Experimental evidences of bio-chemo-mechanical processes in contaminated sediments

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ABSTRACT

The research shows the results of a micro to macro testing programme 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 collected in the basin from the top layer exhibited peculiar geotechnical properties, in terms of plasticity and activity indexes, compressibility and hydraulic permeability. The results of the geotechnical testing were interpreted taking into account the XRD mineralogical results and the chemical composition of the soil matrix. Furthermore, thermogravimetry tests results were examined to explore the nature of the sediment skeleton and of its organic matter content, based on the main thermal reactions occurring within different temperature ranges. Lastly, scanning electron microscopy and mercury intrusion porosimetry were performed to assess the sediment pore size distribution as well as their content in microfossils and diatoms. The original multiscale analysis carried out on some selected sediment samples showed that the biogeochemical degradation of organic matter and the presence of microfossils and diatoms significantly affect the micro to macro behaviour of marine sediments.

Keywords: Contaminated material; Environmental engineering; Laboratory tests

1. Outline of the Mar Piccolo site

The Mar Piccolo (Fig. 1a) is a marine basin with two bays of lagoon features, a total surface area about 20.72 km² and maximum water depth of 13 m. The basin lies in the northern part of Taranto, a town which hosts several strategic industrial sites. The town has been severely polluted in the last decades as to be included within the Italian Sites of National Interest, SIN, which need urgent measures of environmental remediation.

As schematically reported in Fig. 1b, at the sea floor, a thick stratum of soft Holocene sediments overlies the Plio-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 terms of metals and metalloids (e.g. arsenic As, cadmium Cd, chromium Cr, copper Cu, mercury Hg, nickel Ni, lead Pb, and zinc 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 19th century, as result of the waste from local industrial activities (e.g. shipyards, navy, steel and cement plants), together with chemical compounds coming from the surrounding cultivated lands and from uncontrolled sewage discharge pipes. It has been shown that the top sediments (up to 5 m depth) are contaminated by heavy metals (e.g. As, Pb, Cd, Hg, Cu, Zn), asbestos and organic pollutants (PAHs, PCBs, and dioxins) (Cardellinchi et al. 2007, Petronio et al. 2012, Kralj et al. 2016, Cotecchia et al. 2021).

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), 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 actions; iv) providing indications about possible sustainable remediation strategies (Adamo et al. 2018, Vitone et al. 2020, Cotecchia et al. 2021, Roque et al. 2022).

During the above-mentioned campaign, sediment samples for interdisciplinary testing were retrieved from 19 boreholes drilled in the I Bay (S-sites in Fig. 1a). Samples subjected to geotechnical testing were collected down to 39 m below seafloor (bsf), in order to characterise the whole MP system. Most of these samples belong to the Holocene (recent) formations, with the exception of two samples that were taken in the stiff ASP (Cotecchia et al. 2021).
2. Geotechnical features

The geotechnical investigation revealed that 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 envelopes of all the samples taken in the basin do not show significant differences related to depth (Sollecito et al. 2021).

The mineralogical analyses carried out by means of the x-ray diffraction method (Bish and Plötze 2011, Döbelin and Kleeberg 2015) 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%). Additionally, pyrite has been discovered in the sediment matrix, particularly in shallow samples, and is most likely a product of the mineralisation of organic matter under anoxic conditions. As for granulometric composition, also the mineralogical data show 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 characterised by highly variable geotechnical properties. The plasticity index (PI) varies from extremely high to intermediate and the activity index (A) varies from low to high (Fig. 2). In particular, the shallow samples collected down to 1.5 m bsf in the most polluted layer (circles in Fig. 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.

![Figure 1. a) Mar Piccolo basin in the South of Italy: sampling sites of the investigation campaign promoted by the Special Commissioner. b) Hydrogeological sketch of section whose trace is shown in the map (a) - Key: a) Holocene and modern sediments; b) ASP, Sub-Apennine Clay Formation; c) CA, Altamura Limestone; d) MTD, Marine terraced deposits; e) GRA, Gravina Calcarenite Formation; f) fault (after Cotecchia et al. 2021).]

![Figure 2. Activity chart of the samples collected within the basin. The data of the samples selected for the multiscale laboratory testing are highlighted in yellow.]

![Figure 3. Vertical profile of initial void ratio and average compression index of the Mar Piccolo sediments.]

The initial void ratio ($e_0$) and the compression index ($C_c$) decrease significantly with the sampling depth, as expected due to loading with burial (Fig. 3). However,
their variability is particularly relevant for the shallow samples. In this layer of sediments, $e_0$ varies in the range 2.00 – 4.50 and $C_C$ is comprised between 0.57 and 1.23. These parameters reduce with depth up to the ASP values, where $C_C=0.33$ and $e_0=0.74-1.38$ (Sollecito et al. 2019, Sollecito et al. 2021), as reported in Fig. 3.

The geotechnical characterisation has shown that the physical and mechanical properties of the recent MP sediments do not vary solely with the composition of the soil skeleton and the soil deposition-loading history, as expected for uncontaminated recent sediments. Since buried in natural marine environment, locally subject to anthropogenic impact, MP sediments include pore water of marine salinity, which may contain organic matter, diatoms and fossils as well as heavy metals and organic pollutants in concentration also above the law thresholds. All these findings have inspired an original investigation to assess to which extent the bio-chemical processes occurring in real soils influence their index properties and mechanical parameters.

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

Ten samples (full yellow symbols in Fig. 2) were selected for a multiscale laboratory testing, designed to identify and characterise the organic matter, 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 are well representative of the overall variability of the soil properties across the deposit and 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 mineralogic, physical and chemical data revealed the presence of two out-of-trend samples: S12-S and 29-S. It has been found that the sample S12-S has the highest plasticity and activity index despite it includes the lowest CF, Sm content and organic matter content (CF=30.23%; Sm=17.7%; total organic carbon, TOC=5.36%). On the other hand, sample S9-S has the lowest activity index, despite its high CF, Sm content and organic matter content (CF=56.98%; Sm=26.1%; TOC=3.15%). The association of chemical and mechanical data also revealed that both samples are uncontaminated samples and that the most contaminated sample, the shallow S6-S, fits the general trend between composition and index properties (Fig. 2). Liquid limit determinations were carried out also on spiked samples, obtained by mixing unpolluted MP sediments with organic pollutants at different concentrations. The results of the tests on both laboratory spiked samples and polluted ones collected in-situ (i.e. S6-S) showed that pollutants do not cause outliers in geotechnical properties (Sollecito et al. 2021). Given these findings, the reason for the out-of-trend properties of samples S12-S and S9-S have been studied based on other factors, such as their OM nature and microstructural features.

Thermogravimetry (TG) 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.

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 within different temperature ranges (Table 1, Sollecito et al. 2021).

The temperature interval of interest for characterising 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 (Table 1). 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 (Fig. 4) 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 (Table 1).

<table>
<thead>
<tr>
<th>Up to 300 °C</th>
<th>300-850 °C</th>
<th>860-1000 °C</th>
<th>Loss of adsorbed water, dehydration of the interlayer cations of swellable clay minerals</th>
<th>Decomposition of organic matter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dihydroxylation of clay minerals</td>
<td></td>
<td>&gt;600 °C</td>
<td>Biodegradable products</td>
<td>Humic components</td>
</tr>
<tr>
<td>200-650 °C</td>
<td>450-650 °C</td>
<td>Carbonate thermal dissociation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>210-320 °C</td>
<td>400-520 °C</td>
<td>XCO$_2$→ XO + CO$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>270-375 °C</td>
<td>375-430 °C</td>
<td>415-520 °C</td>
<td>&quot;Fresh&quot; OM:</td>
<td>Coal fraction</td>
</tr>
<tr>
<td>-grass litter</td>
<td>-cellulose</td>
<td>-apple leaves</td>
<td>(combustion carbohydrates)</td>
<td></td>
</tr>
</tbody>
</table>
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 (Table 1).

The data in Fig. 4 show that, unlike 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) 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. These data suggest that S9-S sample is likely to be characterised by 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 (Fig. 5a). 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 the S9 sample, 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 the S12-S sample reveal a matrix composed in large part by porous fossils (also relics) and diatoms (Fig. 5b; Sollecito et al. 2021). 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 (Fig. 2). Indeed, as widely reported in the literature (e.g., Tanaka and 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 (Sollecito et al., 2021). The pore size distribution (PSD) of the MP samples selected for the multiscale laboratory testing is shown in Fig. 6. The sediments collected within 1.5 m bsf have a relatively large dominant pore size (DPS), between 2 and 6 μm, higher than that recorded for other soft clays (Hattab et al. 2013, Delage and Lefebvre 1984). As expected, the deep ASP sample has a DPS of 0.29 μm, i.e., close to that of the undisturbed ASP clays sampled in land (Guglielmi et al. 2018). The shallow samples S12-S, S17-S, S8-S, S6-S all exhibit a mild bimodal PSD, with a secondary DPS at about 0.11 μm. The highest frequency of the secondary DPS (0.11 μm) is recorded for sample S12-S, of relatively small CF, as an effect of the high content of microfossils and diatoms. Indeed, bimodal PSD has been found in fossiliferous clays, or in soils rich in diatoms: MIP tests carried out on kaolin (Tanaka and Locat 1999) and Singapore clay mixed with diatoms (Tanaka 2003) showed that diatoms may determine a secondary DPS at 0.07-0.15 μm.

No clear secondary DPS is recorded for the most organic sample, S9-S, which is also the richest one in CF (Fig. 6). The absence of an intra-aggregate porosity in this sample, is likely to be the effect of the sealing of the intra-aggregate pores, determined by the colonies of microorganisms.

4. Conclusion

The research 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 range of different minerals, contain pore water of marine salinity, and may include, also in combination, heavy metals, organic pollutants, organic matter, diatoms and fossils. However, the integration of data has shown that, for the Mar Piccolo site, the anthropogenic pollutants do not impact the micro to macro properties of marine sediments, which instead seem to be influenced by the biogeochemical degradation of organic matter and the presence of microfossils and diatoms. The results of the multiscale investigation here presented represent an original insight in the multiphysics phenomena behind the characterisation of marine sediments with the aim of better addressing the design of remediation measures in polluted sites.
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References


