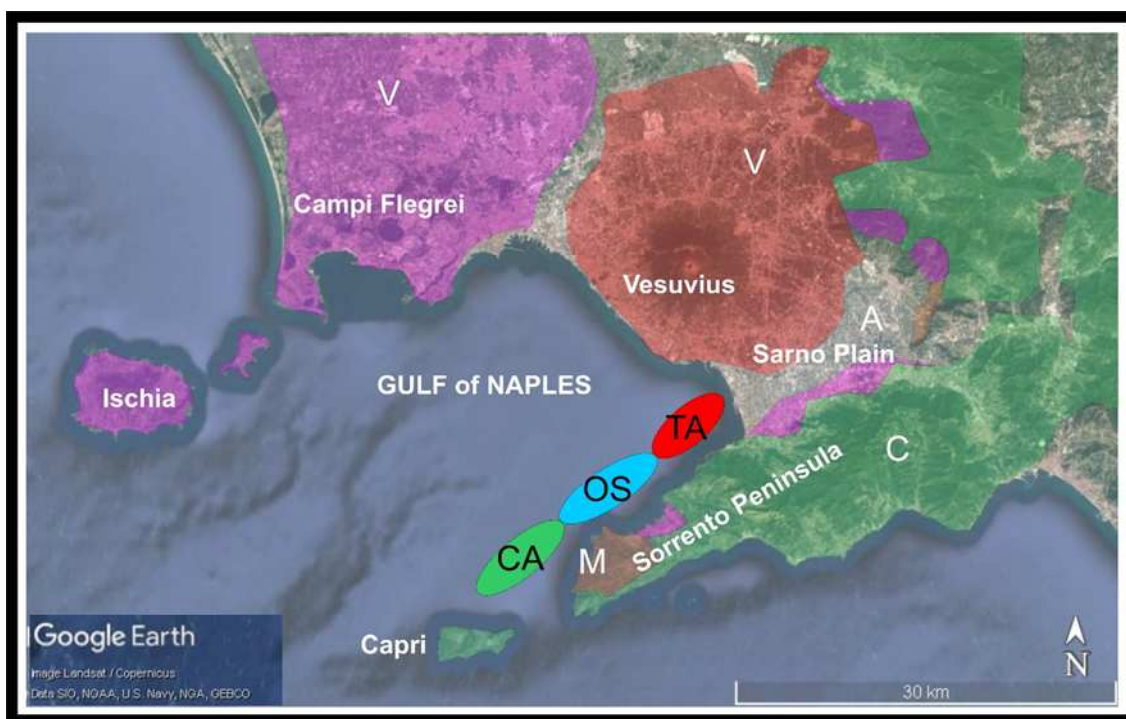


$$y = 131.3x - 19.82$$

$$R^2 = 0.9268$$



Using the “benefit” of graphical representations of Multivariate Techniques utilized, we can summarize as follow:



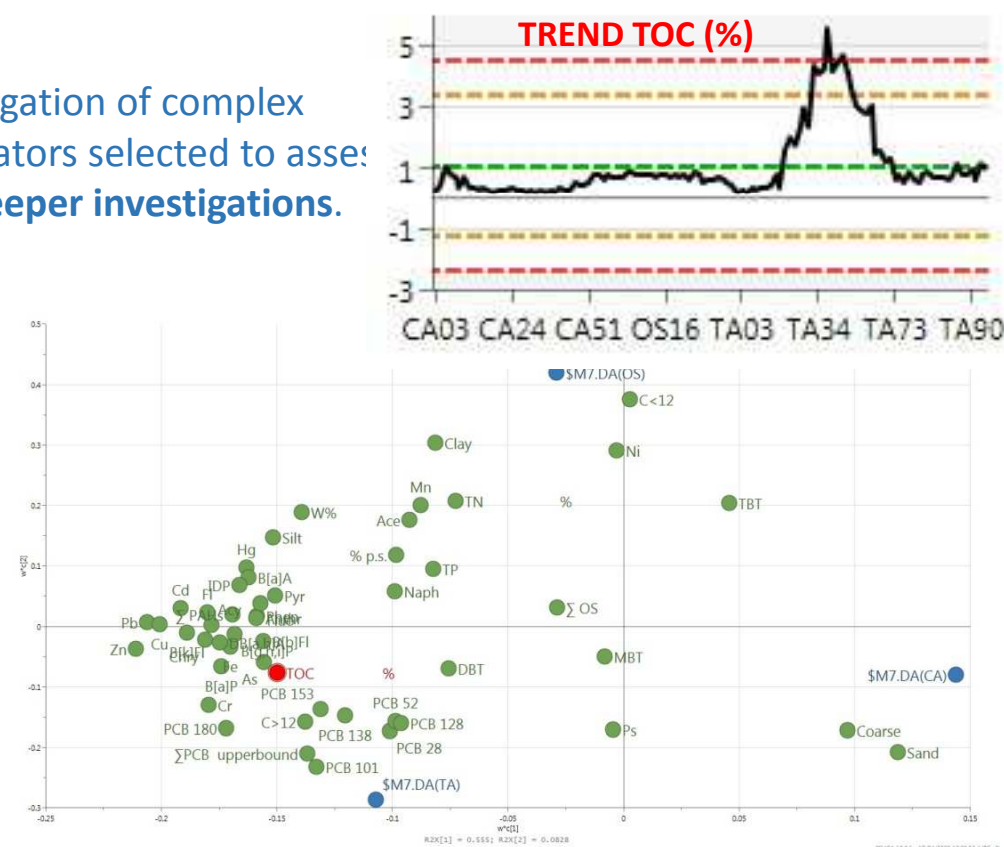
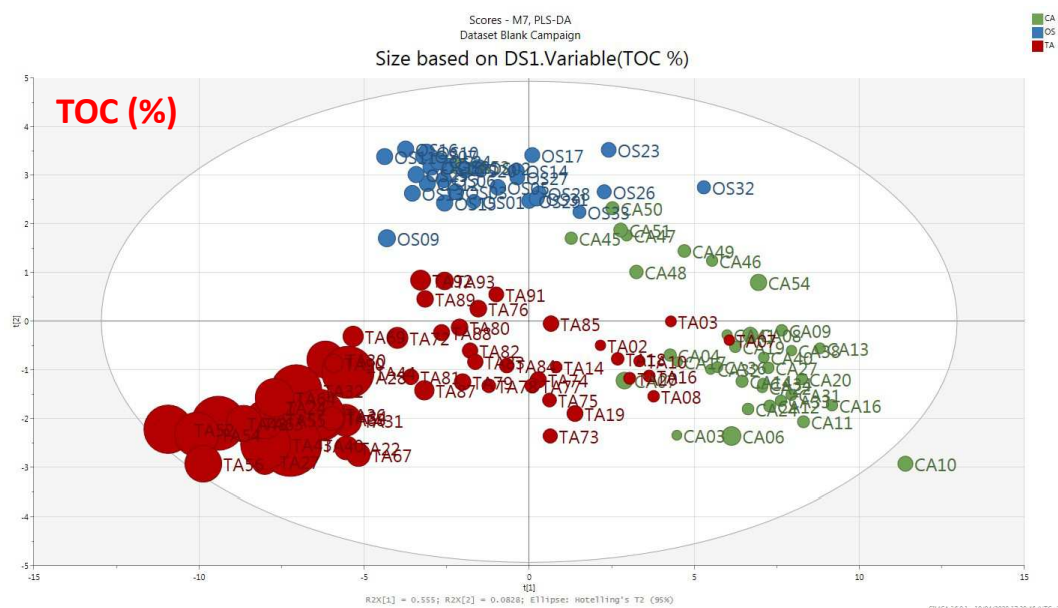
The investigated study area is constituted by three clusters: Torre Annunziata zone (TA in red), Sorrento zone (OS in blue), Capri zone (CA in green), that display different pollution patterns.

The variability of contaminant distribution revealed by Multivariate analyses within TA area, claim for further studies in order to get insight the occurrence of high TOC levels as well as to assess the potential influence of the Sarno river on the contaminant distribution.

CONCLUSIONS

The adopted multivariate approach allowed, through a clear spatial representation of score plots, a deep dive into the large dataset generated by the investigation campaign highlighting the influence of some main factors controlling the contamination pattern, such as **organic matter content (TOC)** and granulometry.

The statistical approach seems to be a **easy-to-use tool** for investigation of complex datasets. It provides **main trends** in the variability of quality indicators selected to assess the pollution status of the study area and to **orient the further deeper investigations**.



THANK YOU!

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