MICRO TO MACRO BEHAVIOUR OF CONTAMINATED MARINE SEDIMENTS: EXPERIMENTAL EVIDENCE OF BIO-CHEMO-MECHANICAL PROCESSES

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Abstract

The research deals with a multiscale investigation carried out on contaminated marine sediments from a natural deposit to assess the effects of bio-chemo-mechanical coupled processes which may act in complex natural environments and affect the geotechnical properties of the clays. The research has been triggered by the emblematic case of the contaminated Mar Piccolo (MP) basin in Taranto (Southern Italy), where the high degree of pollution recorded in the clayey sediments at the sea bottom, has been found to worsen water quality and promote bioaccumulation of pollutants in several species. Several samples of sediments from the top layer exhibited peculiar geotechnical properties, in terms of plasticity and activity indexes, compressibility and hydraulic permeability. While the prime suspect for such unconventional behaviour was the chemo-mechanical coupling between soil skeleton and contaminants, an original laboratory analysis carried out on some selected sediments samples showed that the biogeochemical degradation of organic matter and the presence of microfossils and diatoms significantly affect the micro to macro behaviour of polluted marine sediments.

1. Outline of the Mar Piccolo site

The Mar Piccolo is a marine basin with two bays of lagoon features of total surface area about 20.72 km^2 and maximum water depth of 13 m (Figure 1a). As schematically reported in Figure 1b, at the sea floor, a thick stratum of soft Holocene sediments overlies the Pio-Pleistocene Sub-Apennine clays (ASP, hereafter), the parent formation of most of the sediments deposited in the bays (Cotecchia et al., 2021). The contamination has been logged in the sea water and in the marine sediments in the last two decades, in terms of metals and metalloids, e.g. As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn, and persistent organic contaminants, e.g., polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), total hydrocarbons, which represent possible sources of high risk for the human health. Such contamination has most probably developed progressively in the XIX century, as result of the uncontrolled discharge, in both bays, of the waste resulting from either industrial, or urban activities taking place in the surroundings.
In 2014, the Special Commissioner for the urgent measures of reclamation, environmental improvement and redevelopment of Taranto (Special Commissioner, hereafter), appointed by the Italian Government, promoted an advanced interdisciplinary study of the Mar Piccolo site conditions (i.e. water column and

sediments, called system thereafter), to the aim of: i) deepening the knowledge about the evolution with time of the site pollution; ii) assessing the site environmental risk; iii) identifying the Mar Piccolo portions requiring risk mitigation interventions; iv) providing indications about possible sustainable remediation strategies (Adamo et al., 2018; Vitone et al., 2020; Cotecchia et al., 2021).

During the above-mentioned campaign, sediment samples for geotechnical testing were retrieved down 19 boreholes drilled in the I Bay (S-sites in Figure 1a), from 0 to 39 m below seafloor (bsf) (Cotecchia et al., 2021). Most of the samples were taken in the Pleistocene and Holocene (recent) formation, with the exception of two samples taken in the ASP.

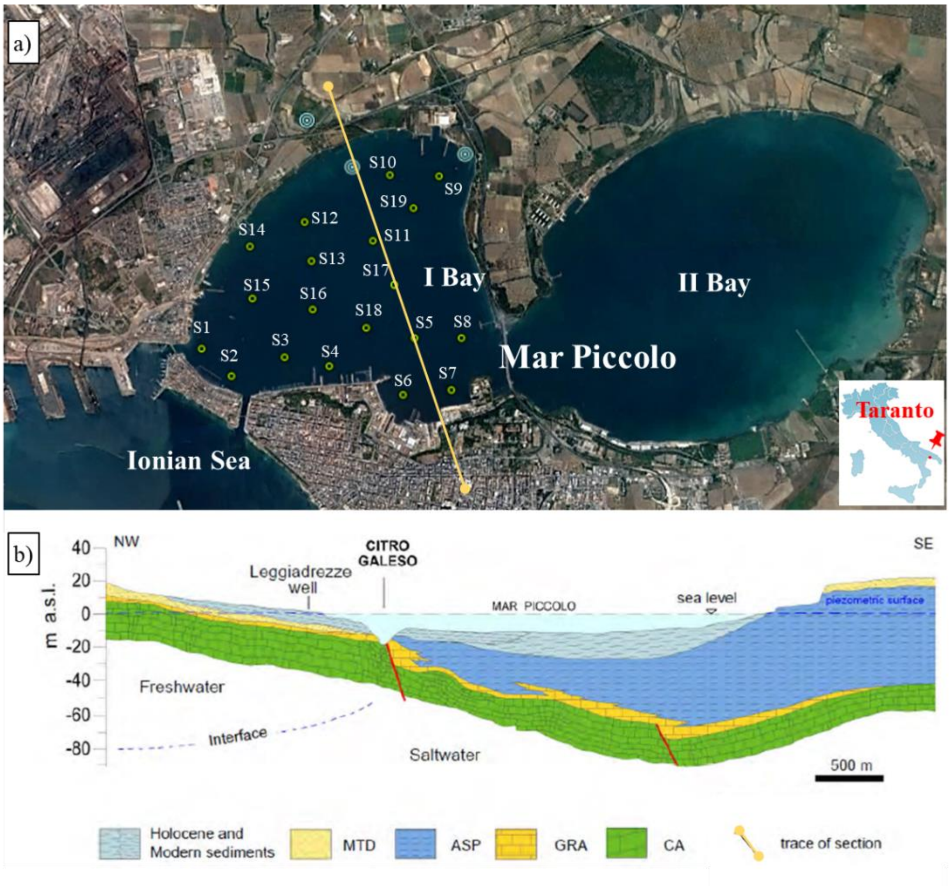

Figure 1. a) Mar Piccolo basin in the South of Italy: boreholes and sampling sites of the investigation campaign promoted by the Special Commissioner (S sites). b) Hydrogeological sketch of section whose trace is shown in the map (a). Key: CA, Altamura Limestone; GRA, Gravina Calcarenite Formation; ASP, Sub-Apennine Clay Formation, MTD, Marine terraced deposits.

2. Standard geotechnical characterisation

The sediments are mostly fine-grained soils, for which the clay fraction (CF) varies between 22.5 and 65.4%, the sand fraction (SF) between 0.5 and 29.4% and the silt fraction (MF) ranges from 30.5% to 69.5%. The grading envelops of all the samples taken in the basin do not show significant differences related to depth. The mineralogical analyses revealed a significant concentration of carbonate minerals, ranging between 28.5-46%; among the clay minerals, smectite (Sm) is prevalent (9-26%), followed by muscovite (i.e., mica group, 7-12%), kaolinite (3.2-5.2%) and chlorite (2.7-3.9%). Pyrite has also been found in the sediment matrix, especially in the shallow samples, probably as a product of the OM mineralisation under anoxic conditions. As for granulometric composition, also the mineralogical data have low variability with depth, confirming that the sediments derive from the erosion and deposition of the ASP clays outcropping inland (Lisco et al., 2015; Vitone et al., 2016; Cotecchia et al., 2021). Despite the homogeneity in composition, the sediment samples from the MP basin are characterized by huge variability of both plasticity index (PI), from extremely high to intermediate (BS 5939:1990) and activity index (A), from low to high (Figure 3). In particular, the shallow samples (circles in Figure 2) exhibit not only the highest variability of both PI (from 34.0 to 78.8%) and A (from 0.60 to 2.49) but also their highest values. The tested sediment samples have revealed a significant variability also in terms of compressibility and permeability (Sollecito et al., 2019a,b; Sollecito et al., 2021).

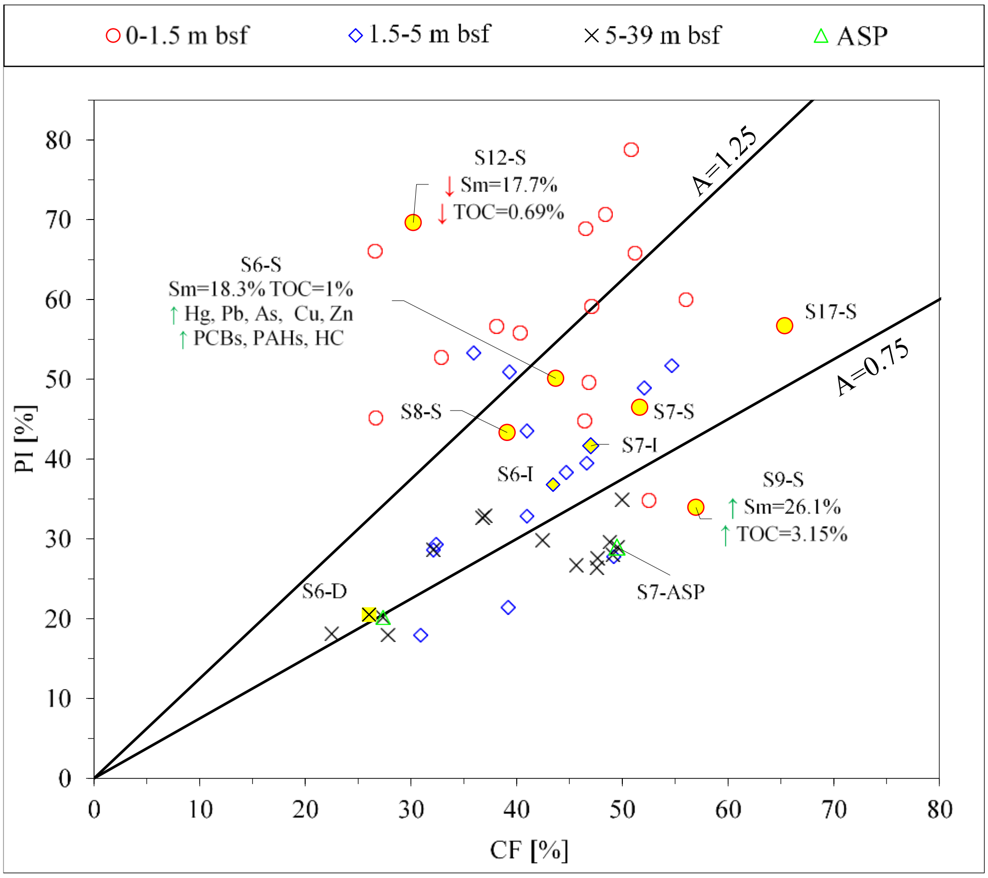

Figure 2. Activity chart of the samples collected within the basin. The data of the samples selected for the multiscale testing are highlighted.

3. Bio-chemo-mechanical processes : integrated and multiscale investigation

Ten samples (highlighted data in Figure 2) were selected for a multiscale laboratory testing, designed to characterise the OM, the microfossils and the pollutants present in the MP sediments and to identify those factors able to affect the geotechnical properties of marine sediments. These samples come from a shallow stratum (i.e., down to 1.5 m bsf, letter 'S' after the borehole number), an intermediate one (depth interval 1.5-3.0 m bsf, letter 'I'), a deep one (depth interval 3.0-39.0 m bsf, letter 'D') and the ASP. The integration of data revealed the presence of two out of trend samples: the sample S12-S of highest activity index despite it includes the lowest CF, Sm content and organic matter content (total organic carbon, TOC), and, on the other hand, sample S9-S of lowest activity index, despite its high CF, Sm content and organic matter content (Figure 2). The association of chemical and mechanical data also reveal that the most contaminated sample, the shallow S6-S, fits the general trend between composition and index properties. Specifically designed spiking tests showed results in line with the data relative to S6-S sample, revealing that the in-situ concentrations of pollutants don't cause outliers in geotechnical

properties.
Given these findings, the reason for the out-of-trend properties of samples S12-S and S9-S have been searched studying other factors, such as their OM nature and their microstructural features.
Total organic carbon and thermogravimetry measurements have been carried out to explore the nature of the sediment skeleton and of its organic matter, along with micro-scale testing. i.e., scanning electron microscopy and mercury intrusion porosimetry.
Thermogravimetry (TG) is a physicochemical technique whereby the samples are heated incrementally in a temperature-controlled device, and their change in physical properties (like the mass) are recorded. Usually adopted to study soil minerals (Emmerich, 2011), TG has been here applied to investigate the features of the organic matter (OM) (e.g., Dell'Abate et al., 2000; Maharaj et al., 2007; Kristl et al., 2016). The thermograms obtained from the tests are expressed as percentage of mass loss against temperature and have been plotted in terms of gradient of mass loss with temperature, i.e., derivative thermograms (DTG). They have been interpreted considering that different thermal reactions occur at different temperature ranges (Sollecito et al., 2021).
The temperature interval of interest for characterizing the OM features is typically between 200 and 650°C, where the main reactions associated with thermal decomposition and oxidation of organic compounds take place. For lower temperature values (T<200°C), the soils should experience the mass loss for dehydration of the clay minerals. Consistently, the DTG curves of the samples here of reference show peak in the rate of mass loss at about 80-100°C (Figure 3) as an effect of the loss of adsorbed water and the dehydration of both the clay aggregates and swellable clay minerals (i.e., smectite). For heating temperatures higher than 620 °C, the mass loss of the soil is related to the process of carbonate thermal decomposition (e.g., Dell'Abate et al., 2000; Maharaj et al., 2007; Kristl et al., 2016). Consistently, the samples with highest total inorganic carbon (TIC), exhibit the most evident peaks in this region.
In the temperature range 220–620°C, large part of the mass loss may be also due to OM degradation. The weight loss at lower temperature (200-450 °C) is associated with the combustion of carbohydrates and poorly altered OM, while that between 375 and 500°C is consequent to the degradation of more complex organic substances, such as humus, lignin, and aromatic compounds.
The data in Figure 3 show that, differently from the other samples, the sample of highest TOC, S9-S, exhibits a peculiar DTG curve with two evident peaks. The earliest DTG peak (270°C), which may result from the oxidation of the recent biodegradable OM, possibly present in the sample. A second DTG peak is recorded in the sample at about 530°C, also suggesting the presence of humic components. Both these peaks are not recorded for the other samples, all of which have lower TOC than that of S9-S and suggest that this sample has a significant amount of recent biodegradable OM, and that the oxidation and transformation of OM is occurring at this site (Sollecito et al., 2021). This hypothesis is also confirmed by the highest content of pyrite found in this sample and detected also through scanning electron microscopy (Figure 4a). Indeed, the formation of pyrite is indicative not only of the anaerobic OM degradation in S9-S, but also of the abundance of the microbial population, which feeds off the organics within the sediments and oxidises the organic matter. Both the organic substances and microbial populations have been recognised to have a binding effect on the soil particles and to aggregate the clay particles (e.g. Varghese et al., 2019). As such, in the case of S9, all the experimental data led to suppose that these substances, which aggregate the clay particles, reduce the plasticity and activity indexes, which would be otherwise much higher given the high CF and Sm contents of the sample.
On the other hand, more than for other samples, the SEM images of S12-S sample reveal a matrix composed in large part by porous fossils (also relicts) and diatoms (Figure 4b). The higher amount in microfossils and diatoms documented for this sample, is recognised to be the source of its out-of-trend values of PI and A, which are not consistent with its low CF and Sm content (Figure 2).
Indeed, as widely reported in the literature (e.g., Tanaka & Locat, 1999; Caicedo et al., 2018), the intraskeletal pore space of the diatoms provides a chamber which can store water that does not participate actively in the measured index property, but that water is included in the measurement of the

water content. The analysis of the mercury intrusion porosimetry confirms the interpretation reported above for both the out-of-trend samples (Sollecito et al., 2021).

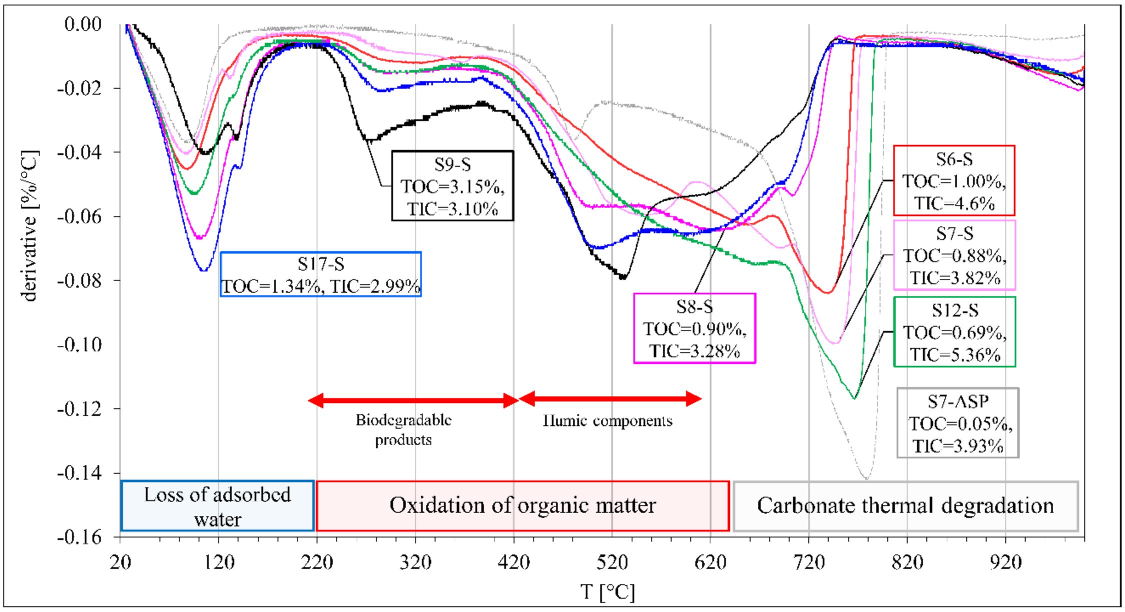

Figure 3. Derivative thermograms of the MP shallow samples and the ASP sample.

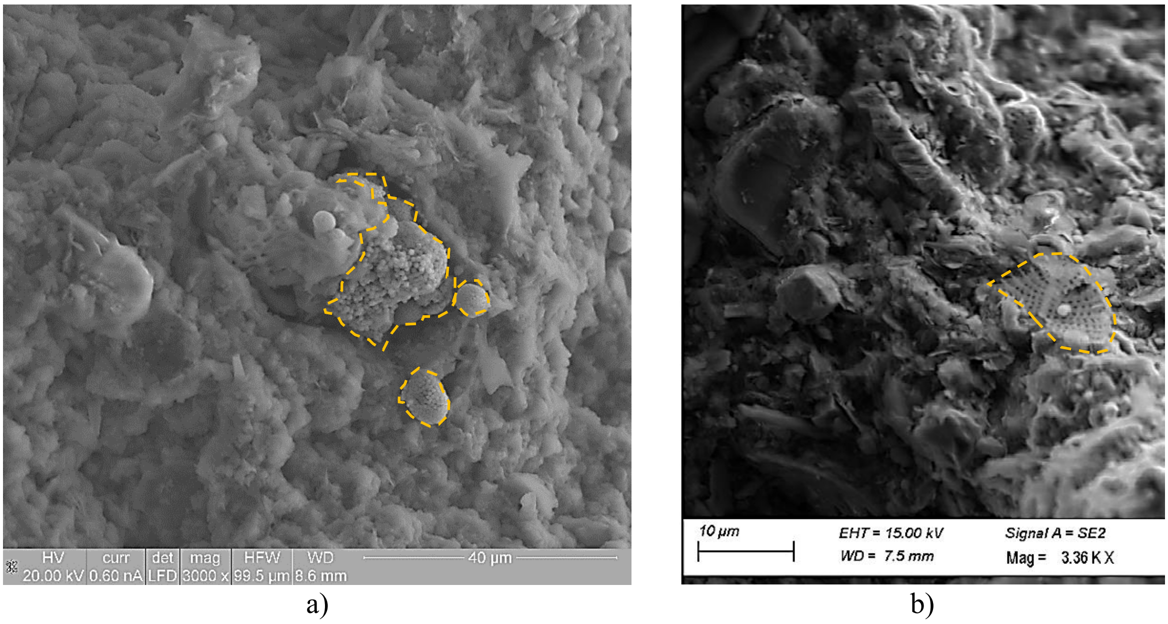

Figure 4. SEM images of a) assemblages of pyrite in S9-S sample, b) one of the diatoms found in S12-S sample.

Conclusion

The research mainly contributes to illustrate the extent to which the geotechnical properties of marine sediments may not depend only on the soil granulometry and mineralogy, especially when they have been recently deposited in complex ecosystems. Indeed, natural marine sediments are usually formed by a pool of minerals, contain pore water of marine salinity, and, may include, all together, heavy metals, organic pollutants, organic matter, diatoms and fossils. The results of the discussed multiscale investigation represent a step forward in supporting both the characterisation of marine sediments through advanced methods and the design of the remediation measures in the case of polluted sites.

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