A CONTAMINATED SITE IN THE SOUTH OF ITALY: GEOTECHNICAL INVESTIGATION OF SUBMARINE SEDIMENTS

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Abstract

The city of Taranto in the south of Italy is one of the areas declared as “at high risk of environmental crisis” by the national government (Italian Law n. 349/86) because it represents one of the most complex industrial sites in Europe, located near urban areas of high population density. During the last 50 years, the complex ecosystem of the Mar Piccolo basin, in the northern part of the city, started exhibiting unconfutable signs of environmental pollution. A number of researchers have shown that also the submarine sediments in the Mar Piccolo contain high concentrations of heavy metals (e.g. Hg, Pb, Cd, Cu and Zn) and organic pollutants (PCBs, PAHs, and dioxins). This experimental research is part of the multidisciplinary studies that aim at the selection of sustainable strategies for the remediation and management of the Mar Piccolo environmental contamination. Specifically, this paper focuses on submarine sediments and reports some results of both the chemical and the geotechnical characterisation.

1. Introduction

The contaminated submarine sediments under study are located in a small protected marine basin, the Mar Piccolo, just behind the coast of the city of Taranto (Fig.1). Originally a greek colony and later capital town of Magna Grecia, Taranto is today one of the most important industrial sites in Europe. The Mar Piccolo is a semi-enclosed basin (total surface of about 20 km²) of lagoon features, of about 13 m maximum water depth, divided into the so-called first and second bosom (Fig. 1). It is presently connected to the Ionian Sea through two channels on the west side. The tidal excursions in the basin are limited, not exceeding 30–40 cm (Cecere and Petrocelli 2009) and there are some submarine freshwater springs (“Citri”), the most important being the Citro Galeso in the northern part of the first bosom (Fig. 1). Tributary rivers flow into the Mar Piccolo; the most important is the Galeso river (first bosom; mean flow about 50000m³/day). Probably, due to the inflow of fresh water, the peculiar morphology and the climatic conditions of the basin, the Mar Piccolo represents an unusual ecosystem from a naturalistic point of view. This is why it has been declared Site of Community Importance since 1995 (Habitat Directive 92/43/CEE). Moreover, it is the most important area of mussel farming in Italy (Caroppo et al. 2012). In this context, the paper first reports an analysis of the site chemical contamination in terms of its spatial distribution and then presents some geotechnical properties of the sediments. In particular, they are discussed focusing on the possible interactions between the presence of contaminants (e.g. salts, metal cations, organic matter) and the soil physical properties.
2. Chemical contamination of the Mar Piccolo sediments

In the last decade, though, several Authors (e.g. ICRAM 2005, ISPRA 2010, Cardellicchio et al. 2007) have provided evidence that the Mar Piccolo submarine sediments contain high concentrations of heavy metals (e.g. Hg, Pb, Cd, Cu, Zn) and anthropic organic contaminants (e.g. PCBs, PAHs), with respect to law limits. Figs 1b-c show statistical distribution of mercury and PCBs concentrations in the first 50 cm below sea floor, compared to chemical measurements. As it can be noted, the chemical data show different levels of contamination, even when measured along narrow verticals (ICRAM 2005 in 170ha area, ISPRA 2010 in the rest of the I bosom). Moreover, the comparison between statistical representation of data and deterministic measurement, shows that the former is useful to highlight a general trend of contamination in a wide area, but representation of raw data is needed to recognise hot spots of contamination.

The chemistry of sediments is also affected by the presence of salt and organic matter. The seawater salinity of the Mar Piccolo ranges between 31g/l and 39g/l depending on the influence of fresh water coming from the submarine springs. The measured salinity of the sediment pore-fluid is 30-32 g/l, even within the deep sediments (e.g. about 18 m below the seafloor). The total organic carbon, TOC, measured in the first 3 m of sediments below the seafloor could reach values of 8% (ISPRA 2010). The highest TOC concentration, higher than those of the Adriatic and Ionian open sea sediments (about 2%; Bartholini 2015), could be due to both the natural and anthropogenic additional sources of organic matter that characterise this specific site. The complex phenomena promoted by this mixture of organic matter as well as coupling effects of OM with other factors (e.g. sediment composition, water salinity and pore water chemistry), contribute to the complex contamination pattern of the Mar Piccolo basin and to their effects on the sediment state and mechanical behaviour.

3. Physical properties of the submarine sediments

The ARPA campaign (Fig. 1a), carried out in 2013-2014, in three sampling sites within a limited area of the first bosom of the Mar Piccolo, was the first one exploring depths larger than 3.8 m below the seafloor and focusing on the geotechnical properties of the sediments. Three borehole verticals (S1, S2 and S3 in Fig. 1a), were sampled up to depths of 8.5, 16.5 and 18.2m below the seafloor, respectively. One undisturbed sample was taken along borehole S2 at 11.5m depth and two undisturbed samples were taken from borehole S3 (16 and 18m depth). Moreover, nearby these boreholes, other three samples (i.e. S1-M, S2-M, S3-M) were taken manually in the first meter of sediments by scuba divers through 101mm diameter PVC samplers.
Composition and physical properties of the sediments are summarised in the Table 1. They were determined in the laboratory according to ASTM standards and taking into account the necessary safety and operational procedures to be used in the laboratory when dealing with highly contaminated geomaterials. The data show that the soils are essentially either clayey silts or silty clays. OM measured according to BS1377 Method, is quite high within the top layer (i.e. 5.0 to 6.0%) and decreases at depth (0.7% at 18m below the seafloor). This is also consistent with the very low specific gravity values of the top layer (Gs=2.56-2.61). The sediments along boreholes S1 and S2 and in the top layer of borehole S3, can be classified as clays of high plasticity (CH; Fig. 2a), whereas the other samples taken at depth from borehole S3 are low plasticity clays (CL). Only sample S3-M can be classified as silt of high plasticity (MH). Peculiar is the very high activity (A=0.5) of the top sediments taken by scuba divers within the top layer, against the other samples taken at depth from borehole S3 which shows that, in contrast with the differences in the activity index recorded between shallow and deep sediments, there is no significant variation with depth of the mineralogical composition, except for the halite and hematite contents. Within the clay fraction a widespread presence of illite, interstratified illite/smectite, I/S, and chlorite/smectite, Chl/S is generally recorded (Vitone et al. 2016). Hence, it emerges that the plasticity and activity indices do not relate solely to the mineralogical composition of the soil skeleton, as observed for natural soils including fresh pore water. Moreover, the mineralogical composition of the top layers cannot justify the measured very high activity index, if the sediment is assumed to be made of a solid skeleton of such mineralogy, saturated with fresh water. It follows that more complex coupling between the soil components and the contaminants present have to be invoked in order to justify the data. It has to be noted that despite their very high LI values, larger than 1.5 in the first 3m, the top sediments are not totally liquid (Fig. 3c) and this feature is again a possible indication of complex interactions between the soil-water components at the different scales. In the...
following, the results of a first exploration of the effects of such complex interactions is reported for these sediments.

4. Chemo-mechanical coupling phenomena

The effects on the geotechnical soil properties of physical-chemical factors, such as salinity and organic and inorganic contaminants, are widely investigated in the literature, even if monomineralic soils (e.g. kaolinite or smectite) are usually examined. According to the Gouy-Chapmann diffusive double layer model, increasing the fluid salt concentration, the forces causing the diffusion of ions away from the clay surface reduce. This causes a reduction of diffusive double layer and prompts the particle flocculation. In terms of index properties, a reduction of the liquid limit, \( w_L \), when pore fluid salinity increases is generally recorded (Di Maio et al. 2004; Petrov and Rowe 1997), especially for active clays. On the contrary, for clays of low activity (illite, kaolinite), such as Drammen clay, Torrance (1975) showed a liquid limit increase with salinity. Effect on soil compressibility and hydraulic conductivity are also recorded (Di Maio et al. 2004, Calvello 2005). In order to determine the fluid content, \( w_f \), and the correct soil specific gravity, \( G_s^* \), equations from ASTM D4542 and BS 1377 have been used. The data in Table 1 show that the presence of salts in the pore water significantly affects both the water content and the specific gravity values.

Furthermore, organic particles can be adsorbed by negatively charged mineral surfaces modifying both the properties of the minerals and those of the organic material itself. If OM content is higher than 3-5\% (Bennett et al. 1985; Leroueil et al. 2007), soils may be characterised by unusually high water contents and plasticity index, with exceptionally low wet bulk densities. High contents of organic matter may be also responsible for peculiar behavioural facets of fine soils: high compressibility, low hydraulic conductivity and strength (e.g. Mitchell and Soga 2005, Keller 1982, Coutinho and Lacerda 1987). The organic matter includes also organic contaminant fluid such as hydrocarbons and PCBs. In the sampling area OM is near 6\%, while organic contaminants, even if above the law thresholds, are present as part for million (Hydrocarbons = 0.16\%, PCBs = 0.0001\%). Beyond the quantities, organic fluids, since characterized by low values of dielectric constant, could strongly influence the electrical forces between the clay particles in fine grained soils, especially at low confinements (e.g. Santamarina et al. 2001, Sridharan 2001, Calvello 2005). Furthermore, the combined effect of the mixture of organic compounds, marine salt water and heavy metals on clay behaviour, should be deeply investigated. From what above, it is reasonable that the organic compounds of the shallow sediments (Table 1) can be responsible, together with the water salinity, for the peculiar geotechnical facets found for the shallow Mar Piccolo sediments and discussed in the previous section.

4.1 Experimental washing procedure and results

The data discussed in the following are the results of an experimental investigation carried out on one sample, S3M, taken during the ARPA campaign (Fig. 1a) within the first meter of sediments near the Navy area. In particular, along the same vertical, for some heavy metals (i.e. Pb, Cu and Zn) and organic contaminants (i.e. PCBs) values exceeding the thresholds have been measured (ICRAM 2005, Bellucci et al. 2016). A new laboratory investigation has been carried out, in addition to the standard geotechnical characterisation performed by Vitone et al. (2016), for a first quantification of the effects of both natural and anthropogenic contaminants (e.g. salinity, organic matter, lithogenic and heavy metals) on the soil physical properties and composition. In Fig.3, the Atterberg limits measured on the sediment sample soon after the sampling in 2014 (Vitone et al. 2016) are reported together with the same limits corrected for the fluid salinity according to Eq. 1. The data show that the corrected values of both liquid limit (\( w_L \)) and plasticity index (PI) are slightly higher than the original ones. The Atterberg limits were determined again on the same sample after having wrapped it in cling film and stored it in the fridge at constant temperature (+4°C) for two years. The 2016 data (path 1 in Figs 3a-b)
show a noticeable increase of both $w_L$ and PI. Since the Atterberg limits are generally reflecting the amount and type of minerals present in a given clay (Skempton 1970), their variability in time is unexpected and suggests that physical changes - probably due to either variation in water salinity, or contaminant degradation processes - have occurred within the sediments.

Figure 3. Sample S3M - Results of the standard tests and the washing experiments on the Atterberg limits and the soil fractions: a) Casagrande's plasticity chart; b) Activity of sample S3M.

This finding prompted an additional laboratory investigation, performing a set of washings with distilled water of the same sample. During each washing, 600g of the sample were left in a glass sedimentation cylinder together with distilled water (total volume of the solution: 1000 ml). The cylinder was turned upside down and back for one minute and then left to sediment for the time necessary to see a clear separation between the fluid and the sediment particles. The salt concentration of the fluid was then measured and the fluid in the cylinder was replaced by distilled water up to the same total volume. This procedure has been repeated six times, until the salinity of the fluid (clearly separated by the sediment) had reached approximately zero. It must be noted that the time necessary to produce the complete sedimentation of the solid particles has been found to increase with decreasing salinity. This is in agreement with the progressive reduction of the forces responsible for the particle flocculation, going on with the reduction of salts, found in the literature for soil slurries. The washed slurry was air dried and the Atterberg limits and particle size distribution were then determined. The whole procedure took about 10 days. The data for the washed sample show an increase in both liquid and plastic limits (see path 2 in Fig. 3a). Moreover, a quite significant increase of the clay fraction (from 28% to 40%) has been also measured, with a decrease of the soil Activity (path 2 in Fig. 3b). The recorded trend is consistent with what reported in the literature (e.g. Di Maio et al. 2004) for active clays. The determination of the Atterberg limits was then repeated on the same washed material, after oven drying at 105°C for 48 hours. Liquid and plastic limits decrease, probably as a consequence of the combustion of the organic matter (path 3 in Figs 3a-b). At some critical stage during oven drying, decomposition of organic matter may occur and this induces a large decrease of $w_L$. In particular, according to the Unified Soil Classification System, an organic clay is a clay for which $w_L$ after oven drying is less than 75% of the $w_L$ value before drying (ASTM D 2217). However, for the tested sample this ratio is higher than 75%, in contrast with the quite high OM contents between 5 and 6% measured on the same sample by BS1377 Method (Table 1). This could be explained if the loss of part of the organic matter (together with cations and salts) during the washing procedure is also inferred. Finally, the washed and oven-dried sediment was re-mixed with the Mar Piccolo marine water and the Atterberg limits were newly determined (path 4 in Figs 3a-b). In this case, the soil exhibits index properties quite similar to those at stage 0. This result is both indicative of the effect of salt on the plasticity of the material and of the permanent loss of other contaminants which make the end and the start points do not coincide (paths 0 and 4).
5. Conclusions

This study represents a first insight into the coupling between physical and chemical properties of submarine sediments from a highly-polluted site in the south of Italy. The sediments are silty clays and clayey silts and their clay fraction is mainly represented by illite-smectite clay minerals. The standard geotechnical characterisation has put in evidence that in the top layer the plasticity and activity indices do not relate solely to the mineralogical composition of the soil skeleton, as observed for natural soils including fresh pore water. Furthermore, it is possible that the very top sediments are not totally liquid despite very high LI values because of the complex interactions between the soil-organic matter-water components. The experiments carried out on one sediment sample taken within the top layer of the Navy area have provided new information about the influence of the natural and anthropogenic contaminants (e.g. salts, metal cations, organic matter) on the soil physical properties (plasticity, activity and soil composition). In particular, unexpected sensitivity of the Atterberg limits to long-lasting fringe-storage (2 years) has been recorded, together with an increment of both the clay fraction and the liquid limit after washing the sample with distilled water. A new campaign is currently ongoing which aims at better focusing on such effects through the analysis of the chemical and geochemical compositions and geotechnical properties of a number samples taken from several sites within the Mar Piccolo.

References


