Geo-chemo-mechanical characterization of a polluted marine basin

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Abstract. The work shows the first results of the characterization of the heavily polluted sediments in the Mar Piccolo basin (Taranto, south of Italy), obtained thanks to an integrated investigation method. In the field of the actions promoted by the Italian Government to select the most sustainable remediation strategies, a multidisciplinary investigation of the site has been carried out involving the reconstruction of the geological set-up of the basin, the analysis of the chemical contamination and the geo-mechanical properties of the sediments collected up to 30 m below the sea floor. The devices and methodologies used for the off-shore sampling, storage and transport of the sediments and for the laboratory testing were specifically designed to obtain the best possible picture of the site. The quality of the soil sampling resulted to be high enough for chemical, geochemical and geotechnical characterization and to develop integrated analyses. With this purpose, the paper discusses preliminary correlations of data, focusing on the geotechnical properties of plasticity that have been interpreted in the light of soil composition and chemical and geological facets of the sediments.

1 Introduction

The site under the study is the Mar Piccolo basin (literally “Little Sea”), a semi-enclosed basin having a total surface of 20.72 km² and 13m of maximum water depth. The basin is divided into the so-called First and Second Bay (Fig. 1) and is located just behind the coast of the city of Taranto (South of Italy). The town is one of the most important industrial sites in Europe, which has been declared ‘at high risk of environmental crisis’ and included into the list of the Sites of National Interest (SIN; [1]), to be subjected to environmental remediation. Probably, due to the inflow of fresh water by submarine springs (e.g. Galeso and Citrello in Fig.1) and tributary rivers, the peculiar morphology and the climatic conditions of the area, the Mar Piccolo represents an unusual ecosystem from the naturalistic point of view and hosts several plant and animal protected species and the most important area of mussel farming in Italy [2].

In 2016-2017 an ample investigation campaign was funded by the Special Commissioner for urgent measures of reclamation, environmental improvements and redevelopment of Taranto (CS_2017 hereafter), aimed to the multidisciplinary investigation of the sediments in the First Bay for the selection of the most suitable remediation strategies [3]. Usually, the environmental campaigns in contaminated sites tend to characterize in more detail the physical and chemical properties of the shallow layer, that is expected to be directly affected by the contamination. The CS_2017 campaign has focused on the geotechnical engineering volume of sediments (i.e. from shallow to large depths) by considering it simultaneously with the chemical composition and the geological and morphological evolution of the whole basin over time.

This inherently interdisciplinary approach addressed the selection of the most sustainable remediation scenarios because on one side allowed the identification of hot-spots along vertical profiles, on the other, supported both the identification of loading factors controlling the spatial migration of contaminants and the reliable assessment of their far-reaching combination effects. Additionally, the sampling and testing procedures have been defined in such a way to enable the data integration, respecting the strict protocols required for the chemical, geotechnical and environmental characterization and the time and cost-efficiency criteria [4].

Fig. 1. Mar Piccolo basin in Taranto (Southern Italy). The green dots in the First Bay correspond to the sampling sites of the investigation campaign (CS_2017).
2 The investigation campaign

One of the main concerns about the sediment characterization has been that of allowing for the highest possible quality of soil sampling for the chemical, geochemical and geotechnical laboratory investigations. Cross-contamination, small changes in the storage temperature, light exposure and volatilization may influence the chemical analyses, which require strict protocols [5]. On the other hand, the sample remoulding and storage at temperatures below +4°C, could seriously compromise the quality of the geotechnical sampling [6]. In order to guarantee both high sampling quality and cost and time optimization for the in-situ campaign, the procedures for off-shore sampling, sample storage on the platform, transport and conservation of tube samplers and sub-sampling were properly defined [4], [7]. Fig. 2a shows the distribution scheme of samples among the chemical, geochemical, environmental technologist and geotechnical laboratories.

For each of the 19 sampling sites in Fig. 1, two twin continuous boreholes, i.e. named A and B (Fig. 2a), were drilled at a maximum distance between each other of 10 m. The sediments collected from borehole A were tested drilled at a maximum distance between each other of 10 m. The sediments collected from borehole A were tested by researchers of environmental technology field, whereas those of borehole B were analysed by geologists and used for chemical, geotechnical and geochemical characterisation. The sample coring within the boreholes was carried out by means of 1.5 m length polycarbonate liners, specifically designed to avoid phenomena of cross-contamination of the sediment through common metallic liners. The polycarbonate liners taken from borehole B were longitudinally cut and the two cores were used for geological, geochemical and mineralogical analyses (first half), and for chemical testing (second half). Moreover, at fixed depths along borehole B, 1.4 m long undisturbed geotechnical samples were collected by means of different devices and methodologies as function of both the sampling depth and the soil consistency. The sediments of medium consistency were usually sampled using Osterberg hydraulic piston samplers, while either Shelby or Denison tube piston samplers were used within stiffer sediment strata. The most polluted shallow layer of sediments (0-1.5m bsf), characterized by very high liquidity index [8], was sampled down borehole M (Fig. 2a) by thin-walled tube samplers, made of transparent polycarbonate, pushed into the soil by a team of expert scuba divers. A portion of each undisturbed geotechnical sample was collected by chemists soon after sampling (Fig. 2b).

3 Results

3.1 Geological and environmental features of the area

The main geological units present in the basin from the bottom to the top are: Cretaceous limestone (Altamura limestone), Upper Pliocene-Lower Pleistocene calcarenites, (Gravina calcarenite, GRA), Lower Pleistocene clays (Sub-Apennine clays, ASP), Holocene alluvial deposits [9]. Except for limestone, during the CS_2017 for the first time several samples were collected from all the formations to reconstruct the geological setting of the basin and its litho-technical features. The two depressions of sub-elliptical shape that constitute the Mar Piccolo are supposed to be ancient river valleys that were incised in the basic formations during the continental phase related to the Last Glacial Maximum (20.000-25.000 years BP, [10]). The valleys were subsequently submerged by the sea during the Holocene marine transgression. The sediments forming the Mar Piccolo basin have been deposited in time-varying environmental conditions, overlying both the ASP and the GRA. Moreover, the recent Carbon-14 dating results show that the top layer of sediments may have suffered a significant remoulding due to both the human activities carried out in the area (e.g. maritime activities and dragging of ship anchors in and around the harbour and the Navy) and the flooding events ([11], [12]).

In the last decade, several Authors (e.g. [13], [14]) have provided evidence that the Mar Piccolo submarine sediments contain high concentrations of pollutants. The chemical characterization carried out during the CS_2017, confirmed that heavy metals (e.g. Hg, Pb, As Cd, Cu, Zn) and anthropic organic contaminants (e.g. PCBs, PAHs, HCs) in the sediments can even exceed the limits set by the law [15]. This is particularly the case within the shallow sediments (0-3m bsf) in some areas of the First Bay [16]. Moreover, the chemical composition of the sediments is also affected by the presence of salt and organic matter. The seawater salinity of the Mar Piccolo basin have been deposited in time-varying environmental conditions, overlying both the ASP and the GRA. Moreover, the recent Carbon-14 dating results show that the top layer of sediments may have suffered a significant remoulding due to both the human activities carried out in the area (e.g. maritime activities and dragging of ship anchors in and around the harbour and the Navy) and the flooding events ([11], [12]).
LOI, EPA 160.4) is found to be highly variable, although a general trend of reduction with depth is recorded: OM ranges between 9 and 18% within 1.5m bsf, it is between 5 and 15%, at medium depth (1.5-5m bsf) and tends to the average value of 7% at larger depth (5-32m bsf). The OM content and its correlation with soil composition can provide supporting information for interpretations of both natural and human-induced contamination [18]. Moreover, due to the small surface area and their negative charge, clay minerals have high attraction for organic or inorganic contaminants, therefore it is supposed that OM and contamination content can impact geotechnical features of sediments [19], [20].

### 3.2 Composition and physical properties of the submarine sediments

The classification of soil according its granulometric composition and its plasticity allows to recognise the engineering category to which it belongs. The geotechnical characterisation of the polluted sediments required the development of innovative solutions to consider the complexities deriving by the highly variable consistency of the sediments, the presence of shells, organic matter and pollutants, and the salinity of the pore fluid [21], [22].

The grading envelope of the 54 samples collected within the First bay of the Mar Piccolo basin (Fig. 3) essentially represents a fine-grained soil, 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%. Specifically, almost all the investigated specimens can be classified as clays with silts, or clayey silts, from sandy to slightly sandy, apart from three samples which testify the presence of a predominantly sandy matrix, located between 1.5 and 5 m bsf in the southwest area of the First Bay. It is worth noting that no significant differences in composition occur between the sediments of the shallow layer (0-1.5m bsf, red curves in Fig. 3) and those at larger depth (i.e. blue curves for 1.5-5m bsf and black ones for 5-32m bsf sediments) [23]. The grading envelop also includes the Mar Piccolo samples belonging to the base formation represented by Sub-Apennine clays, ASP, (green dashed curve in Fig. 3). These data agree with those of the Sub-Apennine clays collected in the Apulian region both on-land (Pappadai Valley, [24]) and in the sea areas (Mar Grande basin, [25], [26]).

A widespread presence of illite, interstratified illite/smectite, I/S, and chlorite/smectite, Chl/S has been detected within the clay fraction of three samples [8]. This finding is similar to what found for the ASP Formation outcropping in the Taranto area, where the clay minerals (46%) are mainly represented by illite ([24] - [28]). All these evidences seem to suggest that there is no indication of significant differences in range of composition not only with depth throughout the basin but also between the recent sediments and the AGA Formation, from which the sediments were originated in consequence of geological processes (i.e. erosion and subsequent deposition, [9], [10]). However, the forthcoming data of mineralogical composition of the Mar Piccolo sediments will better clarify this aspect of the research.

![Fig. 3 Grading curves of the Mar Piccolo sediments.](image)

![Fig. 4 Casagrande’s plasticity chart (a) and Activity chart (b) of the Mar Piccolo sediments.](image)

According to [29], the samples from the deeper (black x in Fig. 4a), intermediate (blue rhombus in Fig. 4a) and AGA (green triangles in Fig. 4a) layers can be classified as fine soils from high (50%<\(w_L\)<70%), to very high
plasticity (70%<\(w_L<90\%\)), except for few samples having CF lower than 30% and \(w_L\) lower than 50% (i.e. intermediate plasticity). In these layers (i.e. deep, intermediate, AGA), the activity for the samples ranges from low (\(A = 0.56-0.75\)) to medium values (\(A = 0.75-1.25\)), as reported in Fig. 4b. On the other hand, the shallow layer of the Mar Piccolo basin (red circles in Fig. 4a and b), where the pollutants reach values often above the legal limits and the organic matter content is high (OM=9-18%), is also characterised by huge variability and highest values of plasticity and activity indexes. In particular, within 1.5 m bsf, \(w_L\) varies between 62 and 117%, PI between 34 and 79% and A ranges from 0.60 to 2.49 (Fig. 4a and b). The activity of the shallow layer is also above the values expected for illitic mineralogy reported by [30] (i.e. Smectites A=1-7; Illite A=0.5-1; Kaolinite A=0.5). The variability of the index properties of the sediments is higher than that of the AGA Formation from which the sediments were originated, as measured either on in-land samples [24] or in submarine samples taken from both the Mar Grande ([25], [26]) and the Mar Piccolo basin (AGA samples). In particular, [25] report that the Mar Grande clays (sampling depth from 1 to 33 m bsf) are characterised by \(w_L\) varying from 38 to 70%, PI from 19 to 40%, and activity values A from 0.49 to 0.93. Similar values were found in the Sub-Apennine Clay Formation in the Pappadai Valley: \(w_L=30-67\%\); PI=11-37%; A=0.42-0.72 [24].

In terms of in situ state, the sediment samples taken within the top 2-3 m bsf have generally natural fluid content much higher than the liquid limit: the liquidity index, LI, varies between 1 and 2.7 (LI\(_{\text{max}}=4\)). In the layer of sediments between 3-5 m bsf, LI is still higher than one (i.e. liquid consistency), ranging between 1 and 2, even when the real consistency of the retrieved material is clearly plastic. At larger depths (5-32 m bsf), LI is either close to one or slightly smaller, indicating a plastic consistency. If compared to the ideal profile of reconstituted Pappadai Clays, the Mar Piccolo sediments exhibit high water content than expected for normally consolidated sediments under their own weight up to 20 m bsf ([5], [30]).

### 3.3 Analysis of chemo-mechanical data correlations

The effects on the geotechnical soil properties of physical-chemical factors, such as salinity and organic and inorganic compounds, are widely investigated in the literature (e.g. [26], [31] - [33]). According to [34], the potential of chemical-mechanical coupling resulted to be greatest in fine-grained soils at low confinement, as for the sediments here of reference, and such coupling may prompt highly variable effects for different clay fabric conditions. Nevertheless, in almost all the literature contributions, spiked monomineralic (e.g. kaolinite or smectite) soils are utilized. The investigation of the Mar Piccolo sediments may provide evidence about the effects of chemo-mechanical coupling phenomena for well-sorted (real) contaminated sediments.

![Graph](https://example.com/graph.png)

**Fig. 5** Liquid limit, \(w_L\) - organic content, OM, data of the Mar Piccolo sediments. Clay content values, sampling depth (a) and the most contaminated samples (b) are also indicated.

With this purpose, the geotechnical properties of the Mar Piccolo sediments were analysed in the light of the available data of organic matter, OM (determined by means of LOI method), heavy metals and organic pollutants concentration. The aim of the analysis was that of identifying correlations between the chemical and the geotechnical data able to explain some of the paradoxes recognised in the soil behavioural facets. As an example of the adopted approach, Fig. 5 shows the variability of liquid limit values, \(w_L\) at different depths with respect to the organic matter, OM, measured according to LOI standards (540° for 4 hours EPA 160.4) on the Mar Piccolo sediments.

The colour intensity of the circular symbols in Fig. 5 has been chosen in order to take account of the range of clay fraction, CF. Moreover, black rhombuses in Fig. 5 indicate samples having the highest CF, i.e. equal to or higher than 50%. In the figure, the samples characterised by CF values lower than 30% (i.e. circles coloured with striped filling mode) include also two samples of sand (SF=67-80%). Furthermore, the samples taken from the top (0-1.5 m bsf) and the intermediate layer (1.5-5 m bsf) have been distinguished by the inner symbols “+” and “-”, respectively (Fig. 5a). The other data refer to deeper samples (sampling depths from 5 to 32 m bsf). Three
samples having the highest values of \( w_L \) are marked with a light blue contour.

Fig. 5a shows that OM is higher in the top soils (OM=9-18%) and tends to reduce with depth, even if, along some boreholes, OM values are still high up to medium depth. Data from the literature testify that OM may absorb water and promote the aggregation of clay-size particles to form a more open fabric [30]. If OM content increases, soils may be characterized by unusually high water contents and plasticity and activity indexes, with exceptionally low wet bulk densities (e.g. [35], [36], [37]). Consistently with the literature, the data show an increasing tendency of the liquid limit as the OM content increases (Fig. 5b):

\[
\textit{w}_L = 4.4 \textit{OM} + 14.6
\]  

(1)

However, for OM > 13% the dispersion of data tends to increase, irrespective of the content of clay, which usually strongly absorbs organic particles [18]. For same OM values, the samples from the top layer are characterised by higher liquid limit than the deeper ones, despite the latter may have similar (or even higher) CF. As an example, two black rhombuses in Fig. 5a, both characterized by CF >50% and the highest OM (18%), have quite different values of \( w_L \), i.e. it is 117% in a top layer sample and 81% in a deeper one. This evidence seems to suggest that, beyond the OM and CF values, the soil response is influenced also by other factors.

The great variability of the liquid limit values is recorded in the shallow layer of contaminated sediments. However, the data of \( w_L \) do not exhibit a clear tendency with respect to the increase of both organic pollutants (red points in Fig. 5b) and different groups of inorganic pollutants (yellow points for samples having high concentration of Hg, Pb; Zn; yellow squares for samples with high concentration of Hg, Pb, Zn, As, Cu). It is suggested that the combination of all these classes of contaminants, associated with the high level of OM and the pore-fluid salinity act in modifying the behaviour of samples in a complex way.

It is interesting to notice that the highest \( w_L \) values are exhibited by three unpolluted samples (blue contour in Fig5a and b), that can also sustain high \( w_L \), despite low CF. These samples are located near the northwest coast of the bay, where a steel factory (i.e. ILVA) pumping plant aspires sea water with a flux of -20.8 m³/sec [16] with a relevant impact on the water circulation within the First Bay [11]. In addition, this area is rich in diatoms [38] and is dedicated to mussel cultivation that is characterised by higher liquid limit than the deeper ones, despite the latter may have similar (or even higher) CF. As an example, two black rhombuses in Fig. 5a, both characterized by CF >50% and the highest OM (18%), have quite different values of \( w_L \), i.e. it is 117% in a top layer sample and 81% in a deeper one. This evidence seems to suggest that, beyond the OM and CF values, the soil response is influenced also by other factors.

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