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EXTENDED ABSTRACT

Marine sediments are identified as an ultimate receptor for many hazardous pollutants produced by the human activities that pose major concerns for human health and the environment. As a result, the definition of the remediation strategies of contaminated sediments has given rise to great scientific and public concern throughout the world, since it represents a huge actual challenge from both a technical and technological point of view.

In this context, the present thesis aims to the assessment of two sustainable treatments for the remediation of contaminated marine sediments of the Mar Piccolo basin, located at north of Taranto, (South Italy). Taranto is one of the most polluted towns in Europe and it has been included into the list of polluted Sites of National Interest (SIN), for which the environmental remediation has been identified as a National priority. The Mar Piccolo is a semi-enclosed shallow coastal basin (total surface of 20.72 km²) with lagoon features, characterized by restricted water circulation and tidal range and by the presence of submarine springs, which discharge fresh water into the basin. All these factors contribute to create a rich and unique marine ecosystem, typical of the transition environments, and make the basin one of the most important area for mussel farming in Europe.

Experimental laboratory investigation has been carried out on sediments contaminated by heavy metals, PAHs and PCBs, to explore the sustainability of two selected remediation technologies: i) in situ reactive capping and ii) ex situ stabilization/

solidification (i.e. S/S). Laboratory-scale experiments with sediment columns have been carried in order to assess the impact of reactive capping on contaminant migration. Lastly, geomechanical laboratory tests were carried out on the polluted sediments improved with absorbent materials, in order to study the effects of in situ mix on sediment behaviour. The experimental results contribute to both improve the understanding of chemo-mechanical processes within marine sediments and support the development of sustainable remediation technologies.

Concerning the ex situ alternatives, leaching tests of S/S treated sediments with both traditional binders (i.e. Portland cement and lime) and green additives (i.e. active carbon and biochar) has been carried out. Most efficient mixtures have undergone a geotechnical characterization, aimed at investigating the mechanical performances in the curing time. The results suggest that appropriate mix designs and curing times could allow us for the reuse of sediments by both improving their geotechnical characteristics and making them environmentally acceptable in accordance to end-of-waste criteria.

The research benefited from the circumstance that the Mar Piccolo represents a “natural laboratory” and an emblematic case in the worldwide panorama of polluted sites. It follows that, although starting from a case history, the study offered the possibility to analyses and tests natural geomaterials altered by the presence of different sources of contamination (i.e. water salinity, organic matter, organic pollutants and heavy metals).

key words: *contaminated sediments, sustainable remediation, reactive capping, stabilization/solidification, beneficial reuse of sediments.*

EXTENDED ABSTRACT

I sedimenti marini sono identificati come il recettore finale per molti inquinanti pericolosi prodotti dalle attività antropiche, sostanze che pongono importanti preoccupazioni per la salute umana e per l'ambiente. Di conseguenza, la bonifica dei sedimenti contaminati comporta una grande quantità di preoccupazioni scientifiche e pubbliche in tutto il mondo, rappresentando un'enorme sfida sia sotto il profilo tecnico che tecnologico.

In questo contesto, la presente tesi è finalizzata alla valutazione di due trattamenti sostenibili per il risanamento dei sedimenti marini contaminati del bacino del Mar Piccolo di Taranto (Italia meridionale). Taranto è una delle città più inquinate dell'Europa ed è stata inserita nell'elenco dei Siti di Interesse Nazionale (SIN), per i quali la bonifica è identificata come una priorità Nazionale. Il Mar Piccolo è un bacino costiero superficiale semichiuso (superficie totale di 20.72 km²) con caratteristiche lagunari, caratterizzato da una limitata circolazione e dalla presenza di sorgenti sottomarine, che immettono acqua dolce nel bacino. Tutti questi fattori contribuiscono a creare un ecosistema marino ricco e unico, tipico degli ambienti di transizione, rendendo il bacino una delle aree più importanti per l'allevamento di mitili in Europa.

Sono state condotte indagini sperimentali, in scala di laboratorio, su sedimenti contaminati da metalli pesanti, IPA e PCB, al fine di esplorare la sostenibilità delle seguenti tecnologie di bonifica: in situ reactive capping reattivo e ex situ stabilizzazione/solidificazione (i.e. S/S). Per valutare gli impatti del capping reattivo sulla migrazione dei contaminanti, sono stati condotti esperimenti in scala di laboratorio con

colonne di sedimento. Inoltre, sono stati effettuati dei test geo-meccanici sui sedimenti inquinati migliorati con materiali assorbenti, al fine di studiare gli effetti di un mix in situ sul comportamento dei sedimenti. I risultati migliorano la comprensione dei processi chimici all'interno dei sedimenti marini e dovrebbero contribuire allo sviluppo di tecnologie di capping attive e sostenibili.

Per quanto riguarda la tecnologia ex situ, è stata valutata la lisciviazione dei sedimenti trattati con tecniche S/S a base di leganti tradizionali (cioè cemento Portland e calce) e additivi verdi (cioè carbone attivo e biochar). Sulle migliori miscele è stata condotta una caratterizzazione geotecnica, finalizzata a indagare le prestazioni meccaniche nel tempo di maturazione. I risultati suggeriscono che le miscele progettate, per appropriati tempi di polimerizzazione, potrebbero consentire di riutilizzare i sedimenti migliorando le loro caratteristiche geotecniche e rendendole accettabili dal punto di vista ambientale in base ai criteri di fine rifiuti.

La ricerca ha beneficiato della circostanza che il Mar Piccolo rappresenta un "laboratorio naturale" e un caso emblematico nel panorama mondiale dei siti inquinati. Ne consegue che, pur partendo da un caso studio, lo studio ha offerto la possibilità di analizzare e testare geomateriali naturali alterati dalla presenza di diverse fonti di contaminazione (ad esempio: salinità dell'acqua, materia organica, inquinanti organici e metalli pesanti).

key words: *contaminated sediments, sustainable remediation, reactive capping, stabilization/solidification, riutilizzo dei sedimenti.*

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LIST OF SYMBOLS

1-D	One-dimensional
AC	Active carbon
As	Arsenic
AV	Average
BC	Biochar
C	Contaminant concentration
Ca	Calcium
cc	Compression index
Cd	Cadmium
CF	Clay fraction
Chl	Chlorite
CH ₄	Inhibitor of methane
CS	Critical state
cs	Swelling index
CSL	Critical state line
Cr	Chromium
Cu	Copper
Cu	Undrained shear strength
d	Diameter of the specimen
δ	Horizontal displacements
Dbio	Bioturbation diffusion coefficient
Ddisp	Effective diffusion coefficient
Dol	Dolomite
Dr	Relative density
Dw	Molecular diffusion coefficient
d ₀	Immediate oedometer settlement (Casagrande curve fitting)
e	Voids ratio

e0	Initial void ratio
ef	Final void ratio
Fadv	Advective flux
Fbio	Bioturbation flux
Fdiff	Molecular diffusion flux
Feld	Feldspar
Fgas	Gas flux
foc	Fraction organic carbon
Gs	Soil specific gravity
Gs*	Soil specific gravity corrected for salinity
H	Longest drainage path at the start of consolidation
h	Initial height of the specimen
Hg	Mercury
HH	Henry's Law constant
I	Illite
k	Coefficient of hydraulic conductivity
K	Kaolinite
kd	Sediment-water partition coefficient
koc	Organic carbon-based partition coefficient
ksw	Partition coefficient between sediment and water
LI	Liquidity index
LOI	Loss on ignition
Logkow	Octanol-water partition coefficients
M	Coefficient of oedometric compressibility
MF	Silt fraction
Mw	Molecular weight
NC	Normally consolidated
Ni	Nickel
OC	Overconsolidated
OCR	Overconsolidation ratio: σ'_p / σ'_v

OM	Organic matter
PAHs	Polycyclic aromatic hydrocarbons
Pb	Lead
PCBs	Polychlorinated biphenyls
PI	Plasticity index
Pv	Vapor pressure
Qz	Quartz
qu	Unconfined compressive strength
R	Ideal gas constant
r	Pore fluid salinity
RCM	Reactive core mat
ρ_{SS}	Suspended sediment density
S	Solubility
SCC	Sedimentation compression line (Skempton 1970)
Sm	Smectite
SF	Sand fraction
TOC	Total organic carbon
Tv	Terzaghi's time factor
V	Vanadium
Zn	Zinc
ZVI	Zero valent iron
w	Water content
w*	Water content corrected for salinity
wf	Final water content
wi	Initial water content
wL	Liquid limit
wL*	Liquid limit corrected for salinity
wP	Plastic limit
wP*	Plastic limit corrected for salinity
ϕ'_{CS}	Critical state friction angle

γ	Bulk unit weight
γ_d	Dry bulk unit weight
γ_w	Unit weight of water
γ_s	Unit weight of the soil grains
γ_{sW}	Unit weight of salt water
σ	Total stress
σ'	Effective stress
σ'_h	In situ horizontal stress
σ'_n	Normal effective stress
σ'_r	Radial effective stress
σ'_v	Vertical effective stress
σ'_p	One-dimensional preconsolidation stress
σ'_y	Vertical effective stress at gross yield in one-dimensional compression
τ	Shear stress
ZVI	Zero valent iron

INTRODUCTION

Anthropogenic factors associated with industrial, urban, agriculture, and recreational activities have led to increasing the emissions of many hazardous chemicals to the aquatic environment. Since many of these pollutants do not naturally exist in marine ecosystems or represent persistent recalcitrant compounds, the natural processes occurring in the environments are neither able to degrade the chemicals effectively nor are quickly enough to prevent accumulation in the system. Several decades of such releases have led to accumulation of pollutants in sediments as well as organisms and biota. In particular, sediment-bound pollutants pose major concerns for human health and the environment, because these contaminants can be re-entering the overlying water and become available to benthic organisms and subsequently enter aquatic food chains. Thus, sediment acts as both carriers and long-term secondary sources of contaminants. The management of these sediments is difficult due to their areal extent, volume and cost and consequences of removal. This has encouraged the development of green and sustainable management approaches.

Among the in situ remediation options, capping turns out to be one of the most sustainable options, i.e. in terms of efficacy, durability and economy. This treatment is the process of placing a layer of clean materials over sediments to isolate the contaminant from the overlying water column and biota, to reduce contaminant flux into the biologically active portion of the sediment, and to create new habitats for aquatic organisms. For the purpose of this dissertation, only the Amended Capping (also sometimes termed active or reactive capping) will be considered, a recent development of traditional (or passive) capping which consist of the use of adsorbent and reactive

materials that, interact with contaminants, enhance cap performance. This technology has the advantage of being able to potentially meet remedial goals faster and also exhibits greater public acceptance than passive containment solutions such as sand capping. However, for the heavily polluted sediments, like the hotspots, or for the case in which dredging is compulsory to reach a desired bathymetric level, ex situ sediment remediation becomes the first choice. In these cases, the beneficial use of dredged materials is highly encouraged. Among the ex situ remediation options, the solidification/stabilization technique is the commonly adopted immobilization option to convert the contaminated sediments to non-hazardous mass, in accordance with the legitimate waste provisions. Treatments allow not only the immobilization of contaminants but also the improvement of the mechanical characteristics, which makes the treated sediments suitable for being recycled as aggregate for road construction, cemented mortars, fill material and blocks or raw material in brick production. The simplest form of treatment is with Portland cement or lime. Nevertheless, the effect of the treatment depends on several factors, such as the quantity of additive, the curing time, composition and physical properties of the sediments, water chemistry. Also, if the sediments are polluted, the contaminants can interfere with the binders' chemistry, compromising the effectiveness of the stabilization. It follows that, for the optimisation of the sediments' reuse, other additives can be used (e.g. carbonaceous adsorbents) depending on the type of contaminants, soil physical properties, composition and the required performance. The described remediation technologies have been successfully applied in several real cases, but their efficacy strictly depends on the sediment and the contamination being treated (specific site conditions). Moreover, theoretical models capturing the chemo-mechanical behaviour of contaminated marine sediments are very limited and are always necessary treatability test in laboratory.

In this context, the research field of the thesis is the Technology for Environmental Protection, involving investigation of sediments sampled down a natural marine deposit, highly polluted by organic (i.e. PAHs and PCBs) and inorganic contaminants (i.e. As, Cd, Cu, Hg, Ni and Pb). This research aims to explore both the efficacy of different types of amended capping for in situ sediments remediation and the efficacy

of different S/S treatments for the reuse of contaminated sediments, in a vision of green and sustainable reclamation.

The scientific issues dealt with involved the understanding contaminant behaviour both in the sediments and in pore fluid, their fate in the environment, the selection of a remedy(s) to remove or isolate the contamination with limited potentially deleterious environmental effects (e.g. waste production or release of contaminants to other compartments). Furthermore, the present study aimed to the assessment of the chemo-hydro-mechanical interactions which develop in a natural marine sediment, with contamination of both natural and anthropogenic origin, treated with traditional binders (i.e. cement or lime) and green additives (i.e. active carbon and biochar).

The experimental data demonstrate the effectiveness of the two remediation technologies investigated. In particular, the present study focuses on: (1) investigating the basic characterization of contaminated marine sediments, (2) studying the effect of reactive capping on the contaminant migration, (3) researching chemical and mechanical properties of treated sediments with different binders and reagents contents, and (4) evaluating the feasibility of treated sediments for beneficial use.

The present study is part of the multidisciplinary investigation carried out on the heavily polluted marine system of the Mar Piccolo basin (Taranto, South Italy), with the aim of identifying the most sustainable strategies for the remediation and management of the environmental contamination. The research was carried out in the field of the activities promoted by the Special Commissioner for urgent measures of reclamation, environmental improvements and redevelopment of Taranto. The research benefited from the circumstance that the Mar Piccolo represents a “natural laboratory” and an emblematic case in the worldwide panorama of polluted sites. It follows that, the study offered the possibility to analyse natural geomaterials spatially altered by the presence of different sources of contamination (i.e. water salinity, organic matter, heavy metals, PAHs and PCBs).

CHAPTER 1. CONTAMINATED MARINE SEDIMENTS

1.1 Introduction

Contaminated marine sediments are a widespread environmental concern in the world, and remediation of these sites has proven to be a significant challenge. Contaminants present in sediments are toxic to aquatic life and biomagnification through the food web can cause detrimental health effects of humans who consume aquatic organisms. Elevated contaminant concentrations in sediments can also limit recreational and economic uses of surface waters.

Common sediment contaminants include PCBs, PAHs, pesticides, nutrients, and metals. Metals of concern typically found in aquatic sediments include arsenic, copper, zinc, lead, cadmium, chromium, nickel and mercury. Once introduced into aquatic sediments, hydrophobic organic contaminants (HOCs) are subject to long-term retention within the sediments. Metals are also stored in the sediment and are typically bound to iron and manganese oxyhydroxides in the oxic layer and to iron/sulphide precipitates in anaerobic regions. Sediments can also serve as contaminant sources.

This chapter will start with a short discussion of sediments and contaminant characteristics and then turn to sediment processes that influence contaminant fate and behaviour.

1.2 Sediment characteristics

Sediments represent the accumulation of soil that has eroded from the terrestrial surface. However, the sediment environment develops much differently than the

terrestrial environment because eroded soils that run off into bodies of water are subjected to a grading process associated with the energy environment. Solids suspended in the water environment may contain significant quantities of sand (particle diameters >0.06 mm), silt ($2\text{--}60\ \mu\text{m}$) and clays ($<2\ \mu\text{m}$). Much fine-grained material may remain suspended in a high energy environment but may settle and accumulate in a low energy environment. Fine-grained deposits are also typically enriched in organic matter. Many contaminants of concern are hydrophobic organics and inorganics that will preferentially associate with these fine-grained sediments and with the organic matter. Thus, many of the most seriously contaminated sediment sites are in low flow, depositional environments that accumulate these fine-grained sediments. Less contamination is typically associated with more dynamic environments in which the sediments are dominated by coarser, faster settling sands (Reible, 2014).

A fine-grained depositional sediment dominated by silts and clays tends to be strongly cohesive, which may limit its tendency to erode under higher flow conditions. A fine-grained depositional environment will also typically be enriched in organic matter relative to terrestrial soils. Surficial sediments may be considerably higher than this range with 10–20% organic carbon not being uncommon. The combination of low permeability (and therefore low exchange with the overlying water) and high organic carbon means that diagenetic processes have a strong influence on the surficial sediment characteristics. Early diagenetic processes lead to the formation of humic and fulvic acids from the degradation of natural organic matter. These are soluble and lead to substantial quantities of dissolved and colloidal organic carbon (10–50 mg/l) in the pore space of the sediments. Diagenetic processes consume a variety of electron acceptors, which dramatically influence the redox environment of the surficial sediments.

Oxygen is typically rapidly consumed by microbial processes and then less desirable electron acceptors are consumed in turn, leading to strongly reduced sediment environments just a few centimeters below the sediment-water interface (Reible, 2014). This may affect the rate of fate processes, such as biological degradation of contaminants in the sediments and the chemical state of metals influencing mobility. The more reduced conditions associated with the elimination of oxygen and the

initiation of iron and sulfate reduction typically slows microbial degradation processes and effectively eliminates degradation of hydrocarbons, which generally proceed rapidly under oxidizing conditions. Iron reduction and sulfate reduction has also been associated with the simultaneous methylation of mercury (Hg) (Compeau and Bartha, 1985; Warner et al., 2003) and carbon dioxide reduction leads to methane formation and gas ebullition. The methane then migrates toward the surface affecting sediment void fraction, strength and, through oxidation of the methane, the oxygen demand of the sediments (Chapra, 1999). Boudreau et al. (2005) describes the growth and migration of gas as a result of methanogenesis. In addition, the reduced nature of fine-grained sediments within a few centimeters of the surface typically limits the vertical extent of macrobenthic activity. The organisms that live at the sediment-water interface are largely limited to the aerobic sediments, although they might extend a portion of their bodies deeper into the sediments or encourage deeper penetration of oxic conditions through burrowing and sediment reworking activities (Reible et al., 1996).

1.3 *Contaminant characteristics*

Contaminants generally include any constituent that can accumulate in the sediments, release of which may dramatically change the biological characteristics of the overlying water. Sediment contaminants are typically strongly hydrophobic and strongly associated with sediment solids. More mobile and soluble contaminants rarely accumulate in sediments. Among the hydrophobic and/or strongly solid associated contaminants of interest are polycyclic aromatic hydrocarbons (PAHs), chlorinated aromatics (such as multiple chlorinated benzenes), polychlorinated biphenyls (PCBs), and heavy metals.

The dominant characteristic of contaminant-solid interactions is physical absorption, characterized by a sediment-water partition coefficient, k_d . The sediment-water partition coefficient is defined by:

$$k_d = \frac{W_s}{C} \quad 2.1$$

where W_s is the solid phase concentration and C is the adjacent water phase concentration. Hydrophobic organic contaminants predominantly sorb into the organic carbon fraction of sediments and thus the sediment-water partition coefficient is often defined as:

$$k_d = k_{oc}f_{oc} \quad 2.2$$

where k_{oc} is the organic carbon-based partition coefficient, a measure of the hydrophobicity of the compound, and f_{oc} is the fraction organic carbon, a single indicator of the sorption capacity of the sediment for hydrophobic organic compounds. This relationship is a good approximation for the sorption of organic contaminants when sorption is dominated by natural organic matter. Natural organic matter is dominated by amorphous carbon, also referred to as soft organic matter. In such cases, the organic carbon-based partition coefficient is related to a measure of the hydrophobicity of the compound. The organic carbon-based partition coefficient is commonly correlated with the octanol-water partition coefficient of the compounds. For example (Baker et al., 1997),

$$\text{Log}k_{oc} = 0.903\text{Log}k_{ow} + 0.094 \quad 2.3$$

Common PAHs exhibit octanol-water partition coefficients ($\text{Log}k_{ow}$) between 3.37 (naphthalene) and 6 or more (e.g., benzo[a]pyrene). Pyrene has a $\text{Log}k_{ow}$ of 5.18 and therefore Equation 2.3 suggests a $\text{Log}k_{oc}$ of 4.77.

Metals do not absorb into the organic fraction of the sediment phase. Instead, metals interact with sediments in a much more complicated manner. Metals can absorb directly onto sediment mineral surfaces, specific species can precipitate onto the solids, and metal cations can be electrostatically attracted to charged sediment surfaces (which are typically negatively charged). These metals can be released by cation exchange with other cations or by acidification of the sediment, which will offset the net

negative charge at the surface. Metal sorption can be described as an irreversibly sorbed fraction (the metal precipitates), coupled with a reversibly sorbed fraction (the exchangeable and adsorbed portion). The most important of the metal precipitates are metal sulfides that are effectively insoluble and form under strongly reducing conditions. Under the reducing conditions in most sediments, that is a few centimeters below the surface and below, these metal sulphides are quite stable. At the surface, however, oxic conditions can lead to sulphide oxidation and release of the metal ions (Hong et al., 2011a). Under static conditions, only the exchangeable and adsorbed portion can partition between the sediments and adjacent porewater. This is generally modelled with an effective partition coefficient, K_{sw} , but this is not easily modelled and changes in pH and oxygen conditions can affect the partition coefficient (Hong et al., 2011b).

1.4 Sediment and contaminant transport processes

1.4.1 Sediment erosion and deposition

Any migration of the sediment, through erosion and resuspension, have a significant impact on contaminant transport. Also, bioturbation, the sediment processing activities of benthic organisms, can also cause sediment migration.

Under high-energy conditions in a stream, significant sediment transport occurs, and individual sediment particles can be carried downstream either by bed load or suspended load transport. During this overturning and migration process, sediment particles are exposed and either scoured and suspended in the stream or reburied by other sediment particles.

Water passing over seabed sediment may reach a high enough velocity to cause the erosion of the topmost layer. In normally consolidated muddy sediment strength increases with depth and therefore, the sediment will be eroded down to a level at which point the strength in the sediment is sufficient to resist the shear. That is to say that continual erosion will only occur when the shear stress is considerably higher than the critical erosion shear strength of the mud (Dyer, 1986).

The contaminant concentration in the overlying water, assuming local equilibrium, is given by:

$$C = \frac{\rho_{ss}W_s}{1 + \rho_{ss}k_{sw}} \quad 2.5$$

ρ_{ss} is the suspended sediment density (or concentration), W_s is the concentration of contaminant on the solids and k_{sw} is the effective partition coefficient between sediment and water. At high suspended concentrations, the overlying water approaches equilibrium with the contaminated sediment bed while at low suspended solids density, the overlying water concentration is directly proportional to the suspended solids density. As shown by Equation 2.5, the concentration and exposure in the overlying water is a function of the concentration of sediment resuspended. The concentration of resuspended sediment is a function of the rate and depth of erosion. The ability to predict the rate of erosion based solely upon physical characteristics of the sediment such as grain size and density remains largely limited to cohesionless, coarse-grained particles. Site-specific measurements of sediment response to shear flows are needed to characterize erosion of cohesive, fine grained sediment.

1.4.2 Porewater diffusion and advection

In a stable sediment bed, the transport processes within the mobile phase in the pore space of the sediments become important. In particular, diffusion, dispersion and advective processes dominate.

Molecular diffusion produces a net flux F_{diff} in the x-direction from a region of higher concentration to one of lower concentration that is often described by Fick's first law:

$$F_{diff} = -D_w \frac{\partial C}{\partial x} \quad 2.6$$

where D_w is the molecular diffusion coefficient of the compound in water. Molecular diffusion in a porous medium such as sediments must be corrected for tortuosity and porosity of the diffusion pathways. Millington and Quirk (1961) suggest a combined correction factor of the porosity to the four-thirds power to account for these effects:

$$F_{diff} = -\varepsilon^{4/3} D_w \frac{\partial C}{\partial x} \quad 2.7$$

A variety of techniques are available for estimating D_w (Schwarzenbach et al., 2003; Lyman et al., 1990). Values of D_w are typically 10^5 - 10^{-6} cm²/s for sediment contaminants.

Advection can be a far more rapid mechanism of contaminant transport. The flow of water in sediments may be upward or downward depending upon local ground-water gradients or both in the case of tidal systems. The advective flux, F_{adv} , is related to the upwelling velocity times the porewater concentration:

$$F_{adv} = VC \quad 2.8$$

Because of natural heterogeneity, the flow of porewater through sediments is non-uniform, resulting in hydrodynamic dispersion. This results in spreading characterized by an effective diffusion coefficient, D_{disp} , similar to molecular diffusion although related to the flow velocity:

$$D_{disp} = \alpha V \quad 2.9$$

The value of α is related to the spatial scale of the heterogeneities in a porous medium. Because the probability of encountering larger heterogeneities increases with travel distance, the value of α is often assumed to be a function of travel distance. A reasonable estimate is 5–10% of travel distance although the sensitivity to this parameter is often not significant for the small travel distances of interest in surficial sediments.

Gas ebullition or nonaqueous phase liquid (NAPL) migration can also influence contaminant migration and retardation by sorption. This is primarily important for organic contaminants. Gas ebullition can carry volatile organic contaminants according to:

$$F_{gas} = V_{gas}H_H C \quad 2.10$$

where H is the Henry's Law constant for the compound and V_{gas} is the volume of gas per unit area exiting the sediment. This assumes that the gas is in local equilibrium with the water and neglects other mechanisms for gaseous transport due to sorption of hydrophobics at the gas-water interface of bubbles (Yuan et al., 2009), or mechanical disruption of the surface by gas (Johnson et al., 2002). Values of V_{gas} typically range from 0 to the order of 1 l/m² per days. The Henry's Law constant for nonpolar volatile organics can generally be estimated by the relationship:

$$H_H = \frac{P_v M_w}{RTS} \quad 2.11$$

where P_v and M_w are the compound vapor pressure and molecular weight, respectively, R is the ideal gas constant, T is the absolute temperature in Kelvin, and S is the solubility of the compound in mass per volume. Due to the relatively small value of H for most hydrophobic compounds of interest, the gas-induced flux is relatively small. A potentially more important concern is the movement of NAPL with gas if the gas moves through a NAPL-contaminated layer.

If a continuing source of NAPL is present, source control efforts are an early and important remedy response. In the absence of gas moving through a NAPL-contaminated layer, however, a NAPL layer is often relatively immobile. Often, the sediment NAPL is often heavily weathered and viscous and the mobile fractions have long since left the sediments. The capacity of the immobile NAPL phase for the organic can also aid in retardation of any chemical migration. Erten et al. (2011) provide a consolidation testing method to evaluate NAPL mobility and expression in soft sediments. This

method could also be used to assess gas release and NAPL release with the gas although the gas release by this test is likely more rapid than in the sediment environment.

1.4.3 Bioturbation

Bioturbation is the normal life cycle activity of benthic organisms that lead to mixing of sediment and porewater in the near surface layer of sediments. These activities influence the fate and behaviour of contaminants and are often the dominant mixing process in stable sediment environments. This is due to the fact that bioturbation typically involves reworking of the surface layer of sediments through particle mixing and is thus not subject to retardation of processes such as diffusion and advection that limit by retardation in the porewater.

The organisms responsible for the most sediment and contaminant reworking are the macrobenthos. Included in this category are deposit feeders that ingest and process sediment for food and are often referred to as conveyor belt feeders in that they ingest sediment at depth (typically 5–10 centimeters [cm] into the sediment) and defecate at the surface building fecal mounds. Burrowing filter feeders similarly move sediment but for the primary purpose of building a protective burrow from which they can actively pump water that they filter for food. The final category of organisms are surface feeders that tend to forage at the surface consuming organic matter or sit on the surface filtering water and have a relatively limited impact on the sediment. *Urechis caupo* is an example of a marine burrowing filter feeder and has been observed to pump an average of 266 ml/min of water through their burrows (Osovitz and Julian, 2002).

The high density of the organisms and their effectively random behaviour suggest that it might be appropriate to model their effect on contaminants as an effective diffusion process in the biologically active zone. The contaminant flux associated with bioturbation in the actively mixed zone is given by:

$$F_{bio} = -D_{bio} \frac{\partial[\varepsilon C + \rho_s(1 - \varepsilon)W_s]}{\partial z} = -D_{bio} \frac{\partial R_f C}{\partial z} \quad 2.12$$

W_s is the concentration of contaminant on the solids in the z direction, ρ_s is sediment density and ϵ is the porosity. The arithmetic means and standard deviation for the bio-diffusion coefficients are 1.23×10^{-7} and 4.31×10^{-7} cm^2/s for freshwater and 3.95×10^{-6} and 5.20×10^{-5} cm^2/s for estuarine systems, respectively.

1.5 *Risk reduction processes*

1.5.1 *Sorption/Immobilization*

The sequestration of contaminants onto solid-phase particles within aquatic sediments is an important attenuation mechanism which removes toxic chemical species from the bioavailable aqueous phase.

Allen (1994) reviewed how metal toxicity to aquatic organisms is proportional to the concentration of free metal ions, emphasizing the significance of sorption/immobilization processes. Metal contaminants exhibit different affinities for each solid-phase sequestering fraction within sediments (Tab. 1.1). In oxic sediments regions, metal sequestration is generally dominated by Fe and Mn oxides and organic matter; whereas dominant sequestration processes in anoxic sediment regions are the formation of metal sulfides and partitioning onto organic matter (Tessier et al., 1994). The sequestration of metals by microbial activity is also possible and has been reviewed in the literature (Gadd, 2004).

The predominant sorbent for HOCs in aquatic sediments is organic matter (Luthy et al., 1997), which includes detritus, lignin, and humic substances (Carlton et al., 1990). Kile et al. (1995) demonstrated a positive relationship between HOC soil-water distribution coefficients for soils and sediments and organic matter content. The ability of organic carbon to indefinitely sequester HOCs has stimulated the idea of organic sorbent addition to sediments to reduce contaminant bioavailability (Zimmerman et al., 2004; Tang et al., 2007). The more suitable models of HOC sorption are the linear and Freundlich isotherms. Substantial time periods may be required to reach equilibrium conditions, however (Pignatello and Xing, 1996), and slow sorption kinetics within sediments can lead to nonideal behaviour and requires more sophisticated process

modelling. Physicochemical nonequilibrium models incorporate rate-limited conditions between the contaminants and sorbents (Brusseau and Rao, 1989), demonstrated to be more representative of natural systems than assumed equilibrium conditions (Weber et al., 1996; Piatt and Brusseau, 1998). Causes for nonequilibrium sorption have been discussed and reviewed extensively (Pignatello and Xing, 1996; Brusseau et al., 1991) and include retarded intraparticle diffusion, intra organic matter diffusion, and slow chemical kinetics.

A contaminant sinks and source, and desorption represents a long-term source (McGroddy and Gschwend, Schneider et al., 2007; You et al., 2006) and a route of contaminant exposure to benthic organisms (Landrum et al., 2007; Shor et al., 2004), despite slow desorption rates (Ghosh et al., 2000 and 2001) and observed hysteresis (Braida et al., 2003).

CONTAMINANT	SEQUESTERING AGENT IN SEDIMENT
Cu	Sulphides Organic matter
Pb	Fe/Mn oxides Sulphides
Cd	Fe/Mn oxides Sulphides Organic matter
Zn	Sulphides
Cr	Fe/Mn oxides
Ni	Iron Sulphides Organic matter
PCBs	Mineral solids Organic matter
PAHs	Organic carbon

Tab. 1.1 - Contaminant sequestering agents found in aquatic sediments (Eggleton and Thomas, 2004).

1.5.2 Transformations

Sediment contaminants can be transformed both abiotically and microbially within sediment beds with some pathways leading to non-toxic end products. Contaminant transformations will be defined here as a change in chemical composition of the contaminant in order to make a distinction from trace metals changing redox state.

Abiotic Transformations

Contaminant transformations at mineral surfaces occur are tied to specific redox conditions. The reduction of nitroaromatic contaminants by iron minerals has been demonstrated and subsequently studied extensively (Elsner et al., 2004; Zwank et al., 2005). The reduction of chlorinated organics has also been documented by zero-valent metals such as zinc (Arnold and Roberts, 1998) and iron (Arnold and Roberts, 2000). These reductions demonstrate how numerous iron minerals, found both in oxic (goethite) and anoxic (pyrite) environments, can abiotically mediate dehalogenation and nitroaryl reduction, two important and environmentally-relevant mechanisms of contaminant transformations.

Mercury methylation has been observed during sulphate reduction (Benoit et al., 2003), which is a detrimental transformation due to the toxicity of methylmercury.

PCBs and PAHs, two classes of HOCs which are traditional sediment contaminants, are observed to be generally recalcitrant to abiotic reactions.

Microbially-Mediated Transformations

Aquatic sediments tend to have active microbial communities due to their ample sources of organic matter, carbon, and electron donor. Bacterial abundance and activity generally decrease with sediment depth due to the prevalence of more recalcitrant carbon sources below the surface (Van Cappellen et al., 1996).

The high levels of bacterial abundance and activity in the aerobic layer promote oxidative contaminant bio-transformations in this region. Hydrophobic organic contaminant classes vulnerable to aerobic biotransformation, and documented within sediments, include petroleum hydrocarbons, PAHs, PCBs, and certain chloroethenes. PAHs

are not degraded as quickly as monoaromatic species but are still susceptible to ring fission via dioxygenase attack (Atlas and Unterman, 1999), carried out by multiple microbial populations (Samanta et al., 2002). Certain PCB congeners are degraded aerobically (Bedard et al., 1987; Maltseva et al., 1999) following initial, anaerobic biotransformations, which increase their aerobic biodegradability and metabolism. The anaerobic, reductive dechlorination of PCBs has been reviewed (Bedard and Quensen, 1995) and recent evidence links PCB dechlorination with bacteria belonging the *Dehalococcoides* group (Bedard et al., 2007). *Dehalococcoides* are also capable of complete reductive dechlorination of chlorinated solvents (e.g., PCE and TCE), which may be introduced into the sedimentary environment via contaminated groundwater plumes. PCE is sequentially dechlorinated by multiple bacterial strains under anaerobic conditions to TCE and dichloroethenes (DCEs), but only *Dehalococcoides* reduce DCEs to vinyl chloride (VC), and finally nontoxic ethene (Cupples et al., 2003). During this process, dissolved-phase chloroethenes serve as electron acceptors for *Dehalococcoides* while the source of electrons is hydrogen (Yang and McCarty, 1998), supplied from the oxidation of organic substrates by fermenting microbial communities (Carr et al., 1998; Fannel et al., 1997).

CHAPTER 2. REMEDIATION TECHNOLOGIES

2.1 Introduction

The management and remediation of contaminated marine sediments is inherently more complex than managing contaminated soil and groundwater sites. Because of the multiple uses and demands placed upon surface waters, it is often difficult to identify the primary goals for contaminated sediments. The primary goal most likely would be elimination of the risks to human health and the environment. However, contaminated sediment remediation could involve societal, cultural, and economic impacts commensurate with human health and ecological risks.

Hence, the choice of approach(es) is generally broad and complex, frequently conflicting, and often controversial. As a result, management and remediation of contaminated sediments is a major issue facing environment policy-makers, scientists, and engineers today.

Sediment remediation techniques are commonly classified as *in situ* (i.e. treatments operating where the contamination is present with no sediment dredging) and *ex situ* (i.e. treatments including sediment dredging or resuspension phenomena to some extent). Nevertheless, dredging still remains an important issue; like for hotspots, dredging activities can heavily remobilize sediment like as the associated pollution via washing out events (Arizzi Novelli et al., 2006; Libralato et al., 2008; Krull et al., 2014; Chakraborty et al., 2014). From 26 dredging projects carried out by the National Research Council (NRC, National Research Council 2007), systematic difficulties were

observed in achieving target clean-up thresholds in addition to the impairment of sediment-associated benthic ecosystem.

The development of cost-effective sediment management strategy requires a multi-approach assessment including in situ treatment alternatives, unless dredging is compulsory to reach a desired bathymetric level. Since they allow sediment remediation avoiding excavation and transport, remediation footprint and cost savings could be significantly optimized. The main disadvantages are related to long-lasting procedures (months or years), uncertainty about the treatment uniformity due to the variability of sediment and aquifer characteristics, and the overall efficiency of the process is more difficult to verify.

According to EPA's "Contaminated Sediment Remediation Guidance for Hazardous Waste Sites" (U.S.EPA, 2005), the current mature and available management strategies are monitored natural recovery (MNR), in-situ management through active capping or active amendment treatment and dredging followed by stabilization/solidification treatments. At some sites, one of the three remediation approaches may serve as the primary approach for remediation, while at other sites, they may be combined together to enhance the remediation performance. Descriptions of each sediment remediation method are provided in these chapter, with emphasis placed on in situ capping and ex situ stabilization/solidification.

2.2 In situ technologies

2.2.1 Overview on in situ technologies

The main advantage of in-situ treatment is that it allows soil and sediment to be treated without being excavated and transported, resulting in potentially significant cost savings. However, in-situ treatment generally requires longer time period, and there is less certainty about the uniformity of treatment because of the variability in soil and aquifer characteristics and because the efficiency of the process is more difficult to verify. The in-situ treatment methods presented involve applying chemical, biological or physical processes to the subsurface to remove or immobilize contaminants without

removing the bulk soil/sediment. Additionally, several of these methods have references to soil and to a much more limit extent to sediment.

Treatment methods can be categorized into three major groups: a) physical/chemical treatment (i.e. in situ stabilisation/solidification, chemical oxidation, electrokinetic separation, soil flushing and sediment capping); b) biological treatment (i.e. phytoremediation, monitored natural attenuation, enhanced natural attenuation); c) thermal treatment (i.e. electrical resistance heating, steam injection and extraction, conductive heating, radio-frequency heating, vitrification).

Physical/chemical treatment uses the physical properties of the contaminants or the contaminated medium to destroy (i.e., chemically convert), separate, or contain the contamination. Physical/chemical treatment is typically cost effective and can be completed in short time periods (in comparison with biological treatment). Equipment is readily available and is not engineering or energy-intensive.

Biological treatment involves the use of microorganisms or vegetation (phytoremediation). Many naturally occurring microorganisms (typically, bacteria and fungi) can transform hazardous chemicals to substances that may be less hazardous than the original compounds. Microorganisms also have been used to alter the valence of some hazardous metals, thereby making them less hazardous and/or less mobile. Several plant species have the ability to bioaccumulate heavy metals found in the soil, and some tree species can sequester, destroy (usually in cooperation with degradative microorganisms in the root zone), and/or evaporate/transpire various organic compounds.

Thermal treatment technologies rely on the addition of heat to the soil to increase the removal efficiency of volatile and semi-volatile contaminants. Vapour extraction is an integral part of these remediation systems to ensure the removal and treatment of mobilized contaminants. In case focusing at areas below groundwater table, the heating cost for all thermal heating technologies rapidly increases and may result in low competitiveness. This is hypothetically one of several reasons behind why it is very sparsely reported on using this group of methods in situ in sediments (besides that part of sediment after electrical treatment usually needs to be dredged and potential

issues using electrical currents under groundwater table only where the remediation shall take place). In situ vitrification is unique among the thermal technologies in that the temperatures used will vitrify soil. The stable glass that is formed by vitrification will immobilize any non-volatile contaminants that are present, including metals and radioactive materials.

2.2.2 *In situ amendment: active mixing and active capping*

Two main approaches could be used to remediate contaminated sediment: (i) active mixing and (ii) thin capping. Active mixing consists of mixing contaminated sediments with natural substrates or other inert materials. In both cases, the bioactive surface layer of sediment is able to transfer contaminants from sediment to strongly binding sorbent particles, reducing their bioavailability to benthic organisms and contaminant flux into the water column and thus the potential general accumulation in the aquatic food web (Ghosh et al. 2011). Thin capping consists of one or more layers of amendment (e.g., sand and NOMs) actively reducing the overall cap thickness required, for example when compared to conventional sand cap (Wessels Perelo, 2010).

In the last two decades, several authors evaluated in situ amendment introducing various sorbents such as activated carbon (AC), organoclay, apatite, biochar, coke, zeolites, and zerovalent iron (ZVI) into contaminated sediments (USEPA, 2013a). Amendments tend to modify sediment geochemistry increasing contaminant binding and stability in order to reduce its risk to human health and the environment. Among all, AC, organoclay, and apatite were identified as particularly promising sorptive amendments for in situ sediment remediation (USEPA, 2013b). But several data about their potential side effects are still missing. Except for AC and ZVI, (eco-)toxicity data are scarce or still unavailable.

As shown in Tab. 2.1 and 2.2, most studies are referred to AC administration. Several laboratory experiments and recent field studies demonstrated that AC showed significant reductions in chemical concentration and biological availability of polychlorinated biphenyls (PCBs) (Zimmerman et al., 2004; Werner et al., 2005; Cho et al., 2009; Beckingham and Ghosh, 2011; Cho et al., 2012), polyaromatic hydrocarbons (PAHs) (Hale et al., 2010; Cornelissen et al., 2011; Hale et al., 2012; Meynet et al.,

2012), and dichlorodiphenyltrichloroethane (DDT) (Tomaszewski et al., 2007) by active mixing and thin capping. Several laboratory studies in column reactors with amendment show the potential for significant reductions in equilibrium pore-water concentration, bioaccumulation in benthic organisms, and contaminant flux into water for polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs). For example, Zimmerman et al. (2004) conducted a 6-month continuously mixed, laboratory study wherein the aqueous PCB concentration was reduced by 92% after contacting 3.4 wt % AC with sediment collected from Hunters Point Shipyard, San Francisco Bay. A laboratory study by Choi et al. (2013) with petroleum-impacted sediment demonstrated the effectiveness of AC amendment to sequester PAHs. Slurry phase experiments with an AC dose of 5 wt % for 1, 2, 8, and 12 months showed up to 99.5% reduction in PAH uptake in polyethylene (PE) samplers. Considering a series of differentially polluted sediment samples, Hale et al. (2010) and Hale and Werner (2010) highlighted that 1–5% AC can reduce the pore water concentration of PCBs, PAHs, DDT, dioxins, and furans from 70 up to 99%. Organoclay effectively removed soluble organics and non-aqueous phase liquids (NAPLs) such as oils, chlorinated solvents, and PAHs (Alther, 2002a, 2002b). Apatite facilitated the immobilization of metals including Cu, Pb, and Zn (Knox et al. 2008). Laboratory results demonstrated that the effectiveness of sorbents in lowering contaminant bioavailability increased with decreasing amendment particle size, growing dose, greater mixing, and contact time (Zimmerman et al. 2005; Ghosh et al. 2011), but it could vary for various amendments with similar surface areas (Tomaszewski et al., 2007).

Considering the Hunters Point Shipyard case study (Tab. 2.1), Choi et al. (2016) focused on the importance of developing and applying decision-making frameworks for in situ sediment AC remediation, including a modelling approach supporting long-term prediction and engineering design. The modelling framework compared various design alternatives for treatment optimization and estimation of long-term effectiveness over 10–20 years under slow mass transfer condition in order to identify the best efficient and cost-effective solution for HOC-contaminated sediment treatment.

Amendment	Sampling site	Experimental conditions	Main findings	Reference
AC	South Basin at Hunters Point Naval Shipyard (San Francisco, USA)	PCB contaminated sediment was contacted with 3.4% (dry weight) AC on a roller for 1 month	87% reductions in aqueous equilibrium PCB concentrations after 1 month and over 90% after 6 months	Zimmerman et al., 2004
AC	South Basin at Hunters Point Naval Shipyard (San Francisco, USA)	PCB contaminated sediment was contacted with 3.4% (dry weight) AC on a roller for 1 month	After 28 days, bioaccumulation in polychaetes is reduced by 82% following 1-m contact of sediment with AC and by 87% following 6-month contact of sediment with AC. Reductions in aqueous PCB concentrations in equilibrium with the sediment were similar to reductions in PCB bioaccumulation	Millward et al., 2005
AC	South Basin at Hunters Point Naval Shipyard (San Francisco, USA)	PCB contaminated sediment was contacted with 3.4% (dry weight) AC on a roller for 1 month	84% reductions in the bioaccumulation of PCBs by the clam <i>Macoma balthica</i>	McLeod et al., 2007
TOG® NDS	Hunters Point Shipyard (San Francisco, USA)	A large-scale device to mix 500 kg of AC into a 34.4-m ² plot to a depth of 1 ft	34% less PCB uptake into semi-permeable membrane devices and 24% less PCB bioaccumulation in <i>Megophrys nasuta</i> after 1 month. Seven months after the AC treatment occurred, the differences further increased up to 62% less in SPMD uptake and 53% less in clam bioaccumulation	Cho et al., 2007

Tab. 2.1 - Summary of active mixing findings with amendments.

Amendment	Sampling site	Experimental conditions	Main findings	Reference
TOG® Filtrisorb® 400 Aquacarb® 830 Aquacarb RS	Lauritzen Channel Point Shipyard (San Francisco, USA)	Large glass bottles were filled with surface sediment followed by the addition of 0.8, 1.6, and 3.2 wt % AC on a dry mass basis	Amendment of field-collected residual sediments with AC resulted in large reductions (>80%) in aqueous equilibrium concentration	Tomaszewski et al. (2007)
AC	Hunters Point Shipyard (San Francisco, USA)	The study design comprised four test plots having a surface area of 34.4 m² each	Successful incorporation of AC into sediment to a nominal 30-cm depth. About 50% reduction in PCB uptake in AC-treated sediment and in pore water even after 13 months post-treatment.	Cho et al. (2009)
AC	Hunters Point Shipyard (San Francisco, USA)	Non-amended reference sediment, sediment with fresh AC, and sediment containing field-aged AC were investigated. The clean AC additions were at levels of 0, 2, 4, and 8% (dw)	Sediment with 2% fresh GAC reduced HOC concentration in pore water by 87–98% compared to non-amended sediment at low spiked PCB concentrations.	Oen et al. (2012)
AC	Hunters Point Shipyard (San Francisco, USA)	Sediment column studies were conducted using sediments with variations in initial AC mixing regimes, AC distribution, AC particle size, pore water movement, and AC-sediment contact time	After 2 years of stagnant contact, the contaminant uptake in polyethylene passive samplers embedded in the columns was reduced by 95–99% for PAHs and 93–97% for PCBs with 5 and 4 wt% AC	Choi et al. (2014)

Tab. 2.1 - (continued).

In order to predict or evaluate the effect of remediation efforts, involving capping of subaqueous contaminated sediments, it is crucial to assess the transport of contaminants from the capped sediment and how it will be affected by the cap (Palermo et al., 1998). Transport of contaminants through the cap can be caused by mechanisms like molecular diffusion, advection of pore water, and bioturbation. Advection of pore water from capped sediment can be driven by two mechanisms: (1) submarine groundwater discharge, and (2) consolidation of contaminated sediment. Advection due to groundwater discharge and tidal pumping is not uncommon and has been reviewed elsewhere (Burnet et al., 2003; McCoy et al., 2009). This mechanism is important when hydrogeological conditions cause release of groundwater through the seabed. However, in many fine-grained contaminated sediments, low permeability suggest that this mechanism will be of limited importance.

A few earlier studies have addressed contaminant transport from consolidating sediments. Moo-Young et al. (2002) studied the effect of consolidation on the migration of pore water and tetrachloro dibenzo-p-dioxin (TCDD) in the cap. They found that pore water from consolidation in a geotechnical centrifuge carried small but significant amounts of TCDD through the cap. Alshawabkeh et al. (2005) developed a model for contaminant mass flux in capped sediments under consolidation. Eek et al. (2007) developed a method to evaluate efficiency of different materials for capping of soft and silty clay sediments collected from Bjørvika (Oslo Harbour) contaminated by heavy metals and organic contaminants. In particular, the efficiency of two different capping material (i.e. crushed limestone and crushed gneiss) and the pore water chemistry during consolidation of capped contaminated material was studied with a modified consolidation cell. The design was based on a modification of the oedometer test, commonly used in geotechnical testing (ASTM D2435). A piston was placed on top of the sample and was loaded with weights in four steps to cover a vertical stress range from 0.7 kPa (weight of piston alone) to 5.0 kPa (the vertical stress of 0.6 m thick layer of capping materials submerged in water). During sediment consolidation, pore water was drained from the surface of the cap and collected in a glass bottle attached to the consolidation cell and inside the N₂-atmosphere (Fig. 2.1a); concentrations of heavy

metals (i.e. Ca, Cd, Co, Cu, Fe, Mn, Ni, P, Pb, and Zn) in the collected pore water samples were determined. The capping of sediments with crushed gneiss increased the release of Ca, Mn, Co, Ni, Cd, and Cu, resulting in negative capping efficiency. Cu and Co were also leaching out from the limestone cap, resulting in negative capping efficiency for these metals. The study shows that the efficiency of capping materials varies significantly and that leaching from natural and uncontaminated materials under certain conditions exceeds leaching from anoxic but heavily contaminated sediments. Exposure to seawater, with high ionic strength and high content of divalent ions, can release a considerable amount of metals from the cap material into solution. For this reason, testing of the leaching properties of a proposed capping material should be an important part of the design work of remediation involving capping of contaminated sediments. Increased leaching of metals from capped sediments has also been reported earlier by Liu et al. (2001). The experimentation was conducted with 17-cm-diameter polycarbonate columns at room temperature to simulate metal transport through sediment and sand capping in the presence and absence of submarine groundwater discharge. However, they presented no data to determine whether this was a direct release from the cap material or if capping increased metal mobility in the sediment. Lenhart et al. (2009) studied the influence of consolidation rate on contaminants migration using a bench-scale consolidation apparatus (Fig. 2.1b) and sediments contaminated with PCBs that were previously dredged from the Grand Calumet River (Chicago). In this study, the influence of capping on contaminant release was studied using three capping materials: quartz sand, activated carbon and organoclay. All of the capping materials produced a decrease in PCB release during consolidation primarily by hindering particle release. The carbon-based materials (organoclay, RCM with organoclay and activated carbon) outperformed the sand. This likely reflects the existence of more attractive particle-particle interactions between the organoclay or activated carbon and the organic content of the sediment. In both studies the loading schedule impacted particle release, with particle release increasing as the consolidation rate increased due to larger load application.

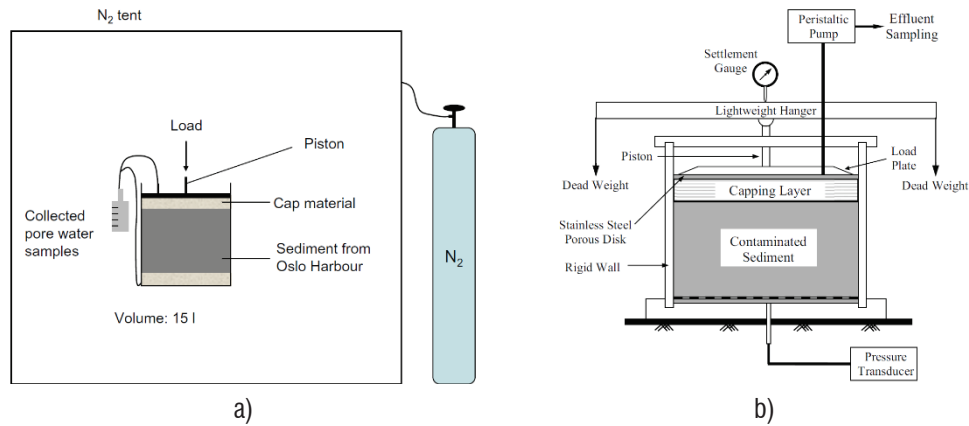


Fig. 2.1 - Schematic diagrams of the consolidation test apparatus (Eek et al. 2007; Lenhart et al., 2009; Lee and Fox, 2009).

Moreover, Lee and Fox (2009) and Lee et al. (2009) conducted consolidation tests to investigate the effect of consolidation on solute transport. They concluded that consolidation can make the solute transport faster. In these tests, they used a miscible tracer to detect the pore fluid mobilization. Contaminants may exist in the pore spaces at different saturation ratios and they may be miscible or immiscible with the pore water. Variation in the pore fluid may influence the physicochemical structure of the soil and affects its consolidation and strength properties. The influence of pore fluid on the characteristics of soils was investigated in several studies. Acar and Olivieri (1989) conducted hydraulic conductivity tests on compacted kaolinite specimens. In this study, it was observed that when organic fluids were permeated through the specimen, the hydraulic conductivity of soils changed. Anandarajah and Zhao (2000) investigated the effect of different pore fluids on the strength of kaolinite. Olson and Mesri (1970) conducted one dimensional consolidation tests on kaolinite slurries as well as illite and smectite slurries. The specimens included one-phase pore fluids, which were water, carbon tetrachloride, and ethyl alcohol. The results showed that the consolidation behavior of kaolinite was governed mainly by the mechanical factors rather than physicochemical effects. The mechanical factors were defined as the strength, flexibility, and surface friction of the soil particles. In addition, the compressibility of kaolinite with

carbon tetrachloride and ethyl alcohol was different than the compressibility of water saturated samples.

Consolidation testing of NAPL contaminated sediments is challenging since they usually are fine grained low strength media with very high water contents. Steward (2007) introduced a new method for specimen preparation of undisturbed NAPL contaminated sediments and conducted consolidation tests using a triaxial setup (initial NAPL saturation of the test samples changed between 0 %–38 %). Moretti (2008) conducted similar tests on NAPL contaminated sediments. The results indicated that consolidation may mobilize the NAPL in sediments. Steward (2007) and Moretti (2008) worked on field samples which varied significantly in terms of the soil type and pore fluid constituents. This heterogeneity made it difficult to derive general conclusions on the consolidation behaviour. Erten et al. (2011, 2012) developed a testing system to evaluate the consolidation potential of contaminated sediments at various oil saturation ratios. Several modifications were made to the standard triaxial setup, specimen preparation and testing procedures so that the testing worked efficiently under low effective stresses and the expelled fluid could be collected for further testing. Six consolidation tests were conducted on a model soft sediment (kaolinite) at different oil saturation ratios (0%-100%). When the NAPL content was higher, generally the soil was stiffer. The oil-wetted and water wetted specimens showed similar consolidation behaviour. The results of tests showed that approximately 0.1 g of NAPL per 1 g of soil solids is unlikely to be mobilized by consolidation. Design of a capping system should be done only for the amount of the NAPL expected to be expelled. This will result in a thinner cap, and lesser amount of work will be required to place the cap material.

Ma et al. (2010) conducted a series of experiments on lagoon and surge pond sediments from a site in south Louisiana contaminated with varying degrees of NAPL to predict the ability to cap the sediments without sediment failure and with containment of the NAPL. 100 mm and 150 mm diameter columns were used to allow the testing on intact core sediments. The results indicated that placement of a cap would result in intermixing in cap sediment interface, and penetration of NAPL and dissolved contaminants into the cap layer due to consolidation. Column diameter did not cause a

significant difference in consolidation rates despite the varying proportion of wall area to column cross-sectional area. Sediments with higher NAPL content (up to 30% NAPL) exhibited a greater degree of intermixing of sediment and cap materials and greater penetration of contaminants. High NAPL content sediments were also more likely to be resuspended by the act of capping leading to contamination of the cap layer. The study demonstrated that traditional sand capping technology is feasible to cap NAPL contaminated sediment but identified the nature and extent of problems to be expected when substantial NAPL is present. Further laboratory column experiments were performed by Gidley et al. (2012) using contaminated sediments and capping materials from a creosote contaminated USEPA Superfund site. Experiments were conducted in 5 cm diameter glass columns with 6 equally spaced 1.5 cm diameter Teflon sampling ports (15 cm apart). Column experiments with a peat amendment delayed PAH breakthrough. The most dramatic result was observed for caps amended with activated carbon at a dose of 2% by dry weight. PAH concentrations in the pore water of the activated carbon amended caps were 3–4 orders of magnitude lower ($0.04 \pm 0.02 \mu\text{g/L}$ for pyrene) than concentrations in the pore water of the source sediments ($26.2 \pm 5.6 \mu\text{g/L}$ for pyrene) even after several hundred pore volumes of flow. Enhancing the sorption capacity of caps with activated carbon amendment even at a lower dose of 0.2% demonstrated a significant impact on contaminant retardation suggesting consideration of active capping for field sites prone to groundwater upwelling or where thin caps are desired to minimize change in bathymetry and impacts to aquatic habitats.

As shown in Tab. 2.3, some patented commercial products are available yet and some of them were applied at full-scale remediation projects like for capping (Tab. 2.2), but every technological approach must be considered on a case-by-case basis. In fact, organoclay® MRM (Tab. 2.3) can enhance the production of methyl mercury in presence of sulphate-reducing bacteria. Short-, medium-, and long-term monitoring surveys should be carried out after remediation activities to verify the amendment stability in sediment within real exposure scenarios

Amendment	Sampling site	Experimental conditions	Main findings	Reference
AC	Trondheim harbour (Norway)	Five experimental were established: no capping; site capped with AC; site capped with AC mixed with bentonite clay; site capped with AC and covered by 5 mm of sand; and cap with sand (5 mm)	Compared to reference field, AC capping reduced fluxes by a factor of 2–10. AC + clay gave the highest AC recoveries (60 vs 30% for AC only and AC + sand) and strongest reductions in sediment-to-water PAH fluxes and pore water concentrations	Cornelissen et al., 2011
AC	Grenlands fjords (Norway)	One very large field was established at 100-m water depth. Target dimensions for cap thickness were 5 cm (limestone and clay only) and 2.5 cm (clay + AC), with an AC amendment of 2 kg/m ² on the clay + AC fields	Sediment-to-water PCDD/F fluxes measured by in situ diffusion chambers were significantly lower at the capped fields than at reference fields in the same fjord, reductions being largest for the limestone (50–90%) followed by clay (50–70%) and the AC + clay (60%)	Cornelissen et al., 2012
AC	Wyckoff/Eagle Harbour (WA, USA)	Laboratory column experiments were performed using contaminated sediments and capping materials (sand + 2% GAC, sand + peat and sand only)	PAH concentrations in the pore water of the AC-amended caps were 3–4 orders of magnitude lower (0.04 ± 0.02 µg/L for pyrene) than concentrations in the pore water of the source sediments (26.2 ± 5.6 µg/L for pyrene) even after several hundred pore volumes of flow.	Gidley et al., 2012

Tab. 2.2 - Summary of thin-layer capping findings.

Amendment	Sampling site	Experimental conditions	Main findings	Reference
AC	Frier fjord (Norway)	The influence of cap thickness (0.5–5 cm) and different cap materials (passive material: coarse or fine limestone or a marine clay; active material: AC or kraft lignin) was tested using a boxcosm. Six plots (5.5 × 5.5 m) were established to determine whether the contaminated sediments can be remediated with thin layers (less than 0.6 cm) of sand amended with activated carbon, without adverse impacts to existing marine habitat.	AC was more efficient than lignin, and a ~90% reduction of fluxes and bioaccumulation was achieved with 3-cm caps with 3.3% AC	Josefsson et al., 2012
AC (SedMite)	Custom Plywood (Anacortes, WA, USA)		Evaluate AC/cap effects in sensitive seelgrass environments	WDOE, 2012
AC (AquaGate)	Puget Sound Naval Shipyard, (Bremerton, WA, USA)	The contaminated area (58 × 35 m) was amended with PAC using the AquaGate™ to improve delivery and decrease the bioavailability of contaminants.	The project showed and validated the placement, stability and performance of AC amendments for treating contaminated sediments in an area with elevated PCB and Hg contamination	Johnston et al., 2013

Tab. 2.2 - (continued).

Amendment	Sampling site	Experimental conditions	Main findings	Reference
AC (BioBlok)	Kirkebukten Bergen Harbor (Norway)	Two types of caps tested in situ (both of which incorporated BioBlok capping products amended with PAC)	It appears that the capping has been effective with respect to reducing leaching of PCB from the sediments. A ~90% reduction of fluxes was achieved.	Hjartland et al., 2013
AC (BioBlok)	Sandefjord Harbour (Norway)	Pilot test has been used to showcase the effectiveness and costs for implementing of a thin-layer capping using conventional materials as well as innovative materials and engineered products.	The study was focused on key elements related to controlled material placement as well as at evaluating short- and long-term remedy effectiveness (reductions in contaminant bioavailability, benthic recolonization, erosion protection, etc.).	Lundh et al., 2013
AC	Trondheim harbour (Norway)	Three types of thin-layer caps with AC were tested in situ, using AC + clay, AC only, or AC + sand. One year after capping, intact sediment cores were collected from the amended plots for ex situ surveys of the capping efficiency in reducing the PAHs and PCBs aqueous concentrations.	AC + clay reduced bioaccumulation of PAH and PCB congeners between 40 and 87% in the worms and between 67 and 97% in the clams. Sediment capped with AC only also led to reduced bioaccumulation of PCBs, while AC + sand showed no reduction in bioaccumulation. Thus, the best thin-layer capping method in this study was AC mixed with clay	Samuelsson et al., 2015

Tab. 2.2 - (continued).

Marketed products	Description	Target	Reference
Organoclay®	A granular, permeable, high-capacity adsorptive material	NAPLs, dissolved weight/low solubility organics mercury and metals	www.cetco.com
Reactive Core Mat®	Active materials encapsulated between carrier textiles, which are adhered together to provide product integrity	According to the active material (e.g. Metals, and Organics)	www.cetco.com
Econo-Hp RCM™	A permeable composite of geotextiles and a non-swelling granular clay compound	Oil and similar organic	www.cetco.com
AquaGate™	Amendments in a thin coating around an inert core	According to the active material (e.g. Metals, and Organics)	www.aquablok.com
AquaBlok™	Low-permeability isolation cap over contaminated sediments in a layer thickness of 6-in. or less	According to the active material (e.g. Metals, and Organics)	www.aquablok.com
SediMite™	An agglomerate composed of a treatment agent (typically AC), a weighting agent (to enable it to sink and resist resuspension), and an inert binder.	PCBs, Hg, dioxins, furans, PAHs, DDT, and other hydrophobic chemicals	www.sedimite.com
TOG®	A virgin GAC	Organics	www.calgoncarbon.com
Filtrisorb® 400	A virgin GAC	Organics	www.calgoncarbon.com
Aquacarb®	A virgin GAC	Organics	www.siemens.com
Aquacarb® 830	A virgin GAC	Organics	www.siemens.com

Tab. 2.3 - Summary of marketed sorbent product.

Reactive materials

The use of chemically reactive materials allows sequestering and/or degrading sediment contaminants, reducing their mobility, toxicity, and bioavailability, performing both containment and treatment to contaminated sediment. The comparison between passive capping and active capping is listed in Tab. 2.4.

Aspect	Capping	
	Passive	Active
Materials	Neutral materials such as sand, silt, clay, crushed rock debris, clean dredged sediments	Active materials such as activated carbon, organoclay, zero-valent iron, zeolite, apatite, biopolymer,
Thickness	About 30–100 cm	About 10–30 cm
Functions	Containment: 1. Physical isolation of contaminated sediment 2. Stabilization of contaminants in sediment 3. Reduction of the flux of dissolved contaminants into the overlying water	Containment and treatment: 1. Physical and chemical isolation of contaminated sediment 2. Sequestration and degradation of contaminants in sediment 3. Reduction of the flux of dissolved contaminants into the overlying water under more complicated conditions
Development stage	Practical stage	Initial stage
Field testing	Substantial	Limited

Tab. 2.4 - Comparison between passive and active materials (Zhang et al., 2017).

A variety of materials are proven to achieve the goals of cap; however, few demonstrated options exist for enhancing contaminant adsorption and degradation processes. Several laboratory experiments and recent field studies demonstrated that a centimeter-thick layer of AC can effectively decrease contaminant flux from sediment to the overlying water (Josefsson et al., 2012; Murphy et al., 2006). Other reactive amendments, such as calcite, zeolite, apatite, organoclay, and biopolymers, can also sequester a variety of contaminants and control their mobility to the water column (Knox et al., 2012; Lin et al., 2011).

Tab. 2.5 summarizes several reactive amendments and the target contaminant classes treated. Typical organic contaminants targeted include dioxins/furans, PAHs, PCBs, and pesticides. Typical inorganic contaminants targeted include metals, such as arsenic, cadmium, chromium, copper, lead, mercury, nickel, and zinc. Specific cap materials are selected based on the remedial objectives, the characteristics of the site, the nature of the contaminated sediments, and the type(s) of contamination present. Reactive capping amendments generally fall into two primary categories: amendments that sequester contaminants (i.e., physically bind and reduce the mobility or availability of contaminants); and amendments that degrade contaminants (i.e., directly alter contaminants into less toxic forms).

Function	Amendment	Contaminant targeted
Sequestering	Activated Carbon (AC)	organics (dioxins/furans, PAHs, PCBs, pesticides)
	Apatite	metals (lead)
	Bauxite	metals (As, Cd, Cr, Pb, Hg, Ni, Zn)
	Barite	metals
	Biochars	organics
	Coal	organics
	Coke	organics (PAHs, PCBs)
	Engineered Polymers	inorganics, organics
	Limestone	metals
	Organoclays	metals, NAPLs, organics (PAHs, PCBs)
	Zeolites	metals (copper, lead, zinc)
Degrading	Bioremediation agents	organics (dioxins/furans, PCBs)
	Biopolymers	metals, organics
	Palladium	organics (chlorinated hydrocarbons, PCBs)
	Zero-Valent Iron (ZVI)	organics (chlorinated hydrocarbons, PCB)

Tab. 2.5 - Reactive amendments for *in situ* treatments.

In order to enhance current capping technologies, different authors have been developed specific formulations of sequestering and degrading amendments. For instance, Choi et al. (2009) focused on the development of AC impregnated with reactive iron/palladium (Fe/Pd) bi-metallic nanoparticles (NPs) (Reactive AC, RAC). RAC is a

smart composite for dechlorination of PCBs. Due to its high adsorption capacity, RAC actively attracts hydrophobic PCBs from sediment matrix (Lofrano et al, 2017).

Reactive mats

The use of active materials into in situ capping allows increasing low adsorption capacity of sand caps and reducing the cap thickness in order to achieve the remediation goals. Amendments can be contained in a mat (Fig. 2.2), applied in bulk onto the sediment surface, mixed in the sediment, added as part of a sand cap, or as a layer within a sand cap. RCM (Fig. 2.2) is a patented permeable composite mat invented by CETCO, a minerals technologies company. It represents a new class of sediment remediation technique, consisting of a reactive layer containing one or more neutralizing or otherwise reactive materials (e.g., organoclay) that is confined between two permeable geotextile layers (Meric et al., 2011). Geotextiles are textiles that are manufactured with biodegradation-resistant synthetic fibers into flexible, porous fabrics. The four most common functions of geotextiles are drainage, separation, reinforcement, and filtration (Martin Bouthot et al., 2004). Due to these functions, the application of geotextiles can effectively inhibit the floating of low-density materials encapsulated in two geotextile layers.

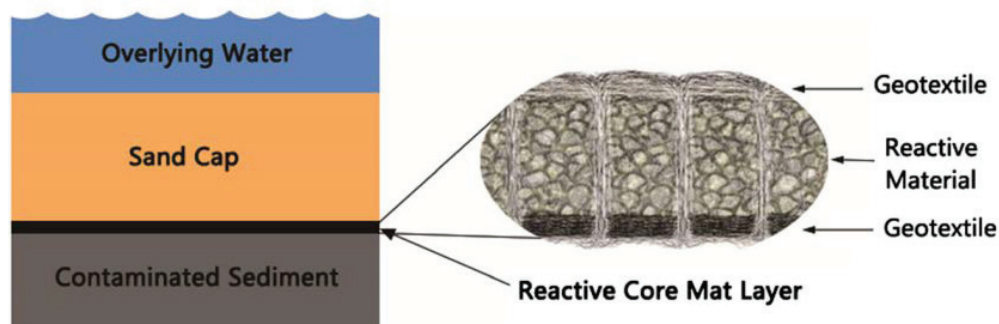


Fig. 2.2 - Field application and schematic of reactive core mat (Zhang et al., 2017).

The same amendment used in the same proportions is generally more effective at isolating contaminants when used in a cap than when placed directly into sediments. Additionally, amendments delivered in a thin layer can minimize an amount of costs since these materials are usually more expensive than traditional materials.

Mats consist of an amendment (or amendments) that are confined between two permeable geotextile layers. These mats allow for accurate placement of amendments with high total organic content and low density that could otherwise become suspended during placement. Synthetic geotextiles also provide a bioturbation barrier, prevent mixing of amendments with underlying sediments, allow a more uniform application of amendments, and reduce erosion. As they are composed of synthetic fibres, they do not easily biodegrade (Olstad and Darlington, 2005).

These mats are generally covered with conventional capping materials and, if needed, armoring layers to provide physical stability and further isolation. A thickness of 10–15 cm of sand or soil acts as an armor layer to protect the underlying thin sorbent layer from erosion forces and provides a habitat for benthic organisms to colonize and lengthen contaminant breakthrough paths (Lampert et al., 2013). Before mat is installed, it is important to remove rocks and debris from the sediment surface to minimize potential damage to the mat and provide a more even surface for placement (Barth and Reible 2008). Differential settling of the mat could lead to ruptured seams and contaminant migration through the seams. In addition, depending on the amendments and components of the mat, they may not sink readily. Although some amendments enclosed in the geotextiles are buoyant, it is possible to use geotextiles with a higher specific gravity or mix a fraction of sand with the amendment to create a mat that is easier to sink (Olstad and Darlington, 2005). Such amendment mats are commercially available from a limited number of companies. However, this approach has been adopted at several EPA superfund site projects with typical thicknesses of 6 and 11 mm.

Granular materials

The commercial product AquaBlok and AquaGate are patented material consisting of individual particles, an aggregate core covered by a clay or clay-sized materials, and polymer coating. For typical freshwater product formulations, AquaBlok's clay component consists largely of bentonite clay. It is a very low permeability isolation layer over contaminated sediments in a thickness of 6 in or less. AquaBlok particles expand when hydrated, and the degree of expansion is determined largely by the product formulation, application rate, and salinity of the hydrating water. After settling to the bottom, the clay absorbs water and swells, thereby reducing the permeability of the surface layer.

The AquaBlok cap has been shown to halt effectively groundwater upwelling in the capped area in a field demonstration (Reible et al., 2006) and remains physically stable and is recolonized with native organisms after 30 months of monitoring following cap placement (Barth et al., 2008). AquaGate composite particle is manufactured using a stone core coated with a combination of bentonite-based clay and powdered activated carbon. This approach increases surface area of the thin activated materials coating later (around the stone core aggregate) and provides uniform delivery/placement of a small amount of reagent over a larger (Fig. 2.3). Because the lighter powder coating materials are bound to an aggregate substrate to form the composite particle, the particle has a very high specific gravity (compared to the coating materials), allowing it to sink rapidly through the water. Specific formulations that incorporate other clay types (e.g., attapulgite) or additives (e.g., plant seeds) are available or can be designed to address site specific (e.g., salinity) or action-specific (e.g., treatment requirements) needs. The material is generally applied as a dry product through the water column to the surface of contaminated subaqueous sediments and hydrates to form a continuous and impermeable isolation cap.

These advantages, as generally claimed, include: (i) low aqueous permeability and transmissivity due to low hydraulic conductivity (on the order of 10⁻⁹ centimeters per second (cm/s) for typical bentonite freshwater formulations); (ii) high degree of cohesiveness and cap uniformity due to coalescing of individual particles on hydration;

(iii) high contaminant attenuation capacity due to binding capacity of the clays used; (iv) contaminant non-specificity due to very low permeability and uniform isolation coverage; (v) high resistance to physical erosion due to cohesiveness; (vi) lower thickness requirements for contaminant isolation due to physical properties of material; and (vii) compatibility with other remediation elements and amendments (e.g., reactive components or seed).

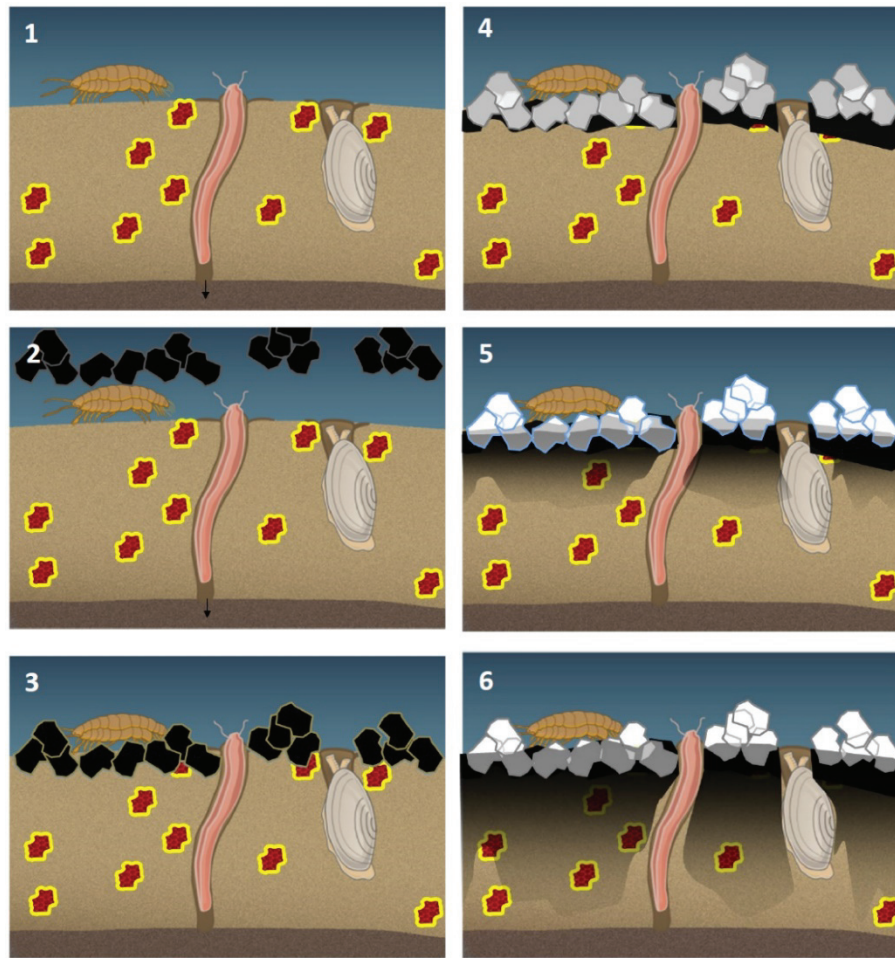


Fig. 2.3 - AquaGate delivery, activated carbon release, and mixing in surface sediment. (1) Pre-installation conditions; (2) the gravitational descent of the amendment coated aggregate; (3) layering of the aggregate on the sediment bed; (4) release of the amendment to the sediment; and (5 and 6) the gradual burial and mixing of the amendment over time (Kirtay et al., 2018).

Placement Methods

Amendments can be contained in a mat, applied in bulk onto the sediment surface, mixed in the sediment, added as part of a sand cap, or as a layer within a sand cap (Fig. 2.4).

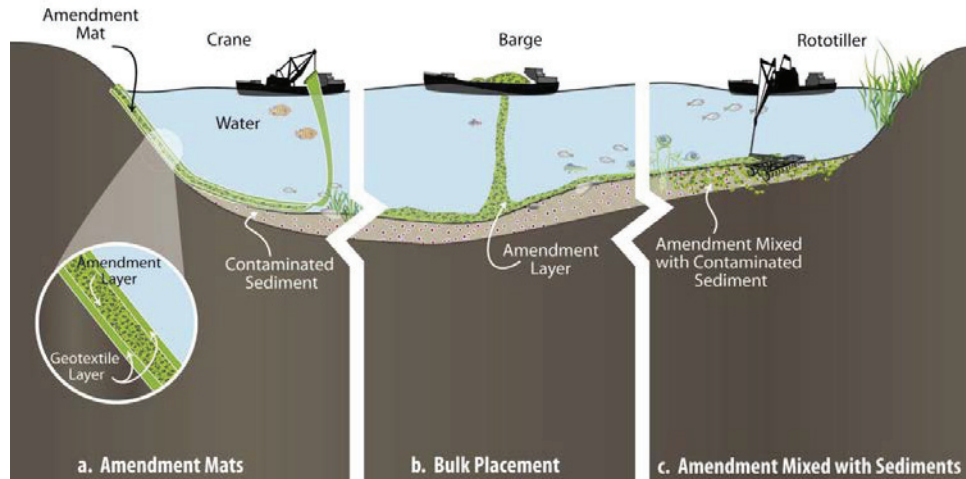


Fig. 2.4 - Placement methods for sediment amendments (US EPA, 2013).

Placing a geotextile or geofabric system (or layer) requires specialized deployment methods such as a vessel with the capability to hold and spool out rolls of the geotextile/geofabric material (Fig. 2.5a) and a mechanism to ensure the material settles on the sediment surface. Before a mat is installed, it is important to remove rocks, debris, and dead trees from the sediment surface to minimize potential damage to the mat and provide a more even surface for placement (Barth and Reible, 2008). Additional factors that affect placement of mats include the type of amendment used in the mat, shoreline accessibility, and the physical nature of the sediment where the mat is placed. Differential settling of the mat could lead to ruptured seams and contaminant migration through the seams. In addition, depending on the amendments and components of the mat, they may not sink readily. Although some amendments enclosed in the geotextiles are buoyant, it is possible to use geotextiles with a higher specific gravity or mix a

fraction of sand with the amendment to create a mat that is easier to sink (Olsta and Darlington 2005).

Amendments can be spread on the sediment in bulk using conventional equipment or equipment that has been modified for aquatic use. At the Anacostia River demonstration, apatite was placed using a clamshell bucket on a barge-mounted crane (Fig. 2.5b). Silt curtains were used to minimize the migration of cap material because of water movement. Equipment such as submerged diffusers, energy dissipaters, submerged discharge points, and tremies can be used to apply amendments evenly to a required thickness (Fig. 2.5c). Amendments can also be applied in bulk with fine-grained soil or sands to provide better dispersion, uniformity, placement controls, and contact time when the required quantity of the amendment is small. Cap system could be placed using a combination of typical cap placement methods and focused placement methods such as diver-assisted placement (Fig. 2.5d).

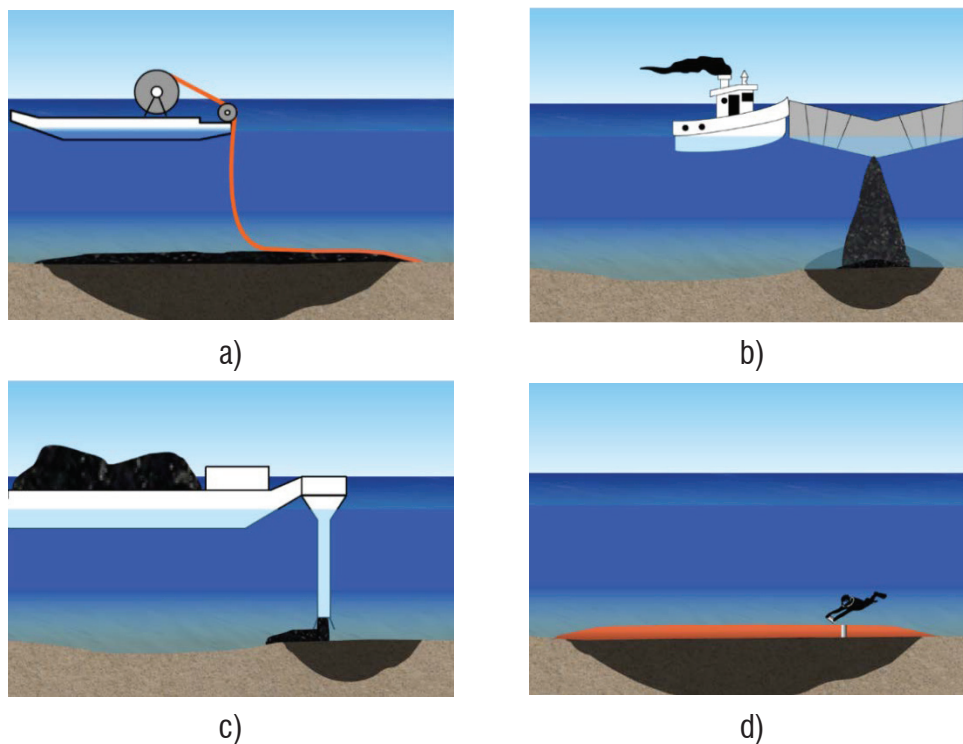


Fig. 2.5 - Placement methods for reactive capping.

Amendments for in-situ treatment are also applied by mixing into the top layer of sediment, effectively achieving at time of placement what benthic organisms may do over time. This can be done mechanically (e.g. by using augers) or by simple settling of higher density amendments through low density surficial sediments. Mixing in the amendments can have advantages such as more uniform application (if done correctly) and setting up of a diffusive flux that prevents breakthrough of contaminants for longer periods of time (Ghosh et al., 2011).

The current, energy, and depth of the waterway may also influence the type of placement method, especially for bulk materials that may become entrained in the water column and therefore be difficult to place accurately. Generally, a longer descent through the water column results in a thinner layer of amendments over a larger area. Delivery may need to be directed closer to the sediment surface in these situations. Slope of the waterway bottom may affect the placement of bulk material, as flat bottom and shallow slopes allow material to be placed more accurately. Currents can affect dispersion during amendment placement, while bottom currents can generate shear stresses on the materials. Depending on the hydrodynamics of the water body, the amendment may need to be protected from erosion. Protection may be accomplished by placing a sand or gravel armoring layer on top of the amendment. The type of material selected for this uppermost layer may also depend on habitat at the site (EPA 2005).

Cost

Cost drivers for active sediment capping technology comprise (1) the required dimensions of the cap (depth, length and thickness), (2) the price of the capping material, (3) the local situation on the site (accessibility, surrounding buildings, underground constructions, type of subsurface, etc.), and (4) the amount of maintenance that is needed to keep the cap active and permeable. Construction costs for the large-scale application (> 400 ha) were estimated to be 22.0 €/m^2 plus the cost of materials. The principal costs within this estimate include monitoring costs (9.10 €/m^2) and construction costs for cap placement (9.10 €/m^2). Furthermore, it is necessary to account

mobilization/demobilization ($\sim 0.9 \text{ €/m}^2$), project management ($\sim 1.8 \text{ €/m}^2$) and miscellaneous (site preparation, construction management, design and permits) ($\sim 1.8 \text{ €/m}^2$). Construction costs for demonstration approaches were estimated to be 182.0 €/m^2 . Tab. 2.6 shows total material cost estimates for several amendments based on the Anacostia River demonstration. According to the reactive core mat vendor, CETCO, costs are approximately 2.50 €/m^2 for mats with activated carbon and 2.00 €/m^2 for Organoclay. The costs of bulk activated carbon is about 1.00 €/m^2 , assuming a typical application of 5 percent activated carbon dry weight to the top 10 cm of sediment. For activated carbon applied using SediMite™, the price is about 2.00 €/m^2 (Menzie-Cura and Associates).

Cap Type (thickness)	Material cost (in 2005)
Apatite (15 cm)	\$ 3.10*
Sand (15 cm)	\$ 0.45*
AquaBlok™ (10-15 cm)	\$ 3.00*
Reactive Core Mat with coke breeze (1 cm)	\$ 1.11
Reactive Core Mat with activated carbon (1 cm)	\$ 2.00
Reactive Core Mat with bulk iron (1 cm)	\$ 1.25
Reactive Core Mat with 10% nano-iron (1 cm)	\$ 3.62
Bulk Activated Carbon (5% AC)	\$ 1.00
SediMite™ Activated Carbon (5% AC)	\$ 2.00

Tab. 2.6 - Estimated material costs for reactive capping (*excludes shipping costs).

2.3 *Ex situ technologies*

2.3.1 *Brief overview*

The main advantage of ex situ treatment is that it generally requires shorter time periods than in situ treatment, and there is more certainty about the uniformity of treatment because of the ability to homogenize, screen, and continuously mix the soil. However, ex situ treatment requires dredging of sediments, leading to increased costs and engineering for equipment, possible permitting, and material handling/worker exposure considerations.

Treatment methods can be categorized into three major groups: a) physical/chemical treatment (i.e. ex situ stabilisation/solidification, chemical reduction, solvent extraction, soil/sediment washing); b) biological treatment (i.e. bioslurry, biopiles, landfarming, composting); c) thermal treatment (i.e. thermal desorption, incinerations, pyrolysis).

Physical/chemical treatment uses the physical properties of the contaminants or the contaminated medium to destroy (i.e., chemically convert), separate, or immobilize the contamination. Chemical reduction/oxidation and dehalogenation (APEG, BCD or glycolate) are destruction technologies. Soil washing, separation and solvent extraction are separation techniques, and Solidification/Stabilisation (s/s) is an immobilization technique. Physical/chemical treatment may be cost effective (depending on site specific conditions) and can often be completed in shorter time periods than by biological treatment methods. Equipment is readily available and is not engineering or energy-intensive. Treatment residuals from separation techniques will require treatment or disposal, which will add to the total project costs and may require permits.

Bioremediation techniques are destruction or transformation techniques directed toward stimulating the microorganisms to grow and use the contaminants as a food and energy source by creating a favourable environment for the microorganisms. Generally, the reactions may be based on oxidation or reduction reactions. Reduction reactions involves heavily halogenated organics (e.g. mostly highly chlorinated solvents, PCBs). Oxidation reactions are most effective in high redox conditions, in

contrary to reduction reactions that need low - very low redox. Sometimes, microorganisms adapted for degradation of the specific contaminants are applied to enhance the process. Biological treatment of PAHs usually is non-effective on 5-ring PAHs and larger. An advantage over the in-situ applications is that in ex situ applications, more toxic by-products during the bioremediation process (e.g., TCE to vinyl chloride) are contained in the treatment unit until non-hazardous end-products are produced. Bioremediation is not yet commonly applicable for treatment of inorganic contaminants (except phytoremediation for reducing heavy metal contents in soils and ground waters).

Thermal treatments offer quick clean-up times but are typically the costliest treatment group. This difference, however, is less in ex situ applications than in in situ applications. Cost is driven by energy and equipment costs and is both capital and operation and maintenance intensive. Thermal processes use heat to increase the volatility (separation); burn, decompose, or detonate (destruction); or melt (immobilisation) the contaminants. Separation technologies include thermal desorption and hot gas decontamination. Destruction technologies include incineration, open burn/open detonation and pyrolysis. Vitrification immobilizes inorganics and destroys some organics.

2.3.2 Solidification/stabilization

Solidification/stabilization (S/S) is an attractive technology for various wastes including sediments by using cement, lime and other binders to reduce their toxicity and improve their strength properties prior to ultimate disposal (Wang et al., 2012; Miqueleiz et al., 2012; Zentar et al., 2012). EPA defines solidification as “a process that encapsulates waste to form a solid material” (US EPA, 1997).

The waste material is converted into solid forms via entrapping within a granular or monolithic matrix by adding appropriate reagents or using a mechanical process during the process of solidification. A chemical reaction is usually involved in the stabilization process to limit the mobility or solubility of the hazardous components in the wastes, and not necessarily alter the physical nature of the waste (US EPA, 2004). The combined application of the solidification and stabilization process ensures the mixing of the contaminated waste materials with the treatment agents, and consequently, both the physical and chemical immobilization of the hazardous components occurs. The

S/S technique is a non-destructive approach to eradicate or inhibit the mobility of contaminants in the waste materials (US EPA, 2004). The ultimate objective of the S/S approach is to complete transformation of the toxic components in wastes into a non-toxic form. However, the objective of S/S technology not only includes limiting the solubility of the contaminant when exposed to leaching fluid, but also improvement of the handling characteristics of the wastes and decreasing the surface area across which contaminant transport might occur is expected through solidifying of the waste materials. The objectives are most likely expected to be achieved via chemical transformation, which result in the formation of new compounds, although chemical changes are seldom occurred during the application of existing S/S approaches (Wiles, 1987).

As noted by Oh et al. (2011) and others, S/S offers several advantages over other treatment technologies, including: i) cost (S/S is comparatively inexpensive, making use of industrial wastes such as fly ash and cement kiln dust); ii) implementability (high water content sediments can be readily treated without further dewatering; amendments can be mixed in barges, eliminating the need for large staging areas and multiple unit operations); and iii) synergistic of processes (the commonly used binding materials are alkaline in nature, further reducing the mobility of metals).

A notable disadvantage of S/S is that contaminants are immobilized, but not destroyed. There is thus potential for future release. Further, oily sediments may not be as readily treated due to the effects of oil on the hydration of cement. Despite these limitations, according to Singh & Pant (2006, as cited in Oh et al. 2011) S/S is recognized as the best demonstrated, available technology for land-based disposal of toxic elements.

The use of treated sediments for other applications (material recovery) is an interesting solution in line with the philosophy of the circular economy (Todaro et al., 2016; Wang et al., 2015). In this regard, Colangelo et al. (2017 and 2015) investigated the recycling of several waste such as municipal solid waste incinerator fly ash by means of cold bonding palletisation based on the use of cement, lime and coal fly ash as components of the binding systems. They showed how the obtained lightweight porous aggregates were mostly suitable for recovery in the field of building materials with

enhanced sustainability properties. Couvidat et al. (2016) studied the feasibility to use dredged sediments as substitute for sand in non-structural cemented mortars. The obtained results confirmed that the reuse of the coarser fraction of a marine sediment offered an interesting valorisation potential as cemented mortars for non-structural applications. Colangelo and Cioffi (2017) analysed the mechanical properties and durability of mortar containing fine fraction of construction and demolition waste (CDW), that generally are problematic waste materials. The use of superplasticizer combined with selective demolition can improve significantly the mechanical properties of mortars produced with CDW aggregate. Recently, Wang et al. (2018) developed a remediation method for contaminated sediment using S/S with calcium-rich/low-calcium industrial by-products and CO₂ utilization. This study represented an additional example of how S/S processes can be a suitable way to transform contaminated sediment into value-added materials. However, the study of this research highlighted the growing importance of assessing the impacts of these new products on the environment.

Many authors in France have used the solidification/stabilization technique to improve the physical, mechanical and environmental properties of dredged sediments from Dunkirk harbour (Aouad et al., 2012; Wang et al., 2012; Zentar et al., 2012), port of Le Havre (Boutouil, 1998), Rouen harbour (Colin, 2003), Port En-Bessin harbour (Silitonga et al., 2010), Cannes harbour (Levacher and Sanchez, 2011; Levacher et al., 2011) and a channel linking Charleroi to Brussels (Scordia et al., 2008). Objectives are focused mainly on: (a) changing the initial fluid flow state of sediments, (b) eliminating or stabilizing the hazardous materials such as heavy metals and organic matters, (c) improving the mechanical performance and (d) producing new geomaterials or granular materials to solve the problem of high-quality resource shortage. Fortunately, the above-mentioned literatures showed that the solidified sediments are suitable and adequate materials for filling engineering, pavement construction, cement production, light-weight concrete production and brick fabrication.

The transformation of dredged sediments into geomaterials is an attractive technology to relieve the shortage of high-quality materials in various projects, such as

coastal highway. This will facilitate the recycling of dredged materials from local sources and save natural soil resources and transportation costs for seaside construction. However, only 5% of the materials generated from recycling operation are used in public works at present (Wang et al., 2013). This data indicates that in the context of sustainable development it is still necessary to study and recycle sediments as renewable geomaterials.

Selection of the reagents and/or additives

The reagent and/or additive to be used for the S/S treatment of contaminated soil is selected based on the end-use goal of the processed material, such as land filling, a resource of aggregate in construction or redevelopment of the sites. The common criteria used for the selection of binder to meet site-specific requirements with the corresponding typical target values (Al-Tabbaa and Perera, 2005) are listed in Tab. 2.7.

Design criteria	Typical target values
UCS	> 350kPa (soaked) at 28 days (US EPA 1986a)
Leachate pH	7–11 (Conner 1990; Harris et al. 1995)
Leachability	in accordance to the EN 12457-2 (2002)
Permeability	< 10^{-9} m/s (as for cut-off walls) (Al-Tabbaa and Perera 2005)
Microstructural analyses	In accordance with the standard test methods; to examine the development of the hydration products and their interaction with contaminants (Al-Tabbaa and Perera 2005)

Tab. 2.7 - Commonly used design criteria and typical target values for the selection of the reagents and/or additives for the S/S application (adapted from Hasegawa et al., 2016).

Inorganic and organic are two broad categories that are used to differentiate the binder systems used for the S/S treatment. The inorganic binder systems include cement, fly ash or blast furnace slag, while the asphalt/bitumen is the common organic binder in use (Al-Tabbaa and Perera, 2006). Besides, there are instances of using

mixed binder systems, e.g., diatomaceous earth with cement and polystyrene, polyurethane and cement, and polymer gels with silicate and lime cement (Wiles, 1987).

The metal-contaminated wastes are frequently processed through cement-based S/S treatment (LaGrega et al., 2001), because the high pH of the cement facilitates the retention of metal cations as insoluble hydroxide salts within the solidified structure. Portland cement (PC) is the most commonly used cement variant for S/S, and the process is executed via mixing of the contaminated mass and PC with or without water depending on the nature of waste (LaGrega et al., 2001). Both the chemical fixation and immobilization via physical encapsulation is expected during the PC-based S/S processing (Al-Tabbaa and Perera, 2006). The binders that have been used as a partial alternative to PC include blast furnace slag and pulverized fuel ash (Al-Tabbaa and Perera, 2006).

The pulverized fuel ash (PFA), which is a siliceous and aluminous material, is used as an alternative binder to PC in the S/S process in conjunction with lime, and the corresponding reactivity depend on the relative fineness of the content and the glass phase ratio (Harris et al., 1995; Neville and Brooks, 2010). The metals in the contaminated soil, if treated with PFA-lime binder, might get chemically immobilized as hydrate complexes (LaGrega et al., 2006). However, the hardening process of PFA is slower (Taylor, 1997) and exhibit reduced sustainability during both leaching and durability tests than that of the PC (Harris et al., 1995).

Bentonite, a naturally-occurring clay as derived from the volcanic ash and having low hydraulic conductivity and high sorption capacity for cations (Matthes et al., 1999) is another suitable binder for the S/S process. The sorption property is attributable to the presence of mineral montmorillonite, which is a di-octahedral smectite and is chemically characterized as a hydro-alumino-silicate. Although it is considered as an advantageous material for treating metal-contaminated wastes, the presence of other organic and inorganic chemicals might alter the sorption ability of bentonite. Hence, it is generally used as a co-additive with other binder, such as PC, etc (Al-Tabbaa and Perera, 2006).

The calcium oxide and calcium hydroxide are the common lime variants, which are used as the S/S binder, and another frequently-used inorganic-type binder (Sherwood, 1993). If the waste material components include alumina and silicates, lime can be used as a standalone binder because those materials can react with lime to generate cementitious solids (LaGrega et al. 2006). However, lime is mostly used as pH-controller additive with the other binders, such as, PC, PFA and clay (Conner, 1990).

In addition to above-mentioned common binders, there are other binders that have been explored for S/S applications, e.g., activated carbon, phosphates, rubber particulates, chemical gellants, saw dust, straw, etc. (Kershaw and Pamukcu, 1997; Ajmal et al. 1998; ITRC, 2011).

The use of agricultural/industrial by-products for soil stabilization has captured extensive interests in recent years (Moon et al., 2013; Tsang et al., 2013). This can be regarded as “green remediation” in a broad sense, because such approach addresses the problems of contaminated soil/sediment while enabling resource recycling and mitigating the overall environmental impact (e.g., carbon footprint and landfill disposal) associated with solid waste management (Tomasevic et al., 2013; Tsang and Yip, 2014).

Effects of binders on soil properties

The chemical reactions involved in the hydration of different types of cement or lime have been described and discussed thoroughly in many papers and textbooks (Taylor, 1997; Boynton, 1980). The various chemical processes involved in soil stabilisation using a variety of binders have also been described in the literature, (Chew et al., 2004; Janz and Johansson, 2001; TRB, 1987), although the focus has mainly been on the two most common binders, cement and lime.

The reactions generated when mixing various binders with soil vary by process, intensity and duration, but in general, exhibit many similar characteristics. As the binder is mixed with the soil, hydration takes place, although slag may need an activator from another binder to start this process. Some reactions may involve cementation starting up directly, while others may lead to further reactions with the soil and its minerals.

The reaction products formed are of somewhat different types. When using lime, which contains large amounts of calcium oxide (denoted C), hydration will occur as the lime comes into contact with the pore water in the soil, resulting in the formation of calcium hydroxide (denoted CH). Some of this calcium hydroxide will be adsorbed onto the soil particles. Ion exchange will take place and the soil will be modified into a somewhat drier and coarser structure due to the slaking process and flocculation of the clay particles that take place (Boardman et al., 2001). The calcium hydroxide not consumed in this process is free to react with the silica (denoted S) and alumina (denoted A) contained in the minerals present in the soil. These reactions, termed pozzolanic reactions, will result in the formation of calcium aluminate silicate hydroxide (CASH), calcium silicate hydroxide (CSH) and/or calcium aluminate hydroxide (CAH). The compounds CSH, CAH and CASH here denote compositions of C, S, A and H in non-specific proportions.

When using cement, primarily CSH is produced, but also, although to a much lesser degree than for lime, pozzolanic reaction products, containing silica and alumina from the soil, are produced. Ground granulated blast-furnace slag, which is a latent hydraulic cement, will react in much the same way as ordinary cement, and lead to the formation of similar hydration products. The fly ash acts mainly as a pozzolanic material, reacting with the calcium hydroxide added to or generated by hydration.

The various binders can be characterised with respect to possible type and rate of reactions by looking at their content of CaO , Al_2O_3 and SiO_2 . In general, the reactivity increases with total content of $\text{CaO} + \text{Al}_2\text{O}_3 + \text{SiO}_2$ of the binders (Taylor, 1997). However, the effects of both major and minor components are complex. For example, the reactivity of MgO in slag is quantitatively equivalent to CaO up to a certain content (Taylor, 1997). Lime, which contains a high proportion of CaO , has a high potential for forming large amounts of reaction products when mixed with soil. However, pozzolanic reactions with soil are normally relatively slow, due to the restricted accessibility of the silica and alumina contained in the soil. In fly ash, the silica and alumina are more easily accessible for reactions with binders that contain calcium hydroxide. The reactions forming CSH upon hydration of cement involve minerals contained in the binder itself

and are thus, as a rule, more rapid than pozzolanic reactions with the soil. In slag, the ratio of CaO to SiO₂ is significantly lower than in cement and, as a result, the build-up of reaction products is normally slower than for cement (Taylor, 1997). In calcium aluminate cements, the high content of alumina will cause much faster reactions than those of Portland cements.

The reactions taking place during hydration generate heat. In general, the slaking of quicklime will produce the largest amount of heat. The total amount of heat generated by soil stabilisation with cement will normally be less than half of that from stabilisation with equivalent quantities of quicklime (Ahnberg et al., 2004). Composite binders of cement and lime can be expected to generate amounts of heat between those of lime and cement, while those of cement-slag and cement-fly ash may generate an amount of heat closer to that of pure cement (Pihl & Kuusipuro, 2004). An increase in temperature will generally increase the rate of the reactions that occur. In the field there will be a significant increase in temperature in the deep-mixed columns, which in turn will affect the rate of the chemical processes taking place. In normal laboratory testing, on the other hand, the effects of heat generation are minor, since the samples are small and are stored at a constant temperature.

Besides the effects of admixtures and temperature on the rates of chemical reactions, these may also be affected by various substances in the soil having retarding or accelerating effects, some of which, but not all, are well known (Taylor, 1997; Kitazume & Terashi, 2002; Horpibulsuk et al., 2003;).

Changes in basic geotechnical properties

Many previous researchers have investigated the effect of cement and lime induced stabilization on the mechanical behaviour of dredged sediments (Miura et al., 2001; Tremblay et al., 2001; Tremblay et al., 2002; Horpibulsuk et al., 2003; Horpibulsuk et al., 2004; Lorenzo and Bergado, 2004; Consoli et al., 2009; Horpibulsuk et al., 2012; Wang et al., 2013; Wang et al., 2014; Wang and Abriak, 2015; Wang et al., 2015; Federico et al., 2015).

Tremblay et al. (2001) concluded that the organic matter can negatively affect the efficiency of artificial cementation on eastern Canada clays. Chew et al. (2004) suggested that the multitude of changes in the properties and behaviour of cement-treated marine clay can be explained by interaction of four underlying microstructural mechanisms: i) the production of hydrated lime by the hydration reaction which causes flocculation of the illite clay particles; ii) preferential attack of the calcium ions on kaolinite rather than on illite in the pozzolanic reaction; iii) surface deposition and shallow infilling by cementitious products on clay clusters; iv) the presence of water trapped within the clay clusters. Wang et al. (2012) proved that cement can improve significantly the bearing capacity and compressive strength of stabilised marine soils, and 6% cement can be considered as an economic and reasonable dosage to stabilise fine soils according to laboratory tests. Federico et al. (2015) analysed the plasticity properties and the compressibility characteristics of clayey sediments, dredged from the Port of Taranto (South of Italy), treated with lime and (or) cement. With respect to the effect of the treatment on the clay plasticity properties, the following conclusions can be drawn: (i) irrespective of both the type and percentage of additive, clay treated for different curing times (up to about 4 years) follows aligned paths in the plasticity chart; (ii) all the plasticity paths are characterized by an increase of w_p and an increment of the consistency index (CI) if, as in this case, the after-curing water content reduces; and (iii) 8% additive and 2 days of curing are sufficient to reduce PI and transform the soil from CH to MH according to USCS classification. The compression behaviour of the treated clay is similar to that of natural untreated clays, i.e. irrespective of the additive used, after 28 days of curing, the compression line of the treated clay is located to the right of the intrinsic compression line (Burland, 1990) of the reconstituted.

In particular, the use of lime will involve a certain degree of expansion upon hydration (Boynton, 1980), whereas the hydration of other binders, as the cement, only causes minor changes in volume (Taylor, 1997). In the laboratory, when mixing dry binders with clay, the density can be expected to be roughly the same or slightly higher than that of the natural, untreated soil. However, density changes in organic soil during stabilisation may be significant (Timoney et al., 2012).

Adding dry binders to a soil will result in a stabilised soil that is not fully saturated. This is the case for laboratory prepared samples, which are normally stored without access to water, and partly also for stabilised soil in the field. The degree of saturation in the field will change to varying degrees with time depending on the pore pressure conditions and the permeability and water absorption ability of the stabilised soil. Since incomplete saturation affects the pore pressure build-up, a decrease in the degree of saturation will lead to an increase in the undrained strength. The degree of saturation of laboratory samples may be of the order of approximately 96-98% in a peat of high-water content when stabilised with a binder quantity of 200 kg/m³, and 93-95% in stabilised high-plastic clays when using a binder quantity of 100 kg/m³ (Ahnberg et al., 2001).

The behaviour of the stabilised soil is affected not only by its water content, but also by its liquidity or consistency index. As in natural soils, a decrease in water content and thus liquidity index, is accompanied by an increase in strength. Both the liquid limit and the plastic limit will also change to varying degrees, largely depending on the type of soil (Federico et al., 2015). The plastic limit normally increases after stabilisation. The liquid limit of soft clays typically also increases after stabilisation, but in some high-plastic and organic soils, it decreases. Examples of changes in water content, w , liquid limit, w_L , and plastic limit, w_P measured in stabilised marine sediments are shown in Fig. 2.6. As can be seen, the plasticity index shows a slight increase at low cement content of 5% or less, followed by a steady decrease as the cement content increases. This can be directly attributed to the different trends in behaviour manifested by the plastic and liquid limits. The plastic limit increases monotonically with an increase in cement content, with a larger rate of increase at low cement content. The 28-day plastic limit is also higher than the 7-day plastic limit. Similar trends have been observed for other lime-stabilized soils that contain a significant amount of clay minerals (Brandl, 1999; Locat et al., 1996) had suggested that one possible reason for this increase is aggregation and cementation of particles into larger size clusters. Another possible reason is the water trapped within intra-aggregate pores. As suggested by Locat et al. (1996), the presence of this intra-aggregate water increases the apparent water content

without really affecting interaction between aggregates. The liquid limit increases significantly at low cement content ($<10\%$) before dropping slightly at higher cement contents.

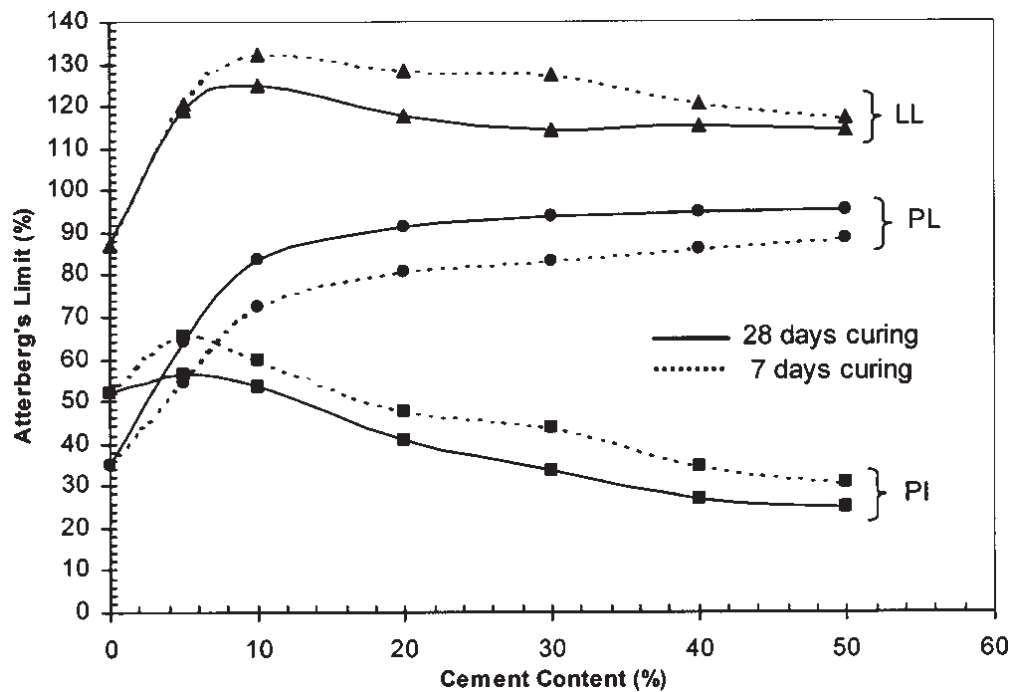


Fig. 2.6 - Effect of cement content and curing time on Atterberg limits for soft marine clay sediments ($w_i 120\%$), (Wang et al., 2004).

In general, change in the liquid limit with cement content seems to depend very heavily on the soil type. Sivapullaiah et al. (2000) reported a similar decreasing trend on lime-treated black cotton soil after 7 days of curing. Kinuthia et al. (1999) also reported a similar trend for lime-treated kaolinite, measured a few hours after mixing. On the other hand, Locat et al. (1996) data on lime-treated Louiseville clay after 100 days of curing suggest a general increase in liquid limit with the lime content. Brandl (1981) reported divergent trends for two soils, with the more plastic soil (containing montmorillonite) showing a significant decrease in liquid limit after 7-day and 270-day curing, and a less plastic soil showing a corresponding increase. The general trend appears to be one of

decreased liquid limit if the untreated soil is highly plastic and increased liquid limit in soil of low plasticity. Taken in light of the mechanisms postulated above, this suggests that, in soils of high plasticity, the encapsulation of the clay clusters by deposited cementitious products has a dominant effect, leading to lowering of the liquid limit. On the other hand, in soils of low plasticity, the presence of entrapped water has a dominant effect, leading to a rise in the liquid limit.

Stabilisation of soil involves a decrease in compressibility and an increase in strength. In general, the stiffness of the stabilised soil will increase more than the strength. The relatively distinct change from large to limited, almost constant, failure strain, mirrors the transition from contractive to dilative behaviour as the strength of the stabilised soils increase. More ductile behaviour with larger strains at failure can be observed for stabilised peat compared with other soft, stabilised soils. This is believed to be caused by a reinforcing effect of the peat fibres. In the oedometer case, where no horizontal displacement takes place, the compression modulus, M , will increase together with the strength. The preconsolidation pressure may be estimated roughly as a factor of about 1.3 times the unconfined compressive strength. The range for this factor has been reported to be between 1.2 and 1.9 (Kwan et al., 2004). This relation is to some extent affected by the overconsolidation ratio of the stabilised soil, i.e. the higher the overconsolidation the higher the factor. Various ways of estimating different compression parameters of stabilised soils have been suggested (Lorenzo & Bergado, 2002), including the vertical yield stress as related to the void ratio (Tremblay et al., 2001; Rotta et al., 2003). Fig. 2.7 shows a schematic variation of the compression modulus with increasing stress, expressed in accordance with the model normally used for calculations of settlements of natural soft soils in Sweden (Larsson et al., 2005). After passing a yield stress, the modulus reaches a minimum value. Thereafter, it increases with further increase in stress and, as an effect of the breakdown of the cementation forces with increasing stress level, is then governed by a modulus number M' of the same magnitude as that of the unstabilised soil (Ahnberg, 1996).

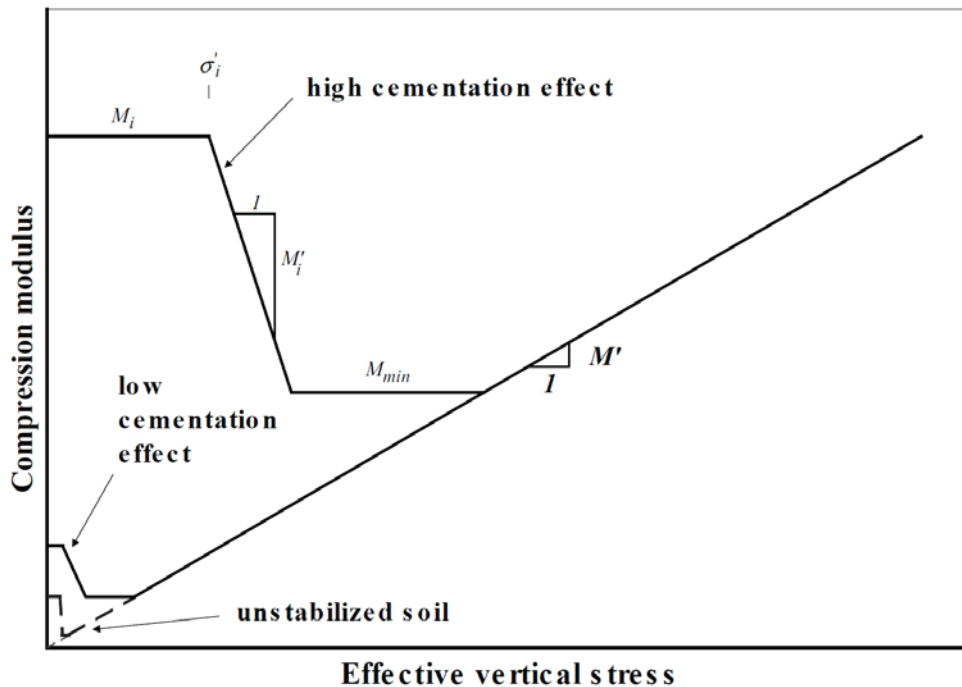


Fig. 2.7 - Schematic variation in compression modulus according to oedometer tests (Ahnberg, 1996).

The permeability of the stabilised soil is often of interest for several reasons. It may affect the pore pressure response at loading and, depending on the rate of loading, influence the extent to which undrained or drained conditions govern the strength behaviour. Furthermore, the permeability will affect possible leakage of binder substances from the stabilised soil, as well as the risk of changes in groundwater conditions, e.g. due to lowering of artesian groundwater pressures. Other important effects, although not directly related to strength, are the influence on the rate of consolidation after construction and the potential impact from leaching of trace elements on the environment. Earlier investigations have reported both increases (Anberg, 2005) and decreases in permeability (Tan et al., 2002) or both depending on the type of binder used. However, these diverging results need not be considered questionable. Depending on the effect of the binder and the time of curing, the macro-structure of the stabilised soil mass and stress conditions, the permeability may be higher or lower than that of the soil before stabilisation. The permeability may thus be very different under field conditions

compared to that measured in the laboratory. In fairly homogeneous stabilised soils, i.e. samples prepared in the laboratory, the change in permeability can be described by an initial change, an increase or decrease, followed by a decrease with time. Initial flocculation and other structural changes will cause a change in the permeability immediately after stabilisation. As a rule, a certain increase in the permeability can be measured, but the addition of large amounts of binders to highly organic soils, and any compaction performed, may cause an initial decrease in permeability. There will then be a decrease in permeability with time, influenced by the continuing formation of different reaction products in the stabilised soil. The rate and extent of this growth will depend on the type and amount of binder and the type of soil and will also be influenced by any retarding substances present in the soil. The initial change in permeability is linked to a change in void ratio and can also be roughly related to the change in water content after mixing and possible compaction. After the initial change, the decrease in the permeability can be related to the increase in strength, which is an indirect measure of the growth of reaction products. The cementation process leads to about the same relative decrease in permeability with increase in strength.

Although it has been observed that the addition of either cement or lime can produce significant effects on the soil index properties (Locat et al., 1996; Russo & Croce, 2011), no definite assessment of such modifications has been identified yet. This is also because the effect of the treatment depends on several factors, such as the quantity of additive, curing time, physical properties, grain size distribution, water chemistry, and, mainly, the soil mineralogical composition (Federico et. al., 2015).

CHAPTER 3. THE MAR PICCOLO OF TARANTO

3.1 Introduction

The Mar Piccolo basin, in the South of Italy, is one coastal marine basin, whose sediments are affected by the presence of high concentrations of organic and inorganic contaminants, that has been included into the list of polluted Sites of National Interest (SIN sites) for which the environmental remediation has been identified as a national priority and required a deepening of the investigation.

The basin represents an ancient river valley, whose geological setting appeared strictly related to the geological evolution of the in-land formation, described in the Section 3.2. A brief description of the environmental features of the basin, of the pollution levels detected by the previous investigations, carried out at least in the first 3 m below the sea floor, and of its economic, social and naturalistic relevance within the territory is reported in Section 3.3.

The chemical composition of the sediments collected in the basin during the last campaign is described in the Section 3.4. It is worth noting that the data obtained should be read in association with the previous environmental characterization carried out in the basin.

3.2 Geological background

The Mar Piccolo (literally “Little Sea”) is an inner sea located on the North of the city of Taranto (south of Italy), with a surface area of 20.72 km², connected to the

open sea (Mar Grande in the Ionian Sea) through two channels, the smaller natural and the bigger artificial (Fig. 3.1). A North-South oriented promontory divides the Mar Piccolo into two sub-circular bays, called hereafter the First Bay and the Second Bay, which have a maximum depth of 12 and 8 m below sea level respectively.



Fig. 3.1 - Map of Taranto coastal area.

The Taranto area is located in the south-western sector of the Apulian Foreland along the Ionian Sea (Fig. 3.1) and the geological setting is strictly related to the geological evolution of the Bradanic Trough and the nearby Apulian Foreland. The area is essentially characterized by a thick Mesozoic carbonate basement, belonging to the Apulian Foreland, overlain by the Bradanic succession, represented by the Plio-Pleistocene transgressive deposits, covered by Pleistocene-Modern fine-grained sediments, which occur in alluvial, transitional and marine settings (Lisco et al., 2015).

According to geological literature (Cotecchia et al. 1989, Cotecchia 2005; Lisco et al., 2015 and references therein), therefore different geological formations could be

distinguished within both the Taranto area and the Mar Piccolo basin, as briefly described below and shown in the map of Fig. 3.2.

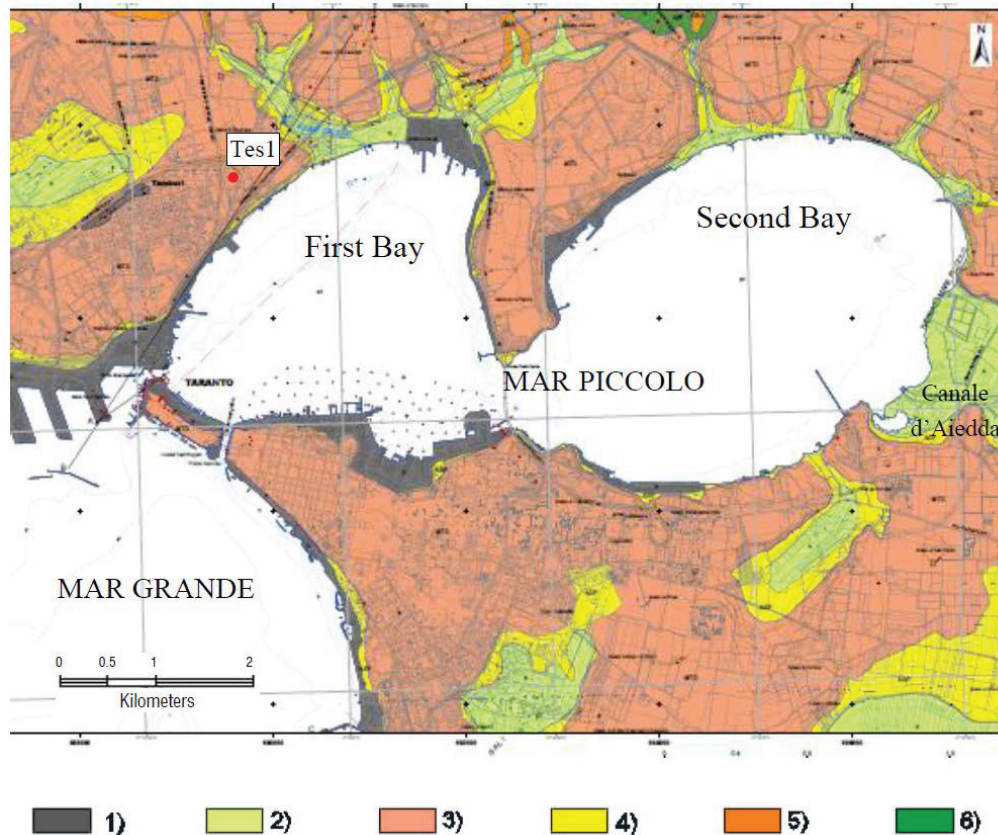


Fig. 3.2 - Geological map of the Taranto area (Lisco et al. 2015). Key: 1) Anthropogenic deposits, 2) Continental deposits (fluvial and palustrine deposits) 3) Marine terraced deposits, 4) Sub-Apennine Clay, 5) Calcarene di Gravina, 6) Calcare di Altamura.

The oldest and deeper formation (Fm) is the Calcare di Altamura Formation (CA, Late Cretaceous), that is represented by a succession of medium to fine-grained limestones, fossiliferous limestones and, subordinately, dolomitic limestones. The CA could be regarded as permeable, due to the fracturing and karstic dissolution phenomena, both affecting the rocks. The top of the CA was recognized at 38.8 m in the in-land borehole named tes1, located at north of the basin, as reported in Fig. 3.2. It is

anticipated that the CA was not intercepted by boreholes collected in the First Bay during the last campaign carried out in the basin (Section 1.3), despite the drilling depth varied between 44.3 m to 11.6 m bsf. Indirect surveys carried out in the First Bay (Cotecchia et al. 1991) suggested that the top of this formation tends to deepen from the Northern part of the bay (i.e. 20 m bsf) to the South (i.e. 80 m bsf).

Outcropping successions are mainly characterized by shallow-marine deposits comprising carbonates of the Calcarene di Gravina Formation, silty clay hemipelagites of the Sub-Apennine Clay Formation and locally regressive coarse-grained bodies.

The Calcarene di Gravina Fm (GRA, Late Pliocene – Early Pleistocene, Fig. 3.2), transgressively overlies the Cretaceous carbonate rocks, and is about 50 m thick. In the area, the GRA consists of bioclastic calcarenites, from white to yellow coloured, mostly with a medium permeability, and with a variable degree of diagenesis. The top of the GRA was recognized at 34.5 m in the in-land borehole tes1 (Fig. 3.2), while in the basin it was found only in the northern part of the First Bay at a depth of 10m bsf, where the calcareous formations are less deep.

The shallow-water calcarenites (GRA) changes vertically and laterally into the hemipelagic deposits of the Sub-Apennine Clay Fm (ASP, Early Pleistocene, Fig. 3.2), which outcrops extensively in Southern Italy. This formation succeeds the carbonate sedimentation on the foreland side of the basin and represents the shallowing of the basin in the other sectors of the Bradanic Trough. Toward the Apennines chain, the ASP covers the Apenninic allochthon, while in the epicenter of the trough the same formation overlays turbidite deposits.

The ASP consists of very stiff grey-bluish marl-silty clays, from 30 to 100 m thick, with fossils and high carbonate contents. Usually, the top part of the formation, is formed by an oxidised yellow-brown clay, that is the product of physical and chemical processes of soil alteration (Cafaro & Cotecchia, 2001). In addition, thin levels of sand and limestone are often observed and carbonate and/or sulphate-rich marks are also present. The deposit, mostly of low permeability, represents the ground substrate of phreatic layers confined in shallow aquifers. The top of the ASP was recognized at 5.2 m in the in-land borehole tes1 (Fig. 3.2), while in the First Bay the top of the ASP

varies between 6.2m and 43 m bsf and has been eroded in the northern area. Usually the shallow portion of the ASP appears highly altered and rich in sand and silt.

Marine, transitional and fluvial terraced deposits (MTD; Middle-Late Pleistocene Fig. 3.2) represent the upper part of the succession outcropping in the Taranto area. They consist of coarse-grained deposits, lying conformably or with an erosional contact on the underlying formations (ASP, GRA e CA). Lastly, Holocene and Modern deposits occur in alluvial and marine settings. In the Mar Piccolo basin, the top of the ASP clays has been eroded, and clayey-silty sediments, occasionally rich in sand, deposited during the Late Pleistocene and Holocene.

The sub-elliptical shape of both Mar Grande and Mar Piccolo derives from the combination of different geological processes, which occurred during the Pleistocene, such as the regional Tectonic uplift (Doglioni et al., 1994), the glacial eustatic sea level variations (Belluomini et al. 2002) and the consequent variations of the hydrographic network energy (Mastronuzzi & Sansò, 2002). The two depressions that constitute the Mar Piccolo are supposed to be ancient river valleys that was incised during the continental phase related to the Last Glacial Maximum (20.000-25.000 years BP; Ashley & Sheridan, 1994; Zaitlin et al., 1994) and then they were submerged by the sea during the Holocene marine transgression (Mastronuzzi & Sansò, 2002).

According to the literature (Lisco et al., 2015), since the Medium Pleistocene the features of the sedimentation environment of the Mar Piccolo varied both in time and space: marine, marine-coastal, river, lagunar and locally continental. In addition, the remoulding of the top layer of sediments that is consequent to the anthropic activities in the area should be considered. The sediments forming the Mar Piccolo basin have been deposited in these time-varying environmental conditions, with an erosional contact on both the ASP and the GRA.

In 2016, the Special Commissioner for urgent measures of reclamation, environmental improvements and redevelopment of Taranto, Dr Vera Corbelli, appointed by the Italian government, promoted an investigation campaign aimed to the multidisciplinary characterization of the Mar Piccolo, and in particular of the First Bay submarine sediments. The features of the litho-technical units have been distinguished within the

Mar Piccolo basin by means of both the visual inspection of the samples collected along the 19 boreholes (Fig. 3.3) and the analysis of the sediment composition and properties, also supported by the lithographic details and the reconstruction of the paleogeographic evolution of the Mar Piccolo sedimentation basin, carried out by the Geology Research Unit of the University of Bari. The present paragraph reports the litho-technical units recognised in the basin.

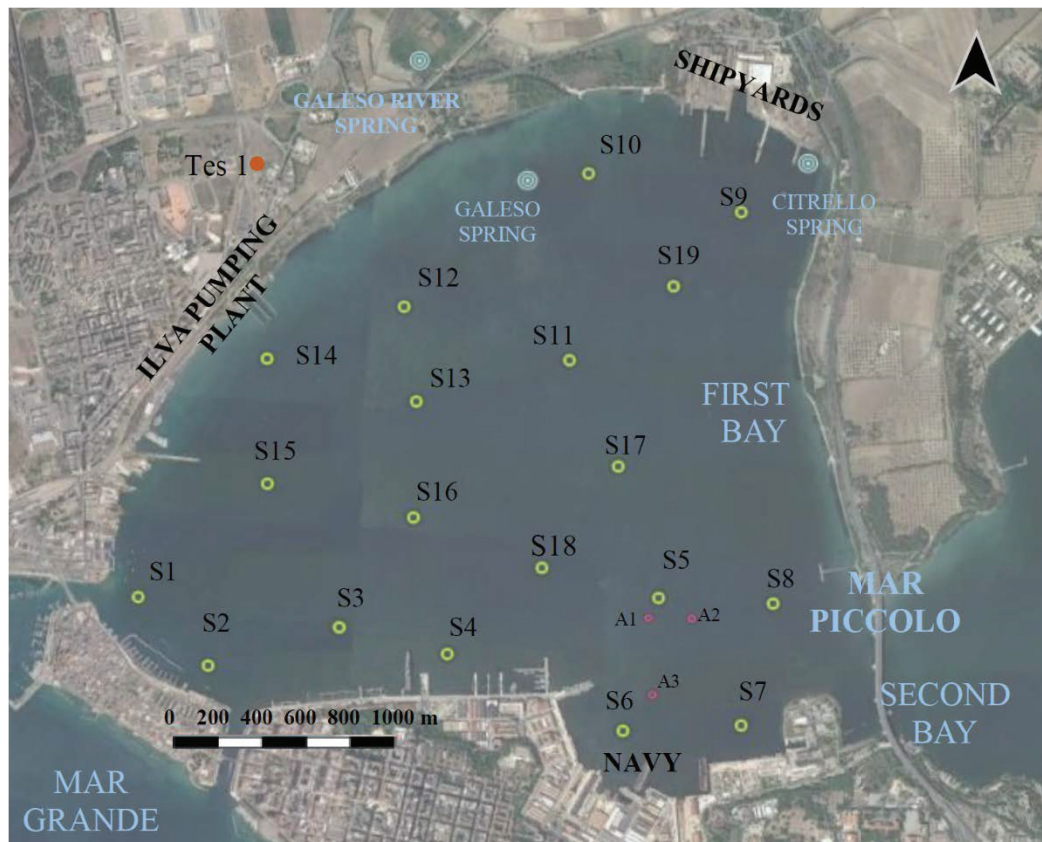


Fig. 3.3 - Sampling sites of the investigation promoted by the Special Commissioner for urgent measures of reclamation, environmental improvements and redevelopment of Taranto in the First Bay: Campaign CS_P (sites S3, S6, S8, S9, S12, S17); campaign CS_2017 (sites from S1 to S19), CPTU (sites S2, S5, S6, S8, S10, S12, S13, S16, S17, S18); in land borehole Tes 1. A1, A2, A3 boreholes from ARPA campaign.

The shallow unit, about 1.5 m thick, is constituted by either clay with silt or sandy to slightly sandy silt with clay. It can be very rich in organic matter and it is characterised by fluid consistency ($q_u < 40$ kPa). Its deposition occurred in recent period in the marine environment. It's worth noting that the soil deposition in the Mar Piccolo basin may have suffered a significant remoulding also due to the human activities carried out in the area. Sediment resuspension occurs regularly in the basin because of important maritime activities and dragging of ship anchors in and around the harbour and the Navy. Furthermore, Mastronuzzi et al. (ARPA report 2014) reported that in recent years hydrodynamic events may have affected sediment deposition in the basin. Indeed, recent significant alluvial events (e.g. 2005, 1996, 1883) caused the arrive into the basin of great amount of water and materials, causing the sea rising. The second unit, on average 6 m thick, is constituted by grey-coloured sandy or clayey-sandy silt or clay with silt, with consistency varying from fluid to soft ($q_u < 80$ kPa). A similar unit outcrops in land, in the northern coast of the First Bay, and includes the coastal-alluvial sediments of the Galeso River. In the southwestern part of the First Bay, this unit has sandy levels, from medium-dense to loose degree of density and it is up to 6.5 m thick.

The two abovementioned soil units have been found in all the boreholes drilled during the present geotechnical investigation. At higher depth the boreholes cross a third unit (i.e. third lithotechnical unit) with complex and variable litho-technical features, deposited mainly in the areas of a paleo-riverbed (Lisco et al., 2015 and references therein). This unit has not been found along some boreholes closer to the shoreline, that are S6 and S7 near the southern coast, S9 at North or S14 close to the western coast. Clayey silt or silty clay alternates with silt and silt with clay, sometimes sandy. Occasionally, layers rich in sand and gravel and peaty levels can be found. The consistency of this unit increases with depth, from very soft at the top ($q_u < 40$ kPa), to soft ($q_u < 80$ kPa) at larger depth. The deeper layers of this unit have firm ($q_u < 150$ kPa) to stiff consistency ($q_u < 300$ kPa), respectively.

A fourth unit, on average 3.8 m thick, has been found locally, along the boreholes S11, S19 and S9 (see legend), S5, S17, S11, S10, S12. It is a sandy silt, or silt

with grey or yellow-grey sand, characterized by variable consistency. Some boreholes (e.g. S19 in G-G') have intercepted pebbles and gravel levels at the transition to the underlying unit, i.e. that of the weathered portion of the Sub-Apennine blue Clay (ASP) formation (fifth lithotechnical unit). This unit consists of either silty clays or clayey (with sand levels) silts of very stiff consistency ($q_u = 200-500$ kPa). Lastly, the sixth unit, hard in consistency, corresponds to the intact portion of the same geological ASP formation. It consists of grey-bluish marl-silty clays that have been found only along some boreholes (S6, S7, S11, S13, S17 e S19).

It is worth noting that in boreholes S9 and S10 the Sub-Apennine Clay is absent, and the fourth unit is in contact with the Calcarene di Gravina formation, which has been intercepted in the area of submarine springs in the northern coast of the First Bay. Finally, although never intercepted by the marine boreholes the calcareous bedrock completes the whole stratigraphy and it is represented by the Calcare di Altamura and the Calcarene di Gravina formations (Sollecito 2019 in prep.).

3.3 *Environmental background*

The environmental setting of the Mar Piccolo basin is the product of both natural and anthropic conditions, which make this site a unique example of environmental resilience where, however, high levels of risk still persist.

The carbonate formation which constitutes the basic formation in the basin holds a deep artesian groundwater body, which discharges fresh water into the sea through several submarine springs (locally called "Citri"), where the clays have been eroded. The most important springs in the First Bay are the "Galeso" (mean flow of 750 m³/s, Fig. 3.4) and "Citrello" (mean flow 350 m³/s,) springs, shown in Fig. 3.4. The freshwater of the "Citri" has a uniform temperature comprised between 18°C and 25°C, therefore, they locally affect both temperature and salinity of seawater, that in the Mar Piccolo is approximately equal to 35,07‰. Moreover, several small tributary rivers flow in the basin, the most important of them is the 'Galeso river' in the First Bay with a mean flow of 50000 m³/day (Cardellicchio et al., 2007 and 2015). Furthermore, the First Bay is the only connected to the Mar Grande (and the Ionian Sea) through the

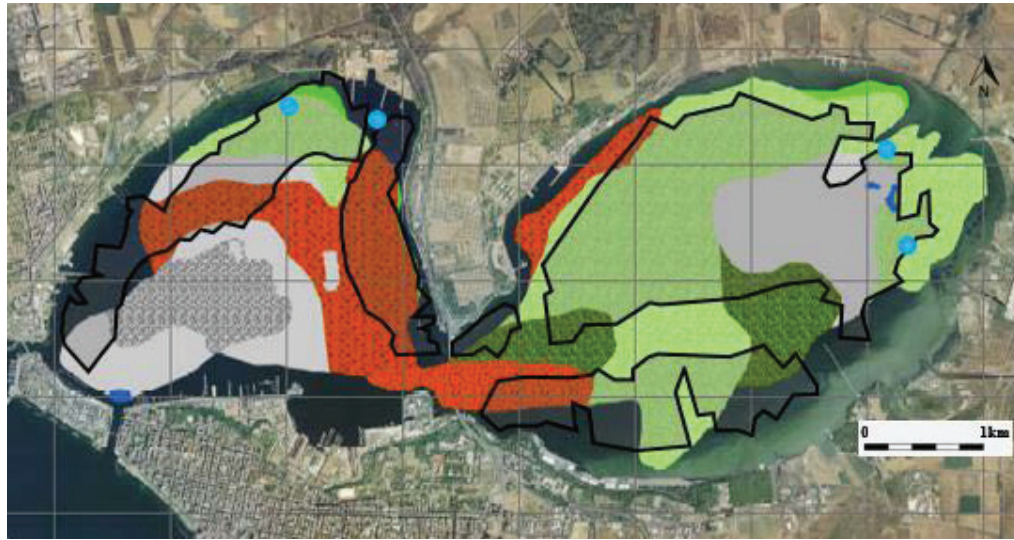
Navigable Channel and Porta Napoli Channel. This is the reason why the Mar Piccolo shows lagoon features, in which the water circulation is restricted, and the tidal range is reduced, not exceeding 30-40 cm (Sollecito 2019 in prep.).



Fig. 3.4 – Swirling seawater in the direction of Galeso Submarine artesian spring in the Mar Piccolo area, located as in Fig. 3.3.

All these factors contribute to create a rich marine ecosystem, typical of the transition environments. The biocenosis map (Fig. 3.5) shows that some portions of the basin are constituted by seabed in which the presence of algae is absent or rare (dark grey and grey areas in the map respectively), while large parts of the seabed are covered by several species of algae and macroalgae. The basin is also considered one of the most important area of mussel farming in Europe, with an annual production of bivalves of about 40000 tons per year (Caroppo et al., 2012), which is prevalent in the First Bay. Fig. 3.5 shows the boundaries of the mussel farming area, where the abundance of pales, used for the mussel cultivation, hosts a rich ecosystem of fouling community. According to WWF Report (2013) and ARPA Puglia Report (2014), in the First Bay of the Mar Piccolo there are many animal and plant species protected by the Barcelona Convention and included in the lists of sensible organisms for preserving

biodiversity (i.e. *Pinna Nobilis* mussel, seahorse, *Caretta caretta* turtle) (Sollecito 2019 in prep.).



*Fig. 3.5 - Biocenosis map of the Mar Piccolo of Taranto. Key: grey and dark grey areas represent seabed without algae and with scarce presence of algae respectively; orange areas represent seabed covered by macroalgae; green areas represents seabed covered by several species of algae, (e.g. *Cymodocea nodosa*); blue areas are covered by debris of shell fragments; black lines define the mussel farming areas; blue circles represent the main freshwater springs 'Citri' (from Technical Report ARPA 2014).*

However, the Mar Piccolo is also an example of Mediterranean coastal marine ecosystem whose biological balances have been modified because of the considerable environmental stress due to the development of human activities. Since the 1960s, the city of Taranto and his coastline have been subject to an intense industrialization process that caused important environmental changes. The presence in the in-land area of the largest steel factory in Europe (ILVA), a major oil ENI refinery one of the largest cement and concrete plant in Southern Italy (CEMENTIR), an into the basin of an abandoned shipyard (built at the beginning of the twentieth century) and a very large Italian Navy port (that has been active for 130 years), a navy arsenal, and other industrial activities, caused high environmental contamination. In addition to industrial sources of pollution, the basin received the discharges of chemicals, drained from the

surrounding agricultural soils in the basin (Caroppo et al., 2012) as more than 80 % of the province of Taranto is used for farming, and of 14 sewage pipes from the nearby towns. Since 2001, 7 of the 14 municipal discharges were fitted out with treatment plants or relocated to the Gulf of Taranto, with the consequent lowering of nutrient discharges and the improvement of the water quality (Kralj et al., 2015).

Various chemical characterization (ICRAM, 2005, ISPRA, 2010; Vitone et al., 2016) and researches have shown so high levels of contamination as to consider the Mar Piccolo of Taranto one of the most polluted areas in Italy (Cardellicchio et al. 2009). The pollution in the sediments is due to both heavy metals (lead, cadmium, mercury, copper, zinc, etc.) (Petronio et al., 2012), and organic pollutants (asbestos, polycyclic aromatic hydrocarbons PAHs, organic solvents, polychlorinated biphenyls-PCBs, dioxins) (Cardellicchio et al., 2007). A more severe condition was found in the First Bay of the Mar Piccolo. Therefore, the benthic communities observed in the Taranto seas are severely affected by the anthropic activity, even if, recently, an improvement of the ecological condition of the basin have been recorded (Cardellicchio et al., 2015). Edible marine organisms were collected in the First Bay of the Mar Piccolo, to investigate contamination level and public health risks, associated with consuming fish and sea-food harvested from these areas. In most species Cd, Pb and PCBs were over the limits set by European Community Regulation (Cardellicchio et al., 2015). In consequence of the high levels of chemicals found in both the water column and water biota, to reduce the risk for human health, both the commercialization and consumption of the mussels coming from the First bay have been prohibited.

The scarce water circulation which characterized the basin also encourages the organic matter sedimentation that plays an important role in the transport and accumulation of pollutants in sediments. The amount of total organic carbon, TOC, in the Mar Piccolo basin may reach values of 8% in the first centimetres, that appear higher than those found for the Adriatic and Ionic stations away from the coast (generally less than 2%). TOC in deep-sea clays reaches values from 1% to 2%, but in coastal areas and estuarine muds it may be as high as 10%. It is worth noting the human activities carried out in the basin may be responsible of a significant in situ remoulding of the sediments,

which could alter the natural process of sedimentation and bioturbation activity. Furthermore, recent alluvial events (e.g. 2004-2006, 1883) caused the arrive into the basin of great amount of materials, which couldn't easily flow away due to the semi-enclosed feature of the Mar Piccolo basin Sollecito 2019 in prep.).

It should be noted that all the chemical and physical characterization carried out in the years in the basin involved at least the first 3 meters below the sea floor, while no data were available about the pollution state of sediments at medium and large depths. Moreover, the only geotechnical data available to characterize the sediment came from three sampling sites within a limited area in the South of the First Bay of the Mar Piccolo, collected in 2013-2014 (ARPA Puglia campaign), when depths larger than 3.8 m below the seafloor were explored for the first time. Peculiar properties were recognized in the sediments and an anomalous variability of soil properties with depth, not consistent with the homogeneity in mineralogy, was noted (Vitone et. al., 2016). This evidence suggested the necessity to investigate the occurrence of complex coupling process between the soil components and the contaminants present. However, the inaccuracy of chemical characterization of the collected samples and the lack of chemical data below 3 m from the sea floor, made not feasible not only the assessment of the coupling phenomena, but even a first selection of sustainable strategies for the remediation and management of the entire basin.

The relatively shallow water level in the Gulf of Taranto yield large amount of mussels *Mytilus Galloprovincialis*. It follows that Taranto seas are a noteworthy economic resource, being the site of intensive mussel farming. In addition to the commercial aspect, this activity has a close connection to the traditions of the city as its history that dates back to the sixteenth century. In fact, the mussel breeder is the oldest job of the tarantine tradition. This industry has grown from the idea of an enterprising local to become a big export earner. Until 2007, the annual output amounted to 30.000 tonnes of mussels. Only a part of the locally harvested seafood was used for home consumption, while most was exported to European Economic Community countries (Cardellicchio et al., 2007). The trade of this typical product renamed "black gold of Taranto", has been repeatedly hit by restrictions because of the strong contamination. The picking

and handling of mussels grown in the first basin (in Italian, Primo Seno), has been forbidden for three years (Decree of the Health Authority n. 1989 of the 22/07/2011) and then its collection and destruction has been ordered (Decree of the Health Authority n. 1765 of the 11/06/2012). Now mussels are still farmed in Taranto Sea, but most of them have been moved to the Mar Grande and all the others can only be kept in the first basin water for the initial phase of ripening, then they need to be moved in the Mar Grande too for the last maturation, in a different temperature and water condition.

3.4 *Chemical composition of sediments*

Previous studies carried out in the Mar Piccolo site (e.g. Cardellicchio et al., 2007; 2009; Petronio et al., 2012), have investigated the pollutants within the first 2-3 m of sediments and they have found high concentration of metals and metalloids (As; Pb; Cd; Hg; Cu; Zn; Cr; Ni; V; Al and Fe), Persistent Organic Pollutants (i.e. PAHs, PCBs and HC). The origin of these contaminants could be related to the presence of human activities carried out in the area. Furthermore, the presence of some compounds (e.g. Cd, Pb and PCBs) in most edible species over the limits set by European Community Regulation, led to the definition of at least some compound as pollutants.

However, the chemical testing programme carried out on shallow soil, at least up to 3 m below the sea floor, prevented both the assessment of the thickness of contamination and the definition of contamination vertical profiles helpful to find the background values of contaminants, which are specific for the deposits.

The new chemical characterization, that is reported in this study, involve instead sampling depths up to 44 m below the seafloor. The data relate to the average depth of each sample tested in the chemical laboratory. The chemical samples were usually 1.5m long. The values were compared with the limits defined by both site-specific law (ICRAM, 2004) and national law (D.Lgs. 152/2006). The values are reported in Tab. 3.1 for each heavy metal considered.

Metals	Unit	Site-specific law ICRAM 2004	National law D.Lgs. 152/2006
As	mg/Kg ss	20	50
Cd	mg/Kg ss	1	15
Be	mg/Kg ss	-	10
Co	mg/Kg ss	-	250
Cr	mg/Kg ss	160	800
Hg	mg/Kg ss	0.8	5
Ni	mg/Kg ss	100	500
Pb	mg/Kg ss	50	1000
V	mg/Kg ss	-	250
Cu	mg/Kg ss	45	600
Zn	mg/Kg ss	110	1500

Tab. 3.1 - Limits of heavy metal concentration.

The concentrations of the persistent organic compounds (Polycyclic Aromatic Hydrocarbons, PAHs, and Polychlorinated Biphenyls, PCBs) are described and compared with the thresholds reported in Tab. 3.2.

Compounds	Unit	Site-specific law ICRAM 2004	National law D.Lgs. 152/2006
PAHs	mg/Kg ss	4	100
PCBs	mg/Kg ss	0.19	5

Tab. 3.2 - Limits of PAHs and PCBs concentration.

3.4.1 *Heavy metals*

Based on the analysis of the human activities carried out in the area and on previous chemical characterization, together with the hazard for human health, the presence of 11 main heavy metals was investigated into the campaign carried out in the Mar Piccolo sediments.

The Arsenic, As, exceeds the site-specific law limit (20 mg/kg ss) within the first meter bsf in the sites S4, S6 and S7. High concentrations have been detected in 1.5 -3.0 m bsf in site S7. In few cases, at higher depth, the concentration approaches the limit. The Cadmium, Cd, exceeds the site-specific law threshold (1 mg/kg ss) only in the case of the shallow sample of the site S4. In the first meter below the seafloor, the concentration of Mercury, Hg, exceeds the site-specific limit (0.8 mg/kg ss) in almost all the sites in the south and in the middle of the First Bay: S2, S4, S5, S6, S7, S8, S11, S15, S16, S17, S18, S19, with values above the law limit (5 mg/kg ss) in sites S4, S6, and S7. The contaminant tends to deepen in sites S7 and S4 since values above the site-specific limit were found up to 3 m bsf. The concentration of Lead, Pb, is beyond the site-specific law limit (50 mg/Kg ss) in the first meter bsf in sites S1, S2, S3, S4, S5, S6, S7, S8, S11, S15, S16 and S18. In S4 and S7, the concentration of Pb exceeds the site-specific limit at 1.3 – 3.0 m bsf. In the first meter below the seafloor, the concentration of Copper, Cu, exceeds the site-specific limit (45 mg/kg dss) in S4, S6, S7, S16 and S18. The concentration of Zinc, Zn, exceeds the site-specific limit law (110 mg/Kg dss) in the sites S2, S3, S5, S6, S7, S16, S18 and with a minor intensity in sites S7 at 2.5m.

Heavy metals clearly exhibited a higher concentration in the first meters below the sea floor with respect to values found below, defining a layer of sediments contaminated by metals due to human contributions, especially in the southern and central areas of the First Bay. More information's have been reported in the report of Environmental Technologies Research Group (Notarnicola et al., 2017).

The mobility and the bioavailability of metals should be carefully considered with reference to the hydraulic conditions of the basin (e.g. the presence of Springs), and events of resuspension and bioturbation which usually occur at the top layer of marine deposits.

Indeed, even if metals tend to form insoluble sulphides (with the following order of solubility $\text{Hg} < \text{Cu} < \text{Pb} < \text{Cd} < \text{Zn} < \text{Ni}$), events of varying nature and extent may, however, induce oxidation of metallic sulphides, resulting in the possible release of metals into the water column and accumulation by biota (Delaune et Smith, 1985; Calmano et al., 1994, Petersen et al., 1997).

3.4.2 *Organic compounds*

The PAHs (e.g. benzo(a)pyrene, fluoranthene), here expressed as summation of the congeners, are Polyaromatic hydrocarbons with benzene cycles. They have low solubility, good stability and strong adsorption in soils and aquifers. With reference to Mar Piccolo basin, concentrations of PAHs above the site-specific limit were found in sites S1, S2, S3, S4 within 1m bsf.

Very high concentrations of PCBs, expressed as the summation of the congeners, were found at the site S4 and S6 in the Navy area, above the value of 5 mg/kg ss (D.Lgs. 152/2006), while sites S16, S19, together with S4 at 3.0 m are polluted by this compound, which has concentration above the site-specific limit (0.19 mg/kg ss).

As in the case of heavy metals, the organic compounds were found in elevated quantity in the shallow layers of sediments, but with respect to heavy metal, the pollution due to persistent organic compounds is strictly about the southern area of the bay.

CHAPTER 4. RESEARCH PURPOSES

The city of Taranto represents one of the most complex industrial sites in Europe. As a consequence of the heavy industrialisation during the last 50 years, the complex ecosystem of the Mar Piccolo area started exhibiting unconfutable signs of environmental pollution enhanced by several uncontrolled discharged sewages, the activities of the Arsenal one of the main naval base of the Italian Navy and the fishing-boat fleet. A number of researchers (e.g. Lerario et al. 2003; ICRAM, 2005; Cardellicchio et al., 2007 and 2009; ISPRA 2010; Petronio et al., 2012; Di Leo et al., 2013; De Gisi et al., 2017a) have shown that also the submarine sediments in the Mar Piccolo contain high concentrations of heavy metals (e.g. As, Hg, Pb, Cd, Cu and Zn) and organic pollutants (i.e. PCBs, and PAHs).

In this context, the study aims at the identification of the most sustainable strategies for the remediation and management of the environmental contamination of the site. Experimental laboratory investigation has been carried out on sediments contaminated by heavy metals, PAHs and PCBs, to explore the sustainability of the following remediation technologies: in situ reactive capping and ex situ stabilization/solidification.

The remediation treatments for marine sediments has the limit of be influenced by the nature of the solid matrix and by grade of contamination; at the present state of the scientific knowledge, it is not possible to fix the application modalities basing only on similar case studies which are present in the literature and on the theoretical knowledge. Therefore, it is necessary a research campaign aimed to investigate the treatment effects and the eventual unfavourable interactions, in order to set up the most sustainable solution.

The intense laboratory testing programme has been carried out on sediments coming from the most contaminated areas of Mar Piccolo (taken up to depths of about 3.0m from the seafloor). Therefore, the experimentation required the design and the implementation of procedures and laboratory equipment to investigate the behaviour of different pollutants in a clay sediment with soft consistency. The experimental plan addresses the following objectives:

- Environmental characterization of contaminated marine sediments;
- Assessment of the transport of contaminants from the sediments in order to either predict or evaluate the main effects of remediation efforts;
- Analysis of the effects of reactive capping on the contaminant migration and the performance of different systems (i.e. permeable reactive mats and reactive granular materials);
- Examination of the competitive multi-contaminant adsorption onto reactive capping;
- Preliminary assessment of the chemical and geomechanical properties of treated sediments when using different types and contents of both binders and reagents;
- Determination of the comparative performance of different reactive materials (i.e. activated carbon, organoclay and biochar) for in situ and ex situ sediment management;
- Evaluation of the feasibility of S/S treated sediments for beneficial use.

CHAPTER 5. RESEARCH PLAN

5.1 Introduction

For achieving the objectives described in Chapter 4 an experimentation study has been made at both laboratories of Chemistry and Environmental Technologies and Environmental Geotechnics of Politecnico di Bari.

The experimentation was divided in two distinct phases with increasing deepening, i.e.: preliminary phase and advanced phase (Fig. 5.1); every experimental phase involved the physic-chemical characterization of samples of contaminated sediments and the execution of experimental treatability tests.

The first phase (preliminary phase) allowed to obtain information on the interaction between the contaminated sediment and the remediation treatments. Special attention has been attributed to the quantification, in different conditions, of the desorption kinetics of contaminants from the sediment (i.e. the migration of contaminants). Moreover, the preliminary phase allowed to definition of the experimental methods, including analytical protocols for the determination of pollutants in different matrices.

The second phase (advanced phase), through an optimized experimentation, allowed to investigate the processes of transport, adsorption and degradation of contaminants over time and to verify the performance of different design solutions, allowing the optimization of the solutions experienced in the previous phase.

The submarine sediment used for the tests has been sampled down from the First Bay of the Mar Piccolo Basin of Taranto. In particular, in the preliminary phase several samples with different contamination have been used; in the advanced phase, all the tests have been performed on a marine sediment made up by mixing several samples from the seafloor up to 1.5 m below, to test different technologies on the same prototype-sample. Laboratory activities involved the environmental characterization of the sediment samples following a screening due to eliminate debris, mussels' shells and anthropic materials.

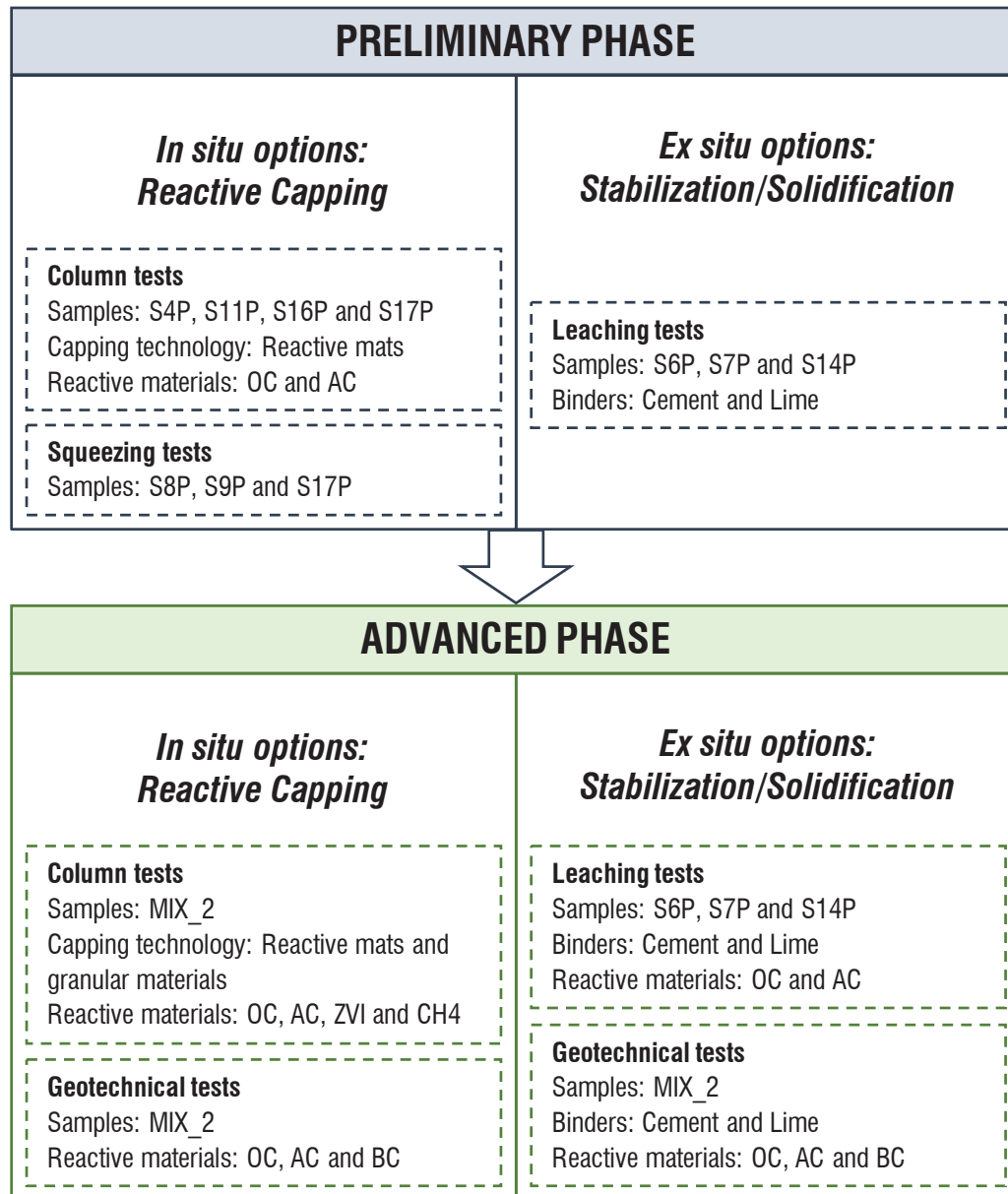


Fig. 5.1 - Research plan. Key: RCM, Reactive Core Mat; AC, Active Carbon; OC, Organoclay; CH4, inhibitor of methane; ZVI, Zero Valent Iron.

5.2 Preliminary phase

5.2.1 In situ options

The treatability tests for in situ remediation options consist in laboratory-scale simulations of the environmental conditions of the study area. The test device was designed, machined and assembled to test the efficacy of several capping solution in different conditions (it will be described in Section 6.4).

In this phase, the experimentation of capping technology (i.e. reactive permeable mats with either organoclay or active carbon) was performed on 4 marine sediment samples with different features (e.g. particle-size distribution, organic matter, classes of contaminants). For each sample 4 scenarios, divided according to the presence of the capping layer or the type of hydrodynamic condition, have been simulated (Fig. 5.2; Tab. 5.1).

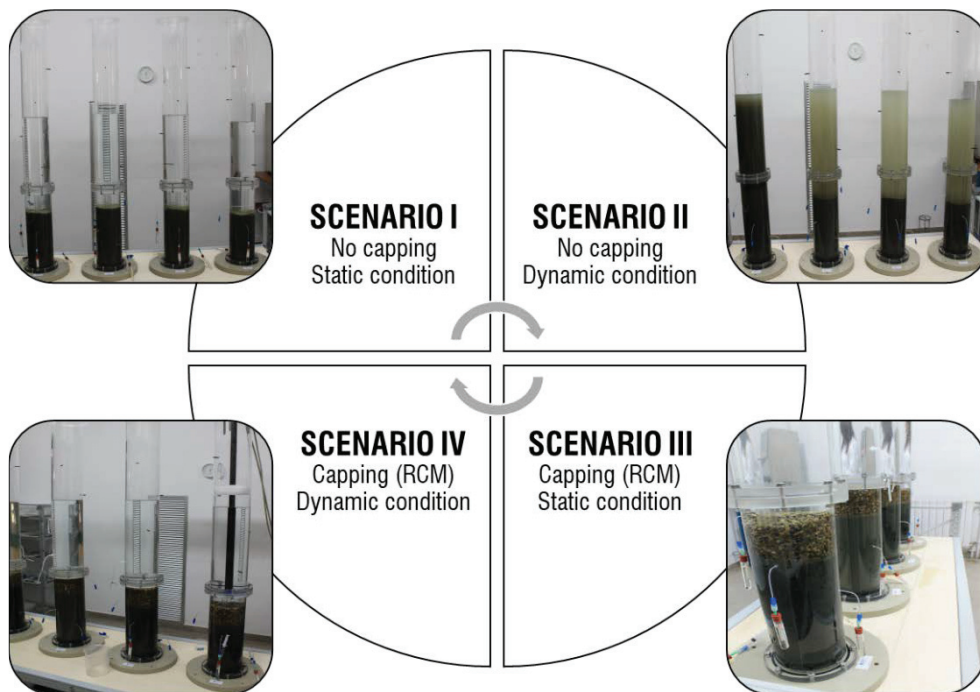


Fig. 5.2 - Experimental plan for column tests (preliminary phase).

SEDIMENT SAMPLES	CAPPING	HYDRODYNAMIC CONDITIONS
S4P	No capping	Static condition
		Dynamic condition
	RCM with OC	Static condition
		Dynamic condition
S11P	No capping	Static condition
		Dynamic condition
	RCM with OC	Static condition
		Dynamic condition
S16P	No capping	Static condition
		Dynamic condition
	RCM with AC	Static condition
		Dynamic condition
S17P	No capping	Static condition
		Dynamic condition
	RCM with AC	Static condition
		Dynamic condition

Tab. 5.1 - Experimental plan for column tests (preliminary phase). Key: RCM, Reactive Core Mat; AC, Active Carbon; OC, Organoclay

The reactors were monitored through the sampling and chemical analysis both of pore water and of water in column. The first sampling, that is representative of the scenario I, has been carried out 5 days after the beginning of the test. Dynamic conditions without capping were explored through Scenario II, to investigate the resuspension into the water column of the contaminated sediment as a consequence of a mechanical driving force. Scenarios III and IV have foreseen the placement of capping layer. In particular, in two columns it has been used a permeable reactive mat with organoclay (OC) and in the other two columns a permeable reactive mat with active carbon (AC). Finally, in these two scenarios, a layer of sand has been placed in order to reproduce an armor layer of bioturbation/protection (Fig. 5.3). Once the capping operations have been completed, a photographic monitoring phase has been started at fixed intervals

(e.g. 0, 1, 6, 12, 24 and 96 h) aimed to try to get a first estimate of sediments' consolidation rate. In analogy to the previous phases, water samples were taken for analysis of heavy metals, PAHs and PCBs (Tab. 5.2). The final scenario (IV) has again planned water stirring in the column and the withdrawal of several samples. At the end of the experiments, the mats used were subjected to chemical analysis of heavy metals, PAHs and PCBs (Tab. 5.2).

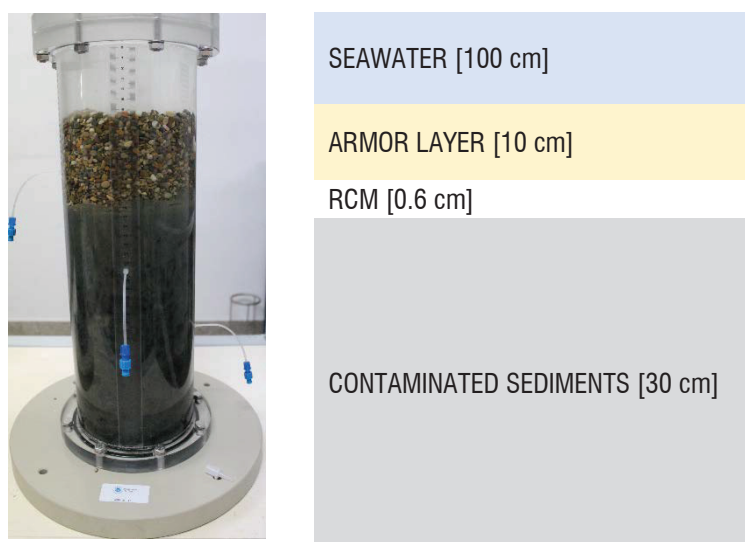


Fig. 5.3 - Capping design (preliminary phase).

Scenario I	<ul style="list-style-type: none"> ➤ Sampling of column water and determination of heavy metals, PAHs and PCBs ➤ Sampling of pore water and determination of heavy metals
Scenario II	<ul style="list-style-type: none"> ➤ Sampling of column water and determination of heavy metals, PAHs and PCBs
Scenario III	<ul style="list-style-type: none"> ➤ Sampling of column water and determination of heavy metals, PAHs and PCBs ➤ Sampling of pore water and determination of heavy metals
Scenario VI	<ul style="list-style-type: none"> ➤ Sampling of column water and determination of heavy metals, PAHs and PCBs

Tab. 5.2 - Samplings and chemical analysis (preliminary phase).

Consolidometer tests (or squeezing tests) were also performed on three sediment samples in order to check the extrusion of contaminated porewater from sediments due to loading, that is the placement of a cap layer. Although the contaminants may be immobilized in sediments effectively by using various capping methods, there is always a concern that these contaminants may migrate into the overlying water due to the consolidation induced by capping (Erten et al. 2011). The capping material represents a load at the top of sediments, that are mainly characterised by liquid consistency (in particular in the top 3 meters below the seafloor). This could also cause stability problems due to the huge consolidation settlements, that might lead to mobilization of the contaminants (NAPL, Azcue et al. 1998; heavy metals, Eek et al., 2007; PCBs, Lenhart et al., 2009; NAPL, Erten et al., 2012) due to the induced advection, but also to mechanical dispersion and diffusion phenomena. Therefore, it is important to determine not only the consolidation properties of the sediments but also the amount and properties of the fluid expelled during the consolidation process under the applied load. In order to contribute to the knowledge in this respect, the apparatus described in the Section 6.7.4 has been designed and realized to test in the laboratory the shallow sediments taken within the first two meters below the seafloor in the Mar Piccolo.

5.2.2 *Ex situ options*

The stabilization and solidification treatments have been made with different binders' typologies (i.e. cement and lime) in order to evaluate the different interaction entities with the contaminated sediments. Furthermore, to investigate the interaction of the sediments' characteristics (e.g. grain size distribution, organic matter and water content) with the binders, 3 sediment samples were treated by using different contents (by dry soil weight) of cement and lime. According to the environmental characterization of the sediments' samples, and through the analysis of scientific papers, the binders' percentages to be used in the mixtures, as well as the main parameters able to condition the phenomena of leaching and hardening, have been identified.

The experimental programme consisted into the preparation and chemical analysis of 3 mixtures for each sediment sample; the mixtures have been obtained by setting binders' content of 15% to the dry sediments. The water to dry material ratio of

the mixtures was imposed equal to 1 (i.e., same as the water to binder ratio determined for optimum workability). Tab. 5.3 shows the mixture design for S/S treatments.

Mix	Cement (C)	Lime (L)	Total binder (C+L)
A	15%	0%	15%
B	7.5%	7.5%	15%
C	0%	15%	15%

Tab. 5.3 - Mixture design for S/S treatments (preliminary phase)

The leaching tests (according to UNI EN 12457-2) have been carried out after different setting times: 1, 7, 14, and 28 days.

5.3 *Advanced phase*

5.3.1 *In situ options*

This phase has involved the optimization of capping solutions and, in particular, two different technologies of reactive capping have been tested. The testing programme aimed to investigate the feasibility and the effectiveness of in situ treatment of a sediment contaminated by heavy metal, PAHs and PCBs (named MIX_2) through the use of reactive permeable mats with either organophilic clay (OC) and active carbon (AC) or with reactive granular materials based on active carbon (AC), zero valent iron (ZVI) and an inhibitor of methane production (named CH4) (Fig. 5.4).

The simulated scenarios are summarised in Tab. 5.4, according to the both the presence of the capping layer and the type of hydrodynamic condition.

The reactors were monitored in static conditions for 20 days, with water sampling in the column for the determination of heavy metals, PAHs and PCBs. At the end of the static phase, the water in the columns has been completely removed in order to take samples of the layers that forming the cap and of the first centimetres of the sediments. The dynamic experimental phase involved the use of a mechanical stirrer in

order to simulate a hydraulic forcing according two different setups: (1) low intensity for a long time (100 rpm for 30 minutes) and (2) high intensity for a short time (300 rpm for 10 minutes). For both setups, water in the column has been sampled at fixed time intervals (1, 6 and 24 hours).

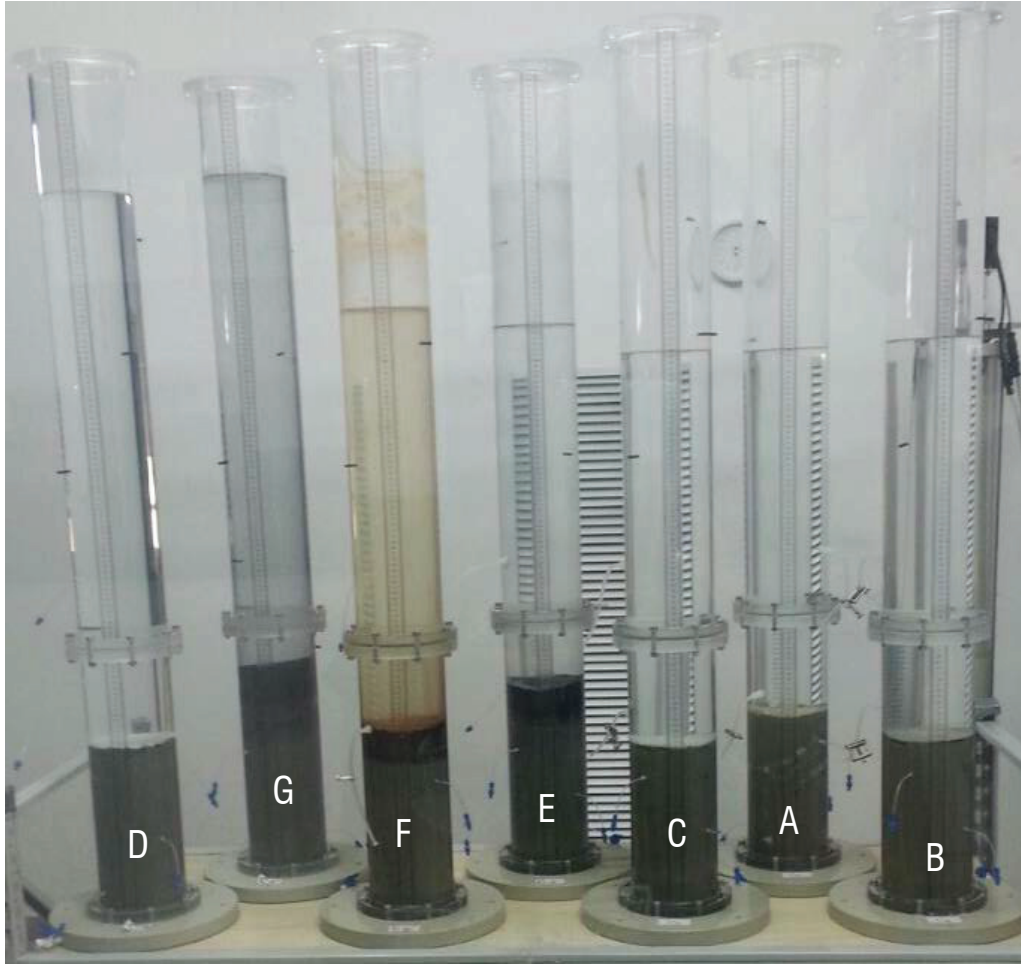


Fig. 5.4 - Capping design (advanced phase).

Key: A) SCENARIO 0: contaminated sediment without capping; B) SCENARIO 1: contaminated sediment capped by RCM with AC; C) SCENARIO 2: contaminated sediment capped by RCM with OC; D) SCENARIO 3: contaminated sediment capped by RCM with OC and AC; E) SCENARIO 4: contaminated sediment capped by granular materials with CH₄ and AC; F) SCENARIO 5: contaminated sediment capped by granular materials with CH₄ and ZVI; G) SCENARIO 6: contaminated sediment capped by granular materials with CH₄, ZVI, AC.

SEDIMENT SAMPLES	CAPPING	HYDRODYNAMIC CONDITIONS
MIX_2	No capping	Static condition
		Dynamic condition
	RCM with OC	Static condition
		Dynamic condition
	RCM with AC	Static condition
		Dynamic condition
	RCM with OC and AC	Static condition
		Dynamic condition
	Granular materials with CH ₄ and AC	Static condition
		Dynamic condition
	Granular materials with CH ₄ and ZVI	Static condition
		Dynamic condition
	Granular materials with CH ₄ , ZVI and AC	Static condition
		Dynamic condition

Tab. 5.4 - Experimentation plan for column tests (advanced phase). Key: RCM, Reactive Core Mat; AC, Active Carbon; OC, Organoclay; CH₄, inhibitor of methane; ZVI, Zero Valent Iron

At the end of the experiments, the capping materials and the first centimetres of sediments have been sampled for chemical analyses (i.e. determination of heavy metals, PAHs and PCB).

Furthermore, to investigate the hydro-mechanical effects of in situ mixing of reactive materials (i.e. the application of reactive materials to the surface of sediments without a diluent capping media), several geotechnical investigations were conducted. In fact, to maximize the benefits of the amendment, it is normally desirable to mix the amendment through the biologically active zone of the sediments; however, the hydro-mechanical effects of these alternatives are not known.

Several specimens were prepared by thorough mechanical mixing of the sediments with different additives (Tab. 5.5). In particular, the research investigated the effects of a treatment with biochar: a low-cost adsorbent and an economic substitute for the activated carbon, thanks to its several unique properties, which make it an

efficient, cost-effective and environmentally friendly material for the contaminants' removal (Oliveira et al., 2017; Silvani et al., 2017).

MIX	SEDIMENT	ADDITIVE
0	100%	0
1	95%	5% Organoclay
2	95%	5% Active Carbon
3	95%	5% Biochar

Tab. 5.5 - Mixture design for in situ mix treatments.

As reported in Tab. 5.6, the geotechnical testing programme included both physical and mechanical investigations (e.g. liquid and plastic limits, oedometer and direct shear tests) on the sediment mixtures. In particular, the testing programme on the treated sediments aimed to investigate their physical properties, composition and state, together with the compression behaviour and the shearing response.

To investigate the effect of the pore fluid composition on the geotechnical properties of the treated sediments, the tests were conducted by using both distilled and seawater.

LABORATORY TESTS	DISTILLED WATER	SEAWATER
Particle-size analysis	✓	
Liquid and plastic limits		✓
Specific gravity	✓	
Oedometer tests	✓	✓
Direct shear tests	✓	✓
Permeability tests	✓	✓
Determination of pH and Eh	✓	

Tab. 5.6 - Geotechnical testing programme (advanced phase, in situ options)

5.3.2 *Ex situ options*

The experimental results emerging from the S/S treatments made in the first stage of experimentation have showed the negative interaction between treatment efficiency and the presence of organic compounds. For reducing these effects, a set of tests, aiming at evaluating the benefits coming from the utilization of adsorbent materials as process additive, have been carried out.

In this phase, the research investigated the effects of treatment of 2 sediment samples (MIX_1 sediment contaminated by heavy metals and MIX_2 sediment contaminated by heavy metals, PAHs and PCBs) with cement and lime enhanced by the addition of adsorbent materials, such as organoclay (OC) and active carbon (AC). Tab. 5.7 show the complete prospect of these samples, made with the same stabilization and solidification procedure described for the preliminary phase.

For several samples leaching tests were carried out, according to the EN standard 12457-2, with different setting times (i.e. 1, 7, 14, and 28 days) for monitoring the progressive change.

After having verified the efficacy of mixtures as environmental remediation solution (Barjoveanu et al., 2018), the best solutions have been submitted to mechanical investigation aimed to verify that the technical characteristics of materials after S/S treatment are appropriate for beneficial reuse. In particular, to validate the applicability of the designed mixtures (in terms of mechanical performance) the treated sediments will be tested using the experimental programme summarised in Tab. 5.8.

Furthermore, to investigate the hydro-mechanical effect of biochar, the same tests reported in Tab. 5.8 were conducted on mixtures composed of either cement or lime (in percentage of 10% compared to the dry weight of the sediments) and biochar (in percentage of 5% compared to the dry weight of the sediments).

MIX	CEMENT (C)	LIME (L)	TOTAL BINDER (B)	ADDITIVE (A)	TOTAL REAGENTS (A + B)
4	10%	0%	10%	0%	10%
5	10%	0%	10%	5% OC	15%
6	10%	0%	10%	5% AC	15%
7	10%	0%	10%	2.5% OC + 2.5%AC	15%
8	0%	10%	10%	0%	10%
9	0%	10%	10%	5% OC	15%
10	0%	10%	10%	5% AC	15%
11	0%	10%	10%	2.5% OC + 2.5%AC	15%

Tab. 5.7 - Mix designs used to S/S treatments (advanced phase). Key: C, Cement; L, Lime; OC, Organoclay; AC, Active Carbon.

LABORATORY TESTS	CURING TIME		
	1 h	14 d	28 d
Particle-size analysis	✓		✓
Liquid and plastic limits	✓	✓	✓
Specific gravity	✓		
Oedometer tests			✓
Unconfined compression tests			✓
Determination of pH and Eh	✓	✓	✓

Tab. 5.8 - Geotechnical testing programme (advanced phase, ex situ options).

CHAPTER 6. MATERIALS AND METHODS

6.1 Introduction

In this chapter there will be a description of the materials and methods used during the experimentation. The intense testing programme aimed to explore the performances of both in situ reactive capping solutions and ex situ stabilization/solidification technologies as sustainable remedial options for contaminated marine sediments from “Mar Piccolo” of Taranto.

Firstly, sediment's chemical-physical properties and their contamination conditions were investigated. As a result, on the contaminated sediments, tests on remediation technologies have been made. In the end, the effects of treatments on the geotechnical properties of the submarine sediments have been evaluated.

Section 6.2 presents the sediments used in the experimental study, including the sampling procedure followed to obtain the marine sediments used of the research. Section 6.3 entails the materials used for the remediation treatments. The design details of the test devices and the associated testing protocols are given in sections 6.4 and 6.5. Section 6.6 includes the details of the analytical procedures followed to analyse the samples of water and sediment collected for each test. Section 6.7 provides the description of the geotechnical tests.

The laboratory tests have been carried out in two laboratories of the Politecnico di Bari, located in Taranto: Laboratory of Chemistry and Environmental Technologies and Laboratory of Environmental Geotechnics.

6.2 Contaminated marine sediments

The marine sediments used for the tests were sampled in the “Mar Piccolo” of Taranto in an integrated campaign - aimed to the multidisciplinary characterization of the contaminated system - prompted by the Special Commissioner for urgent measures of reclamation, environmental improvements and redevelopment of Taranto, Dr Vera Corbelli. Aiming at selecting the most effective and sustainable remediation solutions, the campaign involved experts from several research fields (i.e. biology, chemistry and geochemistry, geology, hydrology and hydrogeology, hydraulic and environmental and geotechnical engineering) and public research institutions (i.e. Politecnico di Bari, University of Bari and National Research Council).

The samples were taken along 19 sites within the First Bay of the Mar Piccolo Basin. They were taken during the preliminary campaign (April 2016), carried out only within the first meter below the seafloor and in ten sites, and the official campaign (from September to December 2016), in 19 sites from the seafloor up to 38 m below. The location of the sampling sites in the basin is reported in Fig. 6.1.

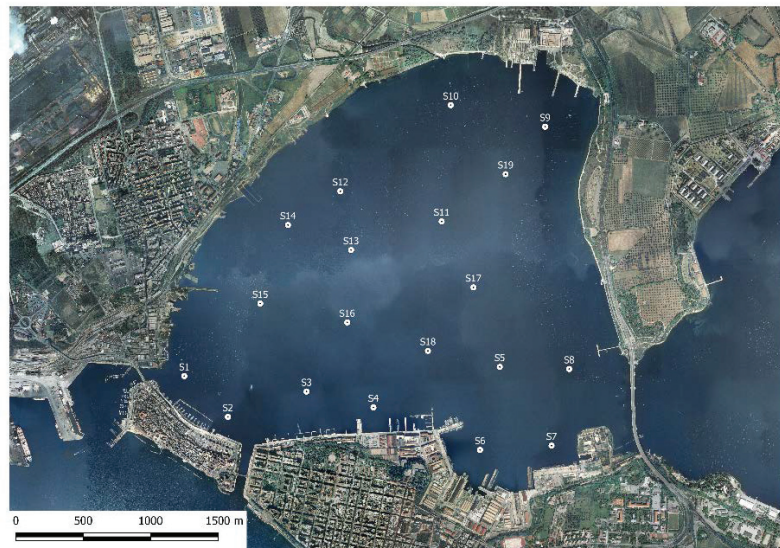


Fig. 6.1 - First Bay of the Mar Piccolo Basin (Taranto), and sampling sites of the investigation promoted by the Special Commissioner for urgent measures of reclamation, environmental improvements and redevelopment of Taranto.

The samples are named according to a protocol created by the Commissioner. For example, in the sample MPI S1A H CL TA, MPI is the location, i.e. the first bay of the Par Piccolo; S1 is the site (i.e. from S1 to S19 in the CS_2017 campaign and the letter P is added to the site name for the CS_P campaign); A identifies the vertical among the different verticals explored by the different research groups (A was the verticals for the environmental investigations); H is a letter identifying the sampling depth (e.g. A applies to samples collected between 0.0 and 1.5 m bsf, B applies to samples collected between 1.5 and 3.0 m bsf); CL and TA are indicating sample in liner for environmental testing (AM and TA were used for manual sampling).

The samples during the CS_P campaign are differently labelled, e.g. S3P_M_A, where P is referring to the CS_P campaign, M_A to manual sampling within the first meter.

During the preliminary investigation campaign, planned with the aim to check the accessibility to the selected areas, and start the laboratory testing, samples of the submarine sediments were taken by a team of expert scuba divers by means of direct push sampling methodology. For this purpose, a new sampling device was specially designed. it consists of 1m thin tube in PVC (0.08 m external diameter) with a screw cap with internal seal for the top while and a pressure cap with drain holes at the bottom. The sampler components are reported in Fig. 6.2.

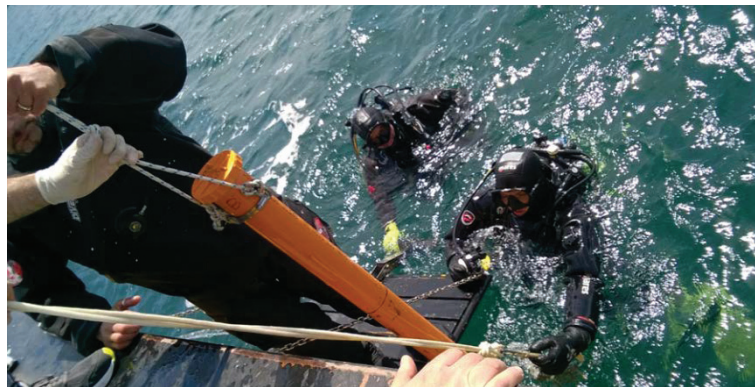


Fig. 6.2 - CS_P campaign: PVC tube used to collect samples within the first meter below sea floor and samples retrieving by means of scuba divers.

During the official campaign the sampling of the sediments within 1.5 m below the seafloor was executed by means of a drilling machine that has been installed on an offshore elevating platform shown in Fig. 6.3. The sample coring within the boreholes was carried out by means of 1.5 m length polycarbonate liners (Fig. 6.4), on purpose designed to avoid phenomena of cross contamination of the sediment through common metallic corers. This ampler has been selected to preserve both the chemical and the geotechnical properties of the materials.



Fig. 6.3 - The drilling machine installed on the elevating platform during the off-shore campaign in the Mar Piccolo.



Fig. 6.4 - Picture of one 1.5 m length polycarbonate liners for environmental testing.

The samplers, properly sealed, were stored in a fridge at a temperature of +4 °C, in order to avoid both loss and alteration of physical-chemical properties of the sediments.

Object of the present study is the most polluted top layer of sediment. Wet sediments were homogenized after removal of large debris and shells (particles larger than 2 cm) and transferred to airtight container that were stored in the dark at +4 °C until use. In particular, in the preliminary phase of the experimentation, the samples of preliminary campaign have been used; in the advanced phase of the experimentation, the tests have been performed on a marine sediment made by mixing several samples of the official campaign, to test different technologies on the same sample.

Tab. 6.1 reports the phase of the experimentation, the name of the sample, the sampling depth (m bsf) and the tested remediation technology.

PHASE	SAMPLE	DEPTH	TECHNOLOGY
Preliminary	S4P_M_A	0.0 – 0.5 m	Reactive capping
	S6P_M_A	0.0 – 0.5 m	Stabilization/Solidification
	S7P_M_A	0.0 – 0.5 m	Stabilization/Solidification
	S11P_M_A	0.0 – 0.5 m	Reactive capping
	S14P_M_A	0.0 – 0.5 m	Stabilization/Solidification
	S16P_M_A	0.0 – 0.5 m	Reactive capping
	S17P_M_A	0.0 – 0.5 m	Reactive capping
Advanced	MIX_1	0.0 – 1.5 m	Reactive capping and Stabilization/Solidification
	MIX_2	0.0 – 1.5 m	Stabilization/Solidification

Tab. 6.1 - Samples of submarine sediments object of the investigation (MIX_1 is a mixture of: MPI S1A A CL TA, MPI S2A A CL TA, MPI S4A A CL TA, MPI S5A A CL TA, MPI S16A A CL TA and MPI S19A A CL TA, sediments contaminated by organic and inorganic compounds; MIX_2 is a mixture of: MPI S3A A CL TA, MPI S7A A CL TA, MPI S8A A CL TA, MPI S11A A CL TA, MPI S15A A CL TA, MPI S17A A CL TA and MPI S18A A CL TA, sediments contaminated by inorganic compounds).

6.3 Materials for the remediation treatments

6.3.1 In situ options

3 types of small-scale test reactive permeable mats (or Reactive Core Mats, RCM) with either organophilic clay (OC) and active carbon (AC) have been used (Fig. 6.5). These mats were constructed by CETCO (company of Arlington Heights, IL) and represent an innovative remediation technique, consisting of a reactive layer containing one or more materials that are confined between a woven backing geotextile and a nonwoven top geotextile. Two of the types of mats, with a 0.6 cm thick, contained a reactive core consisting of mass of either OC or AC per area equal to 3 kg/m^2 . The remaining one mat, with a 1.0 cm thick, contained a double layer of reactive material consisting of OC (3 kg/cm^2) and AC (3 kg/cm^2). Tab. 6.2 below summarizes the properties of the small-scale test mats.

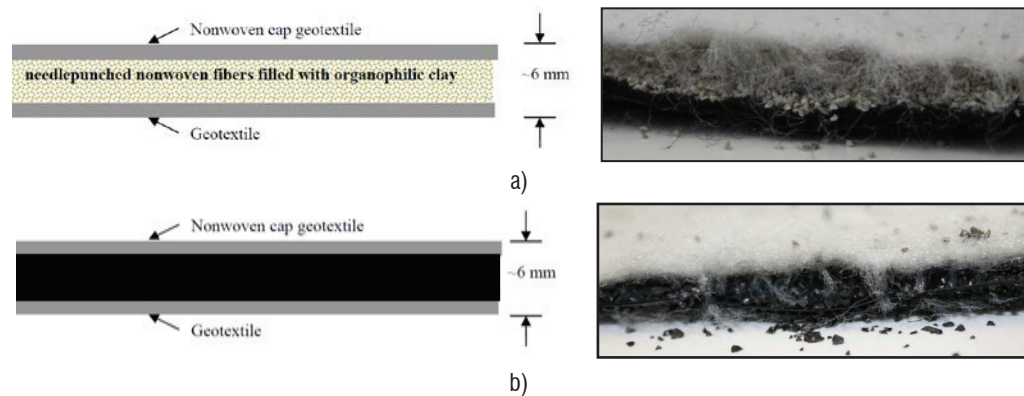


Fig. 6.5 - Reactive permeable mats: a) RCM with organoclay and b) RCM with active carbon.

Reactive permeable mats	Height [mm]	Reactive materials [kg/m ²]	Hydraulic conductivity [cm/sec]
RCM with OC	6	3	1×10^{-3}
RCM with AC	6	3	1×10^{-3}
RCM with OC and AC	10	6	1×10^{-3}

Tab. 6.2 - Properties of small-scale test mats (OC: organoclay; AC: active carbon).

Organoclay PM 199 (CETCO, Hoffman Estates, IL) is a bentonite-originated element modified with quaternary amines that exchanges the surface cation charges of bentonite for organic molecules (Olsta et al., 2006). It possesses unique adsorption behaviour towards aromatic organic compounds (PAHs), free oil and grease (FOGs) and chlorinated hydrocarbons. It has been also verified that OC can have good potential for remediating different metals under real environmental conditions (Meric et al., 2014). This organophilic clay is considered to be most effective to absorb NAPL while activated carbon is more susceptible to fouling in the presence of pure phase organic contaminants and is expected to perform better for dissolved contaminants.

Active carbon (AC), which derives from thermal decomposition of various carbonaceous materials followed by an activation process, is probably the most widely used material among active substances (De Gisi et al., 2017b). Various laboratory studies showed that active sediment mixing with AC can significantly reduce the aqueous concentrations, bioavailability, and bioaccumulation of PCBs, PAHs and several heavy metals (Choi, 2014). LIQPRO CS 1100 was chosen as the GAC in order to have a fair comparison to existing PCB adsorption studies (i.e. McDonough et al., 2007). It is a high performance granular activated carbon manufactured from specially selected coconut shell-based charcoal made by steam activated process. LIQPRO CS 1100 along with efficient micro-porosity makes it suitable for high flow rate applications. Its high surface area ensures superior adsorption of low molecular weight organic compounds. Product is de-dusted during manufacturing process to give excellent clean product.

For in situ mixing, biochar (BC) was chosen as an alternate carbonaceous sorbent, because it has great potential as a low-cost adsorbent for in situ sediment remediation (Silvani et al., 2017; Oliveira et al., 2017). It is a by-product of thermochemical conversion, such as pyrolysis or gasification, of carbonaceous materials (i.e. biomasses and/or agricultural waste) in electric energy. The low-cost adsorbent is emerging as an economical substitute to the activated carbon, thanks to its several unique properties, which make it an efficient, cost-effective and environmentally friendly material for the contaminants' removal (Oliveira et al., 2017). The biochar sample was obtained from Verora GmbH (Switzerland) and it was produced by pyrolysis of mixed

wood saw dust. Its surface area is $250 \pm 50 \text{ m}^2/\text{g}$, with average particle size $< 0.2 \text{ mm}$. The BC used was characterized - in collaboration with ETH of Zurich - other information can be found in literature (Todaro et al., 2019 in prep.).

Physical properties of OC, AC and BC are shown in Tab. 6.3.

Reactive materials	Mesh	Density [kg/m ³]	Surface Area [m ² /g]
Organoclay PM 199	1.00 mm - 0.15 mm	800 ± 100	- ¹
LIQPRO CS 1100	2.36 mm - 0.60 mm	480 ± 30	1150
Verora Biochar	2.00 mm - 0.08 mm	220 ± 22	200 - 300

Tab. 6.3 - Properties for OC and AC. Note: 1) OC absorbs in organic matter is 0.5 kg per kg of OC, surface area is not relevant.

A further one of the technologies tested for in situ sediments remediation is the composite particle approach (reactive granular materials). The composite particles were manufactured by AquaBlok Ltd. (Toledo, Ohio) using a stone core coated with a combination of bentonite-based clay and reactive powder materials. Below is a schematic representation (Fig. 6.6) of the composite particle approach employed by AquaGate for PAC (Powdered Activated Carbon).

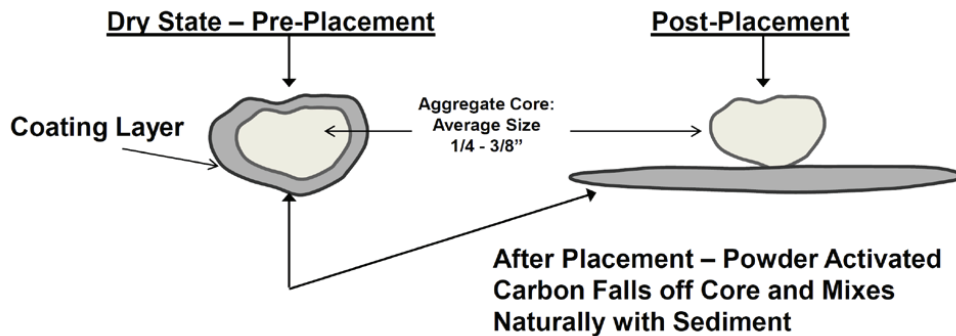


Fig. 6.6 - AquaGate approach.

In particular, 3 types of composite granular materials have been used (Fig. 6.7), namely: (i) AquaGate + PAC 5%; (ii) AquaGate + ZVI 5%; and (iii) AquaGate + Provect-CH₄ 2.5%. The formulations for this demonstration incorporate reactive materials (e.g. 5% Powdered Activated Carbon, PAC, or 5% Zero Valent Iron, ZVI, or 2.5% methane inhibitor, Provect-CH₄) and 10% clay (sodium bentonite), and the remaining fraction of aggregate, by weight. Physical properties of composite materials are shown in Tab. 6.4.

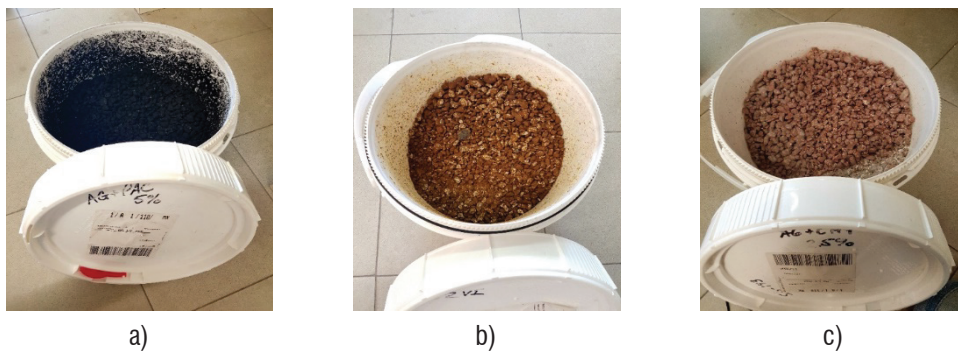


Fig. 6.7 - a) AquaGate + PAC 5%; b) AquaGate + ZVI 5%; c) AquaGate + Provect-CH₄ 2.5%

Reactive materials	Mesh	Density [kg/m ³]	Permeability [cm/s]
AquaGate + PAC 5%	63.5 mm - 95.3 mm	1120 ÷ 1280	$1 \times 10^{-1} \div 1 \times 10^{-2}$
AquaGate + ZVI 5%	63.5 mm - 95.3 mm	1200 ÷ 1360	$1 \times 10^{-2} \div 1 \times 10^{-5}$
AquaGate + Provect-CH ₄ 2.5%	63.5 mm - 95.3 mm	1200 ÷ 1360	$1 \times 10^{-2} \div 1 \times 10^{-5}$

Tab. 6.4 - Physical properties of composite materials.

The PAC particles used for this AquaGate application were 74 μm in diameter or less (i.e., 95% of particles are less than 74 μm). This approach increases surface area of the thin PAC coating later (around the stone core) and provides uniform placement of a small amount of PAC over a larger area than if AC alone were utilized.

Zero valent iron (ZVI) is an electron donor that is used to reduce or indirectly oxidize several contaminants in soil and groundwater. The development of ZVI products

gained a growing interest in environmental remediation with numerous applications all over the world. It is among the most abundant metals of the earth and hence the adsorbents prepared from this metal could be very cost effective. Additionally, iron metals are non-toxic in their elemental form and hence they are environmentally friendly, and no special account should be taken for their application in the soil contaminated site.

Provect-CH₄[®] is a food-grade, natural source of Monacolin K (otherwise known as Lovastatin) that is used to prevent methane (CH₄) production by inhibiting the growth and proliferation of methanogenic Archaea. In environmental remediation applications, it is used as a supplement to conventional enhanced reductive dehalogenation (ERD) and in situ chemical reduction (ISCR) amendments rendering them safer and more effective.

6.3.2 *Ex situ options*

The sediments were treated by adding different contents (by dry soil weight) of several additives, namely Portland cement (C), lime (L), organoclay (OC), active carbon (AC) and biochar (BC).

Portland cement CEM I 42.5 (Italcementi S.p.A., Italy) was used in this study. It is a fine grey powder produced by grinding Portland cement clinker, a limited amount of calcium sulphate and up to 5% minor constituents. The main chemical constituents of clinker are CaO, SiO₂, Al₂O₃ and Fe₃O₃.

In this study, the type of lime used is calcium oxide (CaO), commonly known as quicklime (the product was obtained from Unicalce S.p.A.). The stabilizer is commercially produced finely ground with 99% passing 75 µm sieve and 97% passing 45µm sieve. Hydrated lime, the slaked type of oxide, is equally effective but economically unattractive because much lighter and more voluminous than its reactive type.

OC, AC and BC were used in combination with either cement or lime, these were detailed before (paragraph 6.3.1).

6.4 *In situ options: laboratory experiments for capping treatments*

The experimental set-up (Fig. 6.8) was designed and assembled to test the efficacy of the reactive capping at lab-scale level. The device is an accurate physical model in laboratory-scale of the subaqueous site, used for consolidation and chemical migration tests. The columns used was made of 15 cm inside diameter polymethyl-methacrylate (PMMA) cylinders. They are made up of two sections of different length (50 cm and 100 cm) for facilitating the column handling and cleaning. A porous plate at the base of the columns has been placed in order to allow for water injections into the column through a $\frac{1}{4}$ inch opening. Various sampling ports were present at different heights along the columns for chemical sampling of the effluent to be taken during the test. All the reactors were filled for about 40 cm from contaminated sediment and about 1 m with seawater, previously filtered and chemically characterized (Todaro et al., 2018a).

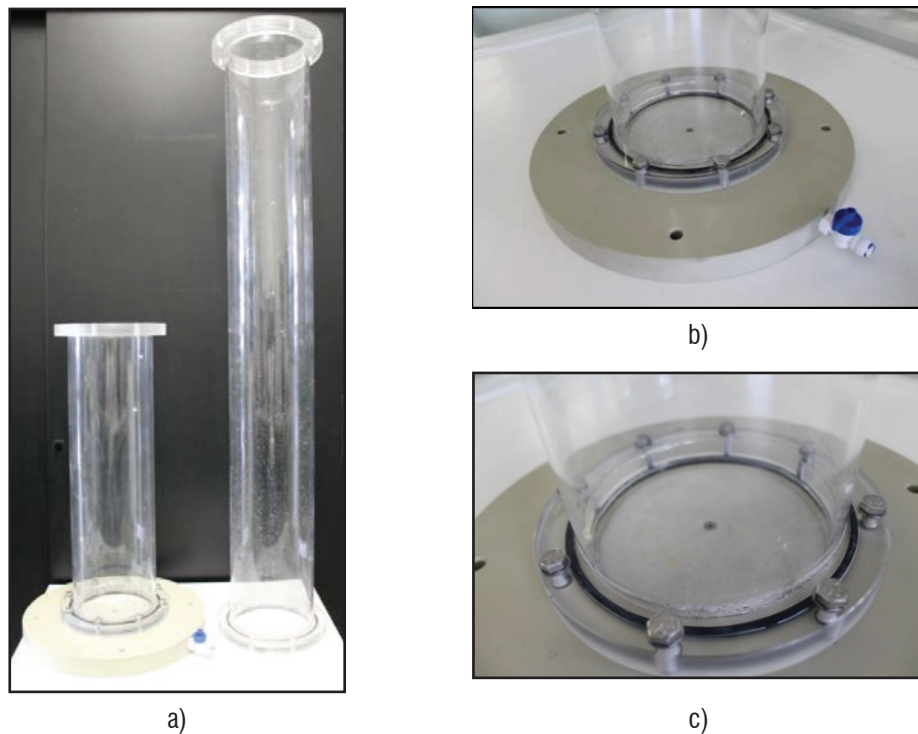


Fig. 6.8 - Laboratory columns used for simulating the in situ capping.

Porewater samples were obtained by Rhizons sampler (Fig. 6.9), distributed by Rhizosphere Research Products (Wageningen, Nederland) or by Ecosearch s.r.l. (Montone, Italy). They are made of a hydrophilic porous polymer tube, with a typical pore diameter of $0.1\ \mu\text{m}$, extended with a polyvinyl chloride tube. The outer diameter of a Rhizon is 2.4 mm, and the filter section has a length of 10 cm. The sampling device has several advantages: low mechanical disturbance of the sediment due to small diameter (2.4 mm), low dead volume (0.5 ml including standard tubing), minimized sorption processes on the inert polymer, no aging during long-term deployments (Knight et al., 1998; Seeberg-Elverfeldt et al., 2005).

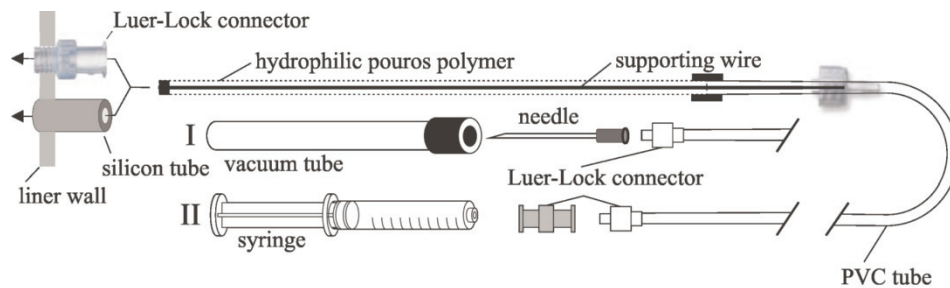
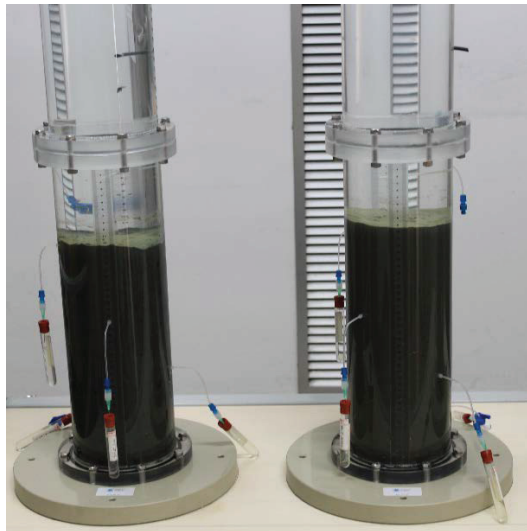


Fig. 6.9 - Photograph of the sampling of pore-water and schematic diagram of a Rhizon (length 10 cm, outer diameter 2.5 mm, dead volume 0.5 ml, pore size $0.1\ \mu\text{m}$) and the devices used for porewater extraction: I) vacuum tubes and II) syringes.

Tests were performed using the columns previously described along with the contaminated sediment and water from Mar Piccolo. Prior to use, seawater was filtered ($0.45\ \mu\text{m}$ membrane filters), analysed and stored in the refrigerator at $+4\ ^\circ\text{C}$. In order to simulate cap placement, water was added very slowly and carefully to not disturb the contaminated sediment already in the column, and then the cap was poured into the column.

Sediment column studies were conducted using two different hydraulic conditions for the water in the column: no water flow (static conditions) and with a turbulent flow (dynamic conditions), made by a stirrer (Fig. 6.10), to simulate anthropogenic activities (i.e. the potential of propellers to erode the thin-layer caps). Depending on the erosive forces presented in a site, two different dynamic conditions were simulated: (i) shaking of water in the column for 30 minutes at 100 rpm and (ii) shaking of water in the column for 10 minutes at 300 rpm.

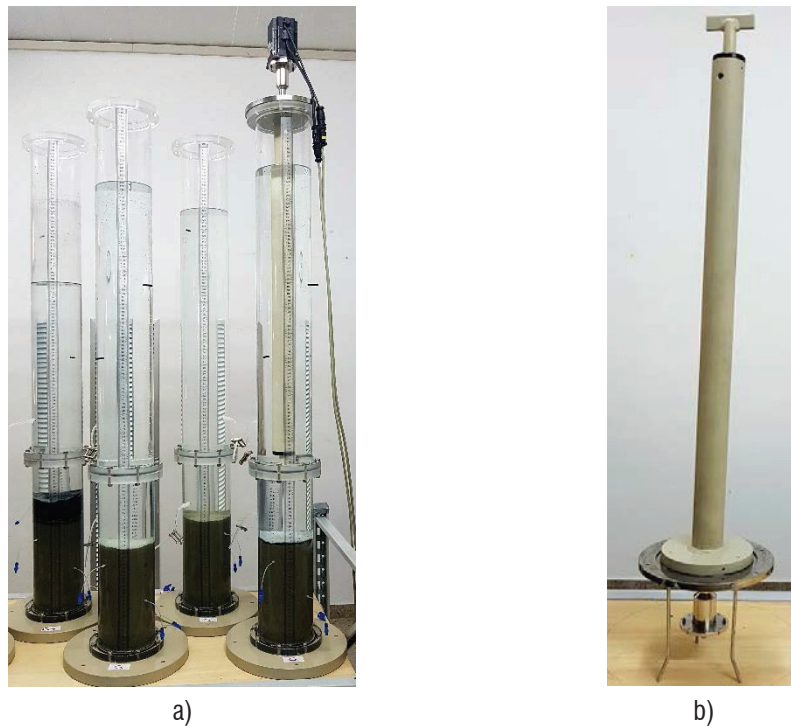


Fig. 6.10 - a) Photograph of the dynamic conditions simulation; b) stirrer.

Seawater samples were taken at increasing intervals (i.e. 0, 7, 14, 28 days) until the end of the test. These tests spanned between 20 to approximately 30 days for static conditions and about 24 hours for dynamic conditions.

During the column tests, sediments consolidation was observed in order to determine the effect of cap placement on the migration of contaminants into the capping layer. The procedure of these tests included setting up the material in the columns, and then measuring the contaminated sediment consolidation over time, using measuring devices permanently attached to column sides.

At the end of tests, the sediments of each column have been sampled and the material in contact with cap has been extruded and sliced for chemical analysis. Before coring could take place, the water was siphoned from the column. Once the water was drained, then the top column addition was removed. After the removal of the top column, the coring was performed (Fig. 6.11).

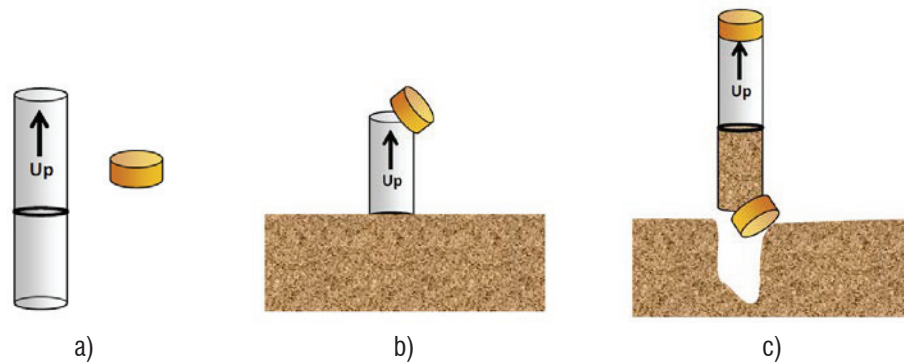


Fig. 6.11 - Operation for sediment sample collection: a) 10 cm long plastic core tubes and 10 core caps; b) insert core tube in sediment until sediment within the core tube reaches the marked line (5-cm depth), then cap the top of the core tube; c) pull the core tube from the sediment, retaining a sediment sample. Cap bottom end of core tube to prevent sample loss as core is pulled out.

In order to evaluate the hydro-mechanical implication of in situ mixing, geotechnical tests were performed. For this remediation option three sorbents were tested: organoclay, activated carbon and biochar; the dose (5% of sorbents) added to the sediments is similar to those applied in different applications (Lofrano et al., 2017). These tests will be described in the following paragraph (i.e. section 6.7).

6.5 *Ex situ options: laboratory experiments for S/S treatments*

The first step of the laboratory experiments for S/S treatments consists in preparing a mixture containing the sediments, the binders (i.e. cement or lime), the eventual absorbent materials (i.e. organoclay, active carbon or biochar) and the necessary quantity of water for the hydration reactions of the binder.

Several specimens were prepared by thorough mechanical mixing of the sediments with the additives. All the materials were initially mixed for 5 min with a standard mixer and, then, a steel trowel was used to ensure a homogeneous paste. In the casting phase, the prepared mixture was introduced into different PVC molds and beaten to get rid of trapped air bubble.

The samples, in the curing phase, were kept at 20 ± 5 °C and 80% humidity (Fig. 6.12) and then put on tests at different setting times, for monitoring the progressive changes (generally, 1 hour, 7, 14, and 28 days).



Fig. 6.12 - Specimens prepared and placed in a temperature-controlled room with 80% humidity.

The testing programme consisted of both chemical (i.e. leaching tests) and physical and mechanical investigations (i.e. oedometer, direct shear and unconfined

compression tests) on the sediment' mixtures after different curing times (i.e. 7, 14 and 28 days).

The sediment mixtures were tested following the experimental programme summarised in Tab. 6.5 (in particular, the mechanical tests will be described in the paragraph 6.7).

PHASE	MIXTURE	TESTS
Preliminary	Sediment + 15% CEM	Chemical
	Sediment + 7.5% CEM + 7.5% LIME	Chemical
	Sediment + 15% LIME	Chemical
Advanced	Sediment + 10 % CEM	Chemical and Geotechnical
	Sediment + 10 % CEM + 5% OC	Chemical and Geotechnical
	Sediment + 10 % CEM + 2.5% AC + 2.5% OC	Chemical
	Sediment + 10 % CEM + 5% AC	Chemical and Geotechnical
	Sediment + 10 % CEM + 5% BC	Geotechnical
	Sediment + 10 % LIME	Chemical and Geotechnical
	Sediment + 10 % LIME + 5% OC	Chemical and Geotechnical
	Sediment + 10 % LIME + 2.5% AC + 2.5% OC	Chemical
	Sediment + 10 % LIME + 5% AC	Chemical and Geotechnical
	Sediment + 10 % LIME + 5% BC	Geotechnical

Tab. 6.5 - Experimental programme for S/S treatments (chemical: leaching tests; geotechnical: physical and mechanical investigations).

Leaching test, according to the EN standard 12457-2, were performed. This procedure can only be applied to granular wastes and sludges which has a particle size below 4 mm and cannot be used for evaluating the leaching grade of the non-polar organic compounds. For several samples, a 40 g portion was sampled and transferred to a polyethylene bottle. Demineralized water was added with a solid-liquid ratio of 1:10 by weight and the bottles was keep in rotation at 12 rpm for 24 h using Rotax 6.8 (Velp

Scientifica) (Fig. 6.13). After 24 h, a short retention time was given to the extraction vessels for the settlement of suspended coarse solids; then, the leachate was filtered for the removal of suspended solids. This test procedure produced an eluate which has been both physically and chemically characterised according to appropriate standard methods. In particular, the eluates were consequently divided into an appropriate number of parts for the different chemical analysis, after having been acidified at a pH equal to 2, through nitric acid, as prescribed by the regulatory for the determination of the metals in outline. The soluble concentrations of heavy metals of interest (i.e. As, Co, Cr, Cu, Ni, Pb, V and Zn) were analysed by using ICP-OES. The analysis directly produces the values of the concentrations in mg/l.



Fig. 6.13 - Rotax 6.8 (Velp Scientifica) used for the leaching tests.

6.6 Chemical analyses

A series of chemical analyses have been performed in order to characterize the remediation materials, to establish the effective degree of sediment contamination and to verify the performances of remediation technologies. The determinations carried out to determine the chemical and physical properties of the different matrices (i.e. marine sediments, adsorbent materials, eluates, seawater, pore water) are listed in Tab. 6.6 according to the standards followed for the measurements.

PARAMETER	MATRICES	UNIT OF MEASURE	STANDARD
Moisture content	Soil	%	EPA 24
Organic content	Soil	%	EPA 160.4
pH	Soil and Water	u.pH	EPA 150.1
Conductivity	Soil and Water	$\mu\text{S}/\text{cm}^2$	EPA 120.1
Inorganic pollutants	Soil and Water	mg/Kg - mg/l	EPA 200.8
Organic pollutants	Soil and Water	mg/Kg - mg/l	EPA 8275A

Tab. 6.6 - Standards followed in the laboratory for each determination.

The oven-drying method was used to determine the moisture contents (u) of the sediment samples. In particular, the samples were weighed and oven-dried at 105°C for 24 hours and w was calculated using the following equation (Eq. 1):

$$u = \frac{W_w - W_d}{W_w} \quad (6.1)$$

where w_w and w_d are the weight of wet sample and dry sample.

The organic content is determined with a similar procedure: loss on ignition (LOI) test. Despite the simplicity of this test, the heating temperature (550°C in an unheated muffle furnace) and the test duration (4 hours or until constant mass is achieved) can significantly alter also the content of inorganic constituents (e.g., some

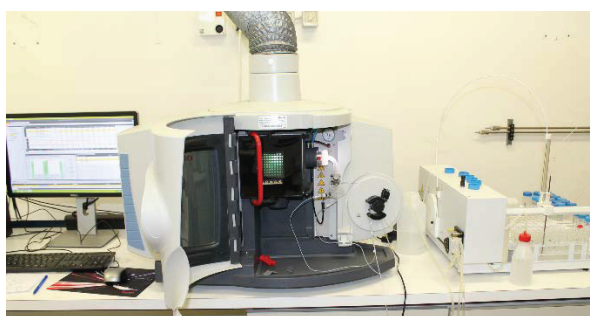
hydrated aluminosilicates) and lead to an overestimation of the organic content. The organic content was determined as:

$$OM = \frac{W_{105^{\circ}C} - W_{550^{\circ}C}}{W_{105^{\circ}C}} \quad (6.2)$$

The pH, Eh and conductivity were measured with electrodes in a Multi-Liner instrument (CyberScan PC5000, Eutech Instruments).

The concentrations of metals were obtained by ICP-OES, Inductively Coupled Plasma-Optical Emission Spectrometry (iCAP 7000 Series - Thermo Scientific, Fig. 6.14a) in accordance to EPA method 200.8 (EPA, 1994).

For total metal determination in sediments (As, Co, Cr, Cu, Ni, Pb, V and Zn), 0.3 g of sediment (dried at 25°C, sieved to <2 mm and homogenized) was digested in a Synthesis Microwave Reaction System (MARS 6 Synthesis, CEM Corporation, Fig. 6.14b) with 2 ml ultrapure water and 8 ml HNO₃ (nitric acid). After digestion, samples were analysed by ICP-OES. Repeatability (three determinations) is lower than 15% at 95% confidence level for all metals. Hydrochloric acid was Sigma-Aldrich (Merck, Darmstadt, Germany). While, the liquid samples (i.e. eluates, seawater, pore water), after acidification (pH = 2) and filtering (0.45 µm sterile acetate nitrate filter), were directly analysed by ICP-OES.



a)



b)

Fig. 6.14 - a) ICP-OES iCAP 7000 Series; b) Digested system, MARS 6 Synthesis.

Ultrapure water with conductivity $<0.1 \mu\text{S}$ was obtained from a MILLI-Q® system (Millipore, Bedford, MA, USA). Working standard solutions of metals were prepared by serial dilution of stock standard solutions of each element (Sigma-Aldrich) containing 1 mg/l in 0.5 M HNO_3 . Normal precautions for trace analysis were always observed. The method quantification limit (MQL) was 0.01 mg/l .

For the determination of the organic compounds total PAHs and PCBs concentrations as well as each compound or homologue group, a Gas Chromatograph - Mass Spectrometer (GC-MS, Thermo Scientific TRACE 1300, Fig. 6.15) and EPA method 8275A was used. For determination in soil matrix, 5 g of samples, dried at 25°C , were extracted with 90 mL of acetone–hexane (1:1) by an Ultrasonic Baths system (VELP Scientific), following EPA method 3541. After extraction, total organic extract was reduced to about 2 mL and then purified by Gel Permeation (Knauer Smartline) to remove polar compounds co-extracted. This last fraction was concentrated and analysed by GC-MS. The relative standard deviation for triplicate analyses ranged from 5% to 15%, while method detection limits for PAHs and PCBs were $20 \mu\text{g/kg}$ and $1 \mu\text{g/kg}$ respectively, for all examined compounds.

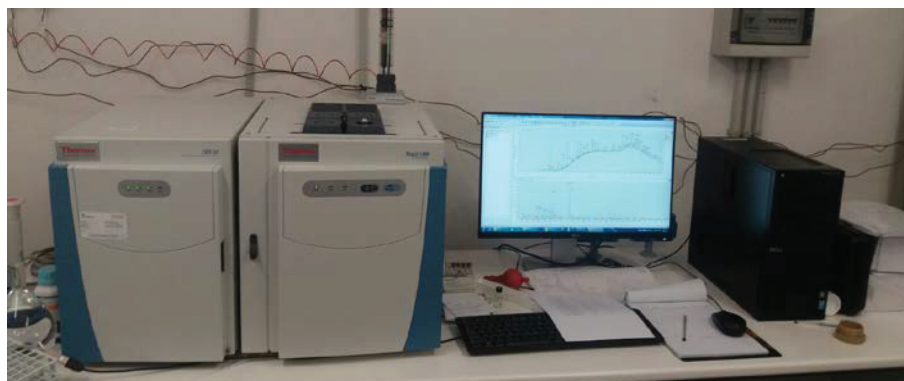


Fig. 6.15 - GC-MS, Thermo Scientific TRACE 1300.

6.7 Geotechnical tests

6.7.1 Composition and physical properties

The tests carried out to determine the composition and physical properties of the sediments are listed in Tab. 6.7, together with the standard procedures followed and the corrections applied to take account of the pore fluid salinity and the presence of shells and mussels. In particular, the presence of pore fluid salinity can play a not negligible on the geotechnical proprieties of the sediments, especially for those characterised by active mineralogy. Clay particles, because of their small size and large surface area, are well known to have a surface charge, hence to be susceptible to surface force interaction manifested by a variety of interparticle attractive and repulsive forces.

TEST	SYMBOL	STANDARD	CORRECTIONS
Water content	w_o	ASTM 2216	ASTM D4542 BS 1377
Atterberg limits	w_L, w_P	ASTM D4318	ASTM D4542 BS 1377
Soil specific gravity	G_s	ASTM D854	STM D4542 BS 1377
Composition	CF, MF, SF, GF	ASTM D422	Presence of shells and mussels

Tab. 6.7 - Summary of the tests performed, standards used and the corrections applied.

The oven-drying method was used to determine the water contents (w) of the sediment samples. In particular, the samples were weighed and oven-dried at 105°C for 24 hours and w was calculated according to the following equation (Eq. 6.3)

$$w = \frac{W_w}{W_s} \quad (6.3)$$

where W_w and W_s are the weight of water and of the soil solids, respectively.

The presence of the water salinity affects the calculation of the natural water content determined by the standard procedures, since the salt crystallizes into a solid during the oven-drying process. For this reason, a correction is proposed from both the Standards (ASTM D4542) and the literature (e.g. Imai et al., 1978; Ho 1988; Le 2008; Lee et al., 2011; Sollecito, 2017). The procedure used to determine the corrected water content of a soft clay which contains salts in its liquid phase is described in the following.

Liquid phase in a saturated element of marine soil is occupied by water in which salt is dissolved, while solid phase is occupied by soil particles. The correct expression of the fluid content, w^* , of the soil element should be, then, defined as:

$$w^* = \frac{W_{sw}}{W_s} = \frac{W_w + W_{salt}}{W_s} = \frac{W_w + W_{salt}}{W_d - W_{salt}} \quad (6.4)$$

where W_{sw} and W_w are the weight of seawater and distilled water, W_s is the weight of soil solids (excluding salt W_{salt}) and W_d is the weight of the oven dried sample at 105°C. The following provides the formulation for the correction of the measured water content, w_m , of a sample once the salinity, r (i.e. the total amount of salt in the marine water), is known (Sollecito, 2017).

$$w^* = \frac{w_m}{1 - r(1 + w_m)} \quad (6.5)$$

The liquid limit and the plastic limit were determined on both the natural sediments and the sediments treated with binders and reagents after 7 and 14 days of curing.

The liquid limit (w_L) is the water content that defines the state in which the soil changes from being plastic to liquid. According to ASTM D4318, a portion of soil sample is placed in cup of the Casagrande apparatus and levelled off parallel to the base (Fig. 6.16). The liquid limit is defined as the water content at which a sample of soil in Casagrande's cup cut by a groove of standard dimensions, will flow for joining the

groove for a distance of 13 mm when subjected to 25 blows from the cup being dropped 10 mm with a rate of two blows per second.



Fig. 6.16 - Procedure for the determination of liquid limit.

The plastic limit (w_p) is the moisture content that defines the physical state in which the soil passes from semi-solid to plastic. The soil sample is modelled with the hands until it dried adequately; w_p is the water content at which a soil can no longer be deformed without crumbling by rolling into 3.2 mm diameter threads (Fig. 6.17).



Fig. 6.17 - Procedure for the determination of plastic limit.

The tests were performed for a sundry moisture contents, from the wetter to the drier states. The samples were not dried before testing because the liquid limit of a soil containing substantial amounts of organic matter decreases dramatically when the soil is oven-dried before testing (ASTM D2487). When additional water was needed, tap water was used. However, when the minimum amount of fluid was added, the new

values of salinity were determinate in order to determine the Atterberg limits at real salt condition. Reduction of water content was accomplished by exposing the material to air currents at room temperature. This method is recommended by the standard (ASTM D4318) for materials containing soluble salts, because it will not eliminate the soluble salts from the test specimens. In addition, concretions, shells, and other fragile particles, were not crushed to make them pass a 425- μm (No. 40) sieve, but they were removed, as suggested by ASTM D4318 standard.

The soil specific gravity was determined according to the standard procedure by using pycnometer (ASTM D854). It is defined as the ratio of the mass in air of a given volume of soil particles to the mass in air of an equal volume of gas free distilled water at a stated temperature (20°C). The values were corrected for salinity by the expression (Eq. 6.6):

$$G_s^* = \frac{\gamma_s}{\gamma_{sw}} \quad (6.6)$$

The grain size distribution of the sediments has been estimated through sieving for particles larger than 75 μm (i.e. retained on the N. 200 sieve) and by sedimentation process (i.e. hydrometer analysis) for the finer ones. Fragments of shells, mussels and fossils were often visible to the naked eye and their presence in the soil matrix was taken into account for the determination of the sediments' composition (Fig. 6.18). The grain size distribution was then obtained either by including or excluding the gravel fraction, mainly represented by mussels, shells and fossils. In the latter case, the weight of the material passing the 1 mm (No. 18) sieve was set to be equal to the total soil weight.



Fig. 6.18 - Material retained to sieve No. 10 (1.68 mm).

6.7.2 Oedometer tests: equipment and procedures

The oedometer (OED) test reproduces, in the laboratory, one-dimensional compression conditions. It is performed to investigate soil compression and swelling (i.e. the relation between effective stress and volumetric strain) or consolidation (i.e. the relation between compression and effective stress), on a cylindrical soil specimen placed when it is restrained laterally while subjected to the application of axial loading steps. Under these conditions, the soil straining and the water flow are allowed only in the vertical direction. The test procedure has been standardized in BS 1377-5 and ASTM D2435. A sketch of the oedometer apparatus is reported in Fig. 6.19.

The oedometer cells used for the present study consist of a rigid ring containing the specimen, which is in contact with two porous stones both at the top and the bottom to allow double drainage. The soil specimen size (50 mm diameter, 20 mm high) used for this study had diameter height ratio greater than two, in order to reduce the effects of side friction (Bishop and Henkel, 1962). The cells are placed on a rigid aluminium base and a loading yoke allows the load transmission from a lever arm carrying the weights to the specimen top cap.

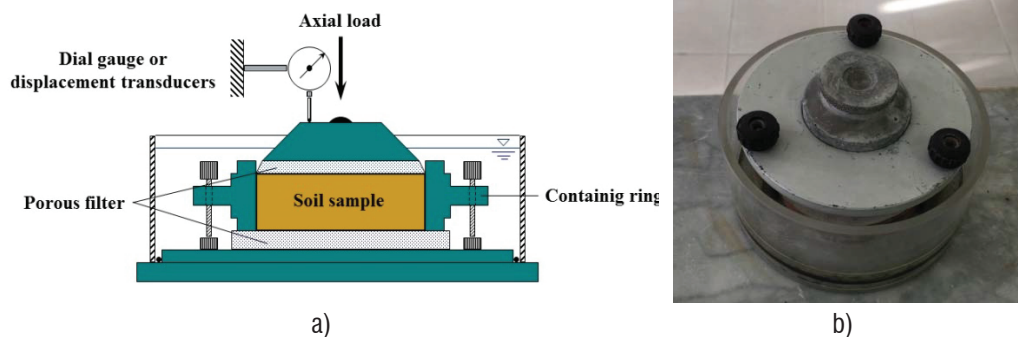


Fig. 6.19 - a) Sketch of the oedometer cell; b) photographs of the oedometer cell.

During the trimming of the specimen, flat and parallel surfaces were ensured to minimize the error due to the imperfect alignment of the top platen with the ring, which can cause misreading of the displacements. The main source of error was derived from the bedding due to the roughness or other imperfections of both the top and base of the specimen. In case of the soft marine sediments under study, also the presence of fragments of shells and mussel represented a cause of disturbance. The initial water content and the specimen dimensions were carefully measured before the setting-up of the tests.

The tests were carried out by exposing natural specimens both to seawater and treated specimens to either tap water or seawater according to the boundary conditions of treatments to be simulated.

The stress and strain conditions are assumed to be axi-symmetric and contact friction between the soil and the ring is assumed to be zero, also thanks to the silicon oil lubrication, carried out before testing, of the inner surface of the steel ring.

During each loading step, the vertical compression or swelling of the specimen under the actual stress is measured by means of a Linear Displacement Transducer (LDT), operating on the loading cap and firmly mounted at the top of the machine. When the axial stress is applied, the specimen of initial height H_0 deforms vertically with time. It ultimately settles of an amount ΔH when the excess pore-water pressure is “completely” dissipated, according to the so-called consolidation process. As lateral strain

is restricted by the stiff ring ($\varepsilon_r = \varepsilon_y = 0$), the volumetric strain, ε_{vol} , coincides with the axial strain, ε_z and it is computed according to equation (6.7):

$$\varepsilon_{vol} = \varepsilon_x + \varepsilon_y + \varepsilon_z = \varepsilon_z = -\frac{\Delta H}{H_0} \quad (6.7)$$

All the oedometer tests were carried out as step-loading type, the duration of each loading step being related to the reaching of a very low rate of settlement (around 0.003-0.005 mm/h) that is when the primary consolidation could be considered to be finished.

At the end of each test the water in the oedometer cell was removed and the specimen was quickly unloaded, in order to restrain swelling. At the end of the test, the specimens were oven-dried at 105°C for at least 24 hours, in order to measure the final water content, and then cut to investigate the presence of fragments of shells in the soil matrix.

In this work, the Terzaghi theory of 1D consolidation (Terzaghi, 1936) has been used to distinguish the soil compression from the compliance and bedding settlements. Accordingly, the curve-fitting method proposed by Casagrande (1936) was applied to compute the starting value for the settlements (d_0) in the oedometer tests, both in loading and in unloading. In the following, the equations of Terzaghi's model of 1D consolidation are briefly recalled as they were considered of reference in the analysis of the oedometer test data.

Based upon the hypotheses of Terzaghi's model (Terzaghi and Peck, 1967), the consolidation process is expressed by the differential equation:

$$C_v \frac{\partial^2 u(z; t)}{\partial z^2} = \frac{\partial u(z; t)}{\partial t} \quad (6.8)$$

where t is time, z is the depth from the drainage boundary and $u(z; t)$ is the excess pore water pressure. The coefficient of consolidation, C_v , is equal to:

$$C_v = \frac{M_v k}{\gamma_w} \quad (6.9)$$

And it is assumed to be constant according to the hypotheses of Terzaghi's model. The solution $u(z; t)$ of Eq. 6.8 by separation of the variables (Taylor, 1948) for consolidation under a stress increment $\Delta\sigma_v$ and constant water pressure at the drainage boundaries, emerged as a Fourier series:

$$u(X; T_v) = \frac{\sum_{n=0}^{\infty} 2\Delta\sigma_v}{M_v \sin(M_v X)} e^{-M_v^2 T_v} \quad (6.10)$$

where M_v is equals to $(2n+1)\pi/2$. In Eq. 6.9 X and T_v (Terzaghi and Peck, 1967; Taylor, 1948) are:

$$X = \frac{z}{H} \text{ and } T_v = \frac{C_v t}{H^2} \quad (6.11)$$

where H is the distance of the undrained boundary from the free drainage boundary ($z=0$). If Terzaghi's assumptions that the soil behaviour is linear elastic, not strain-rate dependant and of constant permeability do not hold in reality, then c_v may change during consolidation and the solution of the consolidation problem in Eq. 6.10 may be not accurate enough.

According to Eq. 6.9, the average consolidation degree in terms of pore water pressures $U_p(T_v)$ is:

$$U_p(T_v) = \frac{\int_0^1 (\Delta\sigma_v - u(X; T_v)) dX}{\Delta\sigma_v} = 1 - \frac{\sum_{n=0}^{\infty} 2}{M_v^2} e^{-M_v^2 T_v} \quad (6.12)$$

and because of the assumption of linear soil behaviour, it is also equal to the average degree of consolidation in terms of settlements $U_s(T_v)$:

$$U_s(T_v) = \frac{\int_0^1 m_v(\Delta\sigma_v - u(X; T_v)dX}{m_v\Delta\sigma_v} = U_p(T_v) \quad (6.13)$$

where m_v is the coefficient of 1D compressibility. It follows that, for given boundary conditions, the model gives a unique expression of the average degree of consolidation of the soil stratum with time $U(T_v)$ ($=U_p(T_v)=U_s(T_v)$; Fig. 6.20) and the soil compression completely defines the process of consolidation, controlled solely by the coefficient of consolidation, c_v . Terzaghi's model was applied to the oedometer test data of this study, by using the Casagrande curve fitting method (Head, 1986). For each loading step, the initial compression d_0 due to apparatus compliance and the settlement related to the average consolidation degree of 50% was calculated as shown in Fig. 6.21 (Head, 1986). The coefficient of consolidation for $U=50\%$ was calculated as:

$$c_v = \frac{0.197H^2}{t_{50}} \quad (6.14)$$

where H is the distance of the undrained boundary from the free drainage boundary. The 1D stiffness M_v ($=1/m_v$), was calculated as:

$$M_v = \frac{\Delta\sigma_v}{\Delta\varepsilon_v} \quad (6.15)$$

where ε_v is the vertical strain at the end of the compression step.

The corresponding coefficient of hydraulic conductivity (k) was derived from Eq. 6.7.

During the oedometer tests, the secondary compression coefficient c_α was also calculated as:

$$c_\alpha = \frac{\Delta e}{\Delta \log(t)} \quad (6.16)$$

In the present study the bulk weight of water has been substituted by the bulk weight of seawater γ_{sw} , i.e. 10.05 kN/m³.

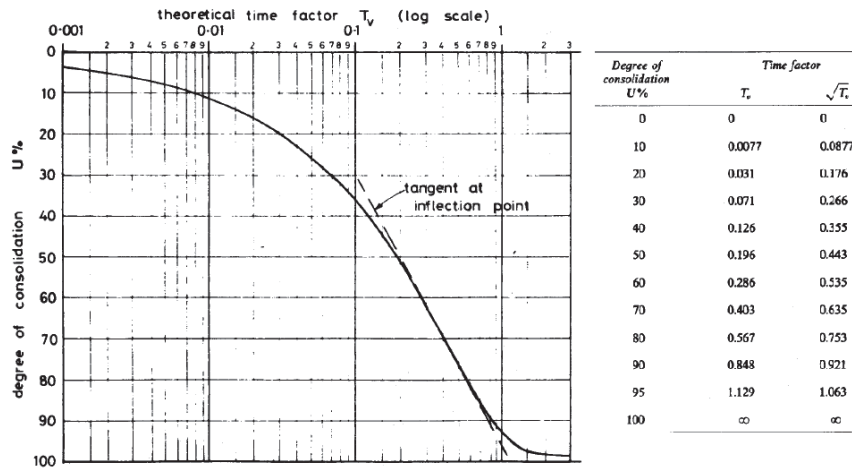


Fig. 6.20 - Terzaghi's model: $U\%-T_v$ relationship (after Head, 1986).

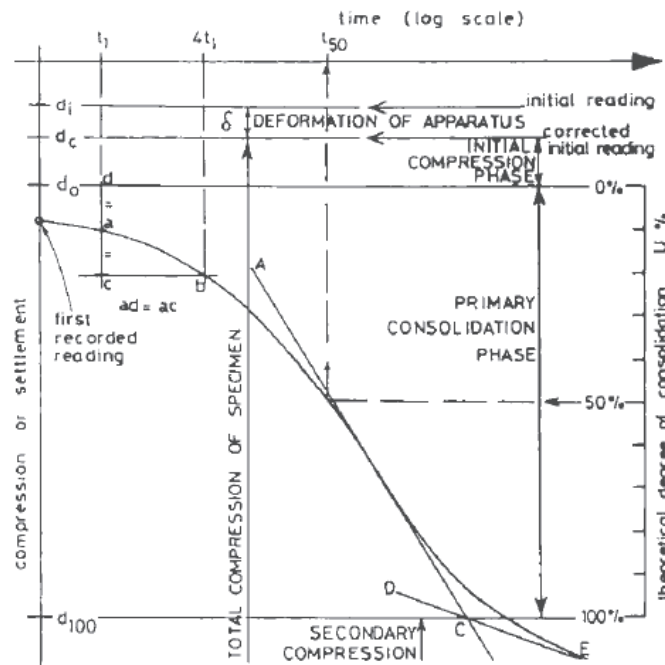


Fig. 6.21 - Casagrande's curve fitting method (after Head 1986).

The indexes of recompression (i.e. c_r), compression (i.e. c_c) and swelling (i.e. c_s) are usually expressed as the ratio between the total variation of void ratio, Δe , and the corresponding loading effective stress increment in the semi-logarithmic plot (i.e. $\Delta \log \sigma'_v$):

$$c_r, c_c, c_s = \frac{\Delta e}{\Delta \log(\sigma'_v)} \quad (6.17)$$

6.7.3 Direct shear tests: equipment and procedures

The essential features of the direct shear tests (DST) apparatus are illustrated in the sketch in Fig. 6.22, whereas the test procedure is detailed in BS 1377-7, BS 1377-8 and ASTM D3080. The specimen has a square cross-section 60 mm long at each side and 20 mm thick, it is confined in a metal box known as the shear box, split horizontally at mid-height, into two halves. A vertical force, N , is applied to the specimen through a loading plate and shear stress is gradually applied on a horizontal plane by causing the two halves of the box to move relative to each other, the shear force, T , being measured together with the corresponding shear displacement, Δ .

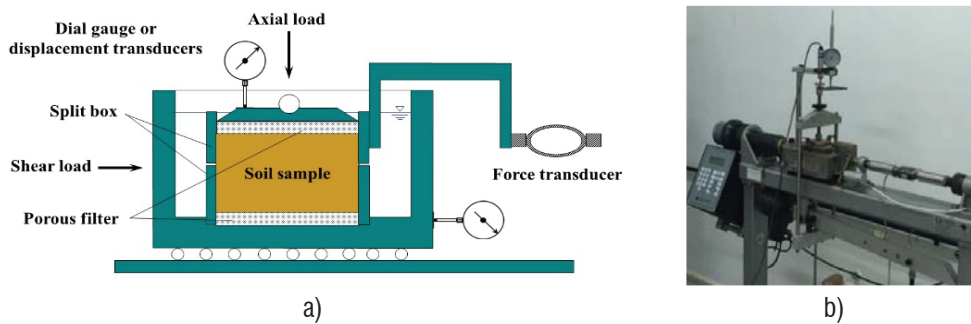


Fig. 6.22 - Direct shear test apparatus: sketch (a) and photograph (b) of one of the apparatuses present in the geotechnical laboratories of the Politecnico di Bari.

During the setting up of the apparatus, on the inner sides of the split shear box and on the surface between the two halves a film of grease was applied to reduce the

friction during both the consolidation and the shearing phases. Subsequently, the specimens, prepared by the cutting edge of the direct shear sampler, were carefully pushed into the box. With the aim to allow free drainage from the specimen, porous plates were placed both at the top and at the bottom of the specimen and the porous plates were protected by filter papers. As for the oedometer tests, the box was filled with seawater, to avoid flux of water and ions from the specimen. At first, the specimens were compressed applying a loading sequence from the restrained swelling condition. The compression curves obtained from the first phase of the DST were compared with the corresponding ones derived by the OED tests for each sample. After the consolidation phase, the shearing phase started applying a relative displacement between the two halves of the box, since the lower half is fixed and the upper one can move at constant rate. The shearing force, T , exhibited by the specimens, which react to the shear box displacement, was measured by means of load cells, while the corresponding shear displacement, Δ , together with the change in specimen thickness, ΔH , were measured by means of two LDT, installed on the box and on the loading cap, respectively.

Since the usual shear box apparatus provides no control of drainage and no provision for measuring pore water pressures, a constant rate of displacement of 0.00144 mm/min was set in all the DS tests to ensure a drained shear phase and determine the consolidated-drained shear strength parameters. It follows that horizontal displacements of 8 mm were reached in 92 hours (shearing phase).

Both the values of the shear stress, τ , obtained as force, T , divided by the cross-section area A , and the vertical displacements, ΔH , recorded during the shearing phase, were plotted against the horizontal displacements, Δ . The maximum values of shear stress were plotted against the vertical effective stress for each test. The effective shear strength parameters were then obtained from the fitting of either the stress peak or the critical state points.

6.7.4 *Squeezing tests*

Mechanical testing of soft contaminated sediments is challenging since they usually are fine-grained soils characterised by very low consistency and high fluid content. If in oedometer tests and direct shear tests the specimens are contained in a rigid mould, the preparation of undisturbed laboratory specimens for triaxial tests at the in situ state has been almost impossible for the top sediments, i.e. those at high fluid content and their liquid consistency ($LI > 2$). Furthermore, although contaminants may be removed from sediments effectively by using various remediation methods, there is always a concern that these contaminants may mobilize and migrate into the overlying water (e.g. Erten et al. 2011). A cover or cap to be placed in situ at the top of the contaminated deposit is one of the possible types of remediation strategies. However, the cap itself represents a not negligible load, especially for top sediments of liquid consistency. This could cause stability problems due to the huge consolidation settlements, that might lead to contaminants' migration (e.g. Azcue et al. 1998), due to advection, mechanical dispersion and diffusion phenomena. Therefore, it is important to determine not only the consolidation properties of the sediments but also the amount and properties of the fluid expelled during the consolidation process under the applied load. In order to contribute to the knowledge in this respect, the apparatus in Fig. 6.23a has been designed and realized to test in the laboratory the shallow sediments taken within the two meters below the seafloor in the Mar Piccolo. This apparatus allows to simulate the processes naturally occurring within the sediments, when pore fluid flows out as the soil is subjected to load. Moreover, differently from standard oedometer tests, this apparatus offers the possibility to collect the outcoming fluid to be analysed in order to acquire information about the mobility of the contaminants.

To adapt a conventional consolidometer setup for consolidation of very soft contaminated sediments, some modifications had to be implemented. The environmental consolidometer (Fig. 6.23) is constituted by a stainless-steel pedestal, equipped at the base with a hole for the installation on the seat and drainage lines to allow the outcoming of the pore fluid during the consolidation phase. The drainage lines are connected to thin polycarbonate tubes for the collection of pore fluid, which ends up in an

HDPE bottle. A transparent polycarbonate tube 5 mm thick was used instead of a standard metallic tube, since polycarbonate is non-reactive with most contaminants, and it has higher stiffness if compared with other plastic materials. Furthermore, the transparency of the tube allowed to inspect the formation of air bubbles in the specimen during the test. In the study, tubes of 40 mm diameter x 200 mm height were used. The presence of the o-ring ensured the connection between the tube and the pedestal. Porous stones at the top and bottom surface of the specimen were here substituted by thin aluminium disks made by perforate sheet to avoid the absorption of contaminant by the stone. A disk of filter paper was used to avoid the loss of material through the drainage lines. As in the oedometer, a loading yoke allows the transmission of load from a lever arm carrying the weights to the specimen top cap. The top cap in contact with the specimen inside the tube during the vertical settlement, was connected to the loading system by means of a little ball bearing, which allows to ensure the contact between the top cap and the specimen during its vertical settlements. Vertical displacements have been recorded by using an electrical transducer LDT.

The consolidometer tests were carried out on 4 samples collected within the first meter below the seafloor by means of thin tube in PVC 1-m long (CS_P). A portion of the sample has been cut and a 40 mm diameter tube, has been slowly pushed into this portion of sample. The inner surface of the tube was previously covered with a film of grease to reduce the side friction. The material was transferred into the environmental consolidometer by means of a wooden dolly. An on-purpose designed rigid ring assured the co-axiality with the tube of the consolidometer during the setting up of the test. Specimens were consolidated from approximately their in situ state to maximum vertical effective stress, σ'_{vmax} equal to 100 kPa, by means of successive load increments, each doubling the previous value.

After one-dimensional consolidation, the specimens were extracted and trimmed to the triaxial specimen dimension. The dimension and the weight of the specimens at the end of the tests were recorded. The pore fluid outcoming from the apparatus during the consolidation phases were collected in the HDPE bottles and subjected to chemical analyses.

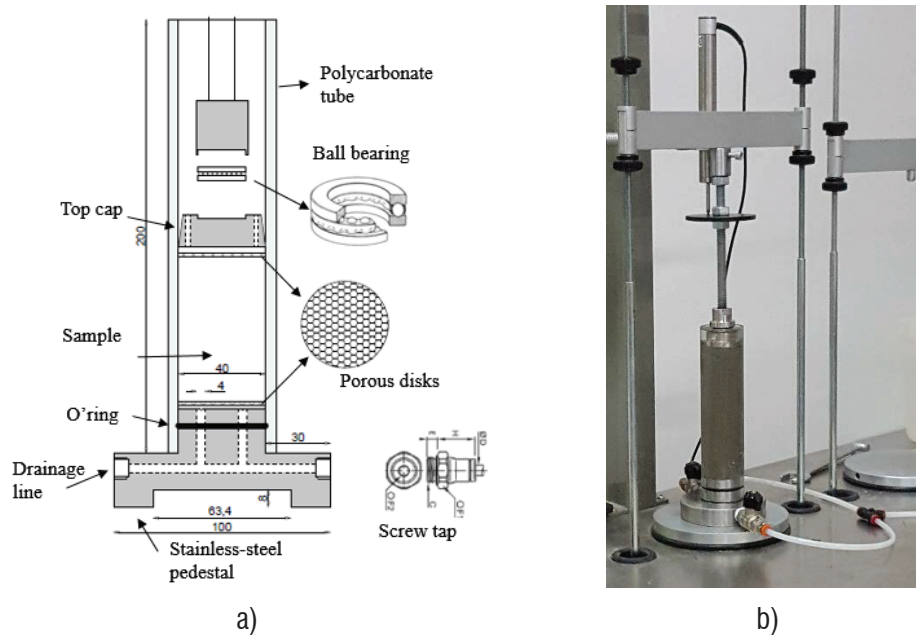


Fig. 6.23 - a) Schematic section of the environmental consolidometer (the dimensions are expressed in mm); b) apparatus present in the geotechnical laboratories of the Politecnico di Bari.

6.7.5 Unconfined compression test

The unconfined compression (UC) test is by probably the most popular method of soil shear testing because it is one of the fastest and cheapest methods of measuring unconfined compressive strength.

A cylindrical soil sample (with the length-to-diameter ratio on the order of two) without any confining pressure, is subjected to an axial compressive load until failure occurs. These tests were performed on both natural and treated (after 28 days of curing time) specimens according to the testing programme reported in Table. Immediately after mixing, the water content of the mixture was measured, and the stabilized sediment was placed into plastic moulds (cylindrical shape, 45 mm in diameter and 100 mm in height) in 3 layers (Fig. 6.24a). For each layer, the mould was tapped about 50 times against the floor, which followed the standard specified by the Japanese Geotechnical Society (2009). The specimens were placed in the triaxial load frame (Tritech

50kN, Controls S.p.A.) and the axial force was measured by means of a load cell of Imperial College type. Axial displacements were measured by LVDT transducers (Fig. 6.24c). The standard displacement transducer has a maximum travel length of 50 mm; its body is fixed to the loading ram, while the piston is allowed to move jointly to the cell and measures its movement. Accounting for corrections for the compliances of the apparatus, the accuracy of such displacement measurements is about 0.05%.

The tests were performed in accordance with ASTM D2166 for both the natural and treated sediments at 28 days of curing time. UC testing was performed at a rate of 5 mm/min until failure as the maximum deviator stress observed during testing.

The Unconfined Compressive Strength (q_u) is defined as the ratio of the Failure Load (P) to the cross-sectional area of the soil sample (A_c), if it is not subjected to any lateral pressure (Eq. 6.18).

$$q_u = \frac{P}{A_c} \quad (6.18)$$

The changed average cross-sectional area at a particular deformation during the test was calculated using the following equation (Eq. 6.19).

$$A_c = \frac{A_0}{(1 - \varepsilon)} \quad (6.19)$$

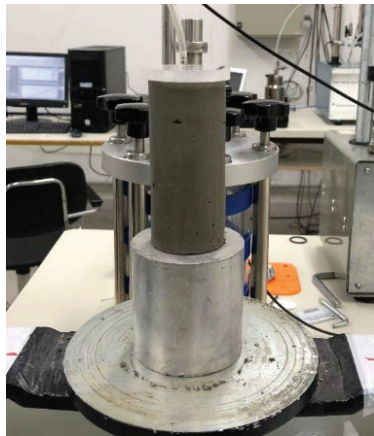
where ε is axial strain ($\varepsilon = \Delta L/L$).

The undrained shear strength is defined as the half of the compressive strength (Eq. 6.20).

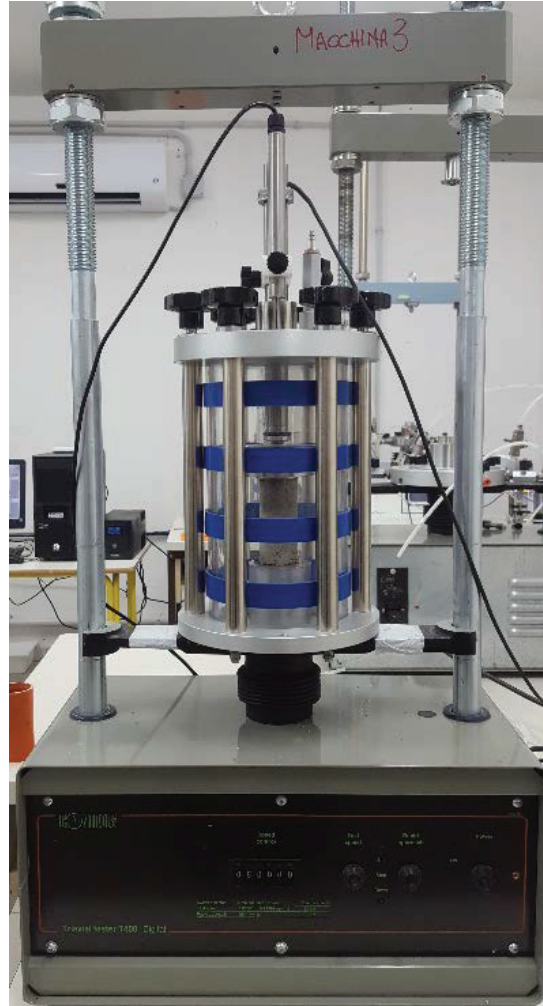
$$c = \frac{q_u}{2} \quad (6.20)$$



a)



b)



c)

Fig. 6.24 - Phases of preparation of the UC specimens: a) casting phase; b) specimen before testing phase; c) apparatus present in the geotechnical laboratories of the Politecnico di Bari.

CHAPTER 7. RESULTS AND DISCUSSION

7.1 Introduction

In this chapter, the laboratory test results obtained during the various experimental phases carried out at the laboratories of Chemistry and Environmental Technologies and Environmental Geotechnics of the Politecnico di Bari are presented. Specifically, Section 7.2 presents the results of the tests performed for the preliminary phase allowed to obtain information on the interaction between the contaminated sediments and the remediation treatments. Columns experiments and squeezing tests were carried out to investigate the applicability of permeable reactive mat for in situ remediation of contaminated sediments and the mobility of contaminants, while leaching tests allowed to verify the S/S treatments. Section 7.3 shows the experimental data of the advanced phase that allowed to both investigate the processes of transport, adsorption and degradation of contaminants over time and to verify the performance of different design solutions, allowing their optimization with respect to those of the preliminary phase. In addition to column tests for in situ options and leaching test for ex situ options, geotechnical tests were carried out on the best remediation solutions.

7.2 Preliminary phase

7.2.1 In situ options

Contaminated sediments

The sediments used for the tests were characterised by the composition and physical-chemical properties reported in Tab. 7.1. They are essentially fine-grained soils, for which the clay fraction, CF, varies between 37.21% (S17P sample) and 56.98% (S9P sample), sand fraction, SF, between 3.35% (S8P sample) and 14.84% (S14P sample) and the silt fraction, MF, ranges from 39.04% of the S9P sample to 55.33% of the S11P sample.

The chemical characterisation (Tabb. 7.2 - 7.4) showed that they were polluted by heavy metals, PAHs and PCBs. In particular, the values of contaminants are compared with the limits defined by both site-specific law (ICRAM, 2004; in yellow in the Tabb. 7.2, 7.3 and 7.4) and Italian National Law (D.Lgs. 152/2006; in red in the Tabb. 7.2, 7.3 and 7.4). The most contaminated samples (i.e. S4P, S11, S16P and S17P) were used for column tests to study the effects of capping solutions by means a reactive permeable mat; S8P and S9P samples were instead used for squeezing tests.

Parameter	Unit	S4P	S8P	S9P	S11P	S16P	S17P
pH	u. pH	8.91	9.12	9.16	9.20	9.11	9.31
Eh	mV	-100.9	-113.5	-114.6	-117.8	-116.9	-122.7
Conductivity	mS/cm	3.26	4.85	4.09	4.09	3.64	3.78
Moisture content	%	51.98	52.64	51.82	53.83	51.78	54.17
Ashes at 550°C	%	76.61	80.25	82.89	81.19	81.46	82.48
Organic matter content	%	23.39	19.75	17.11	18.81	18.54	17.52
Particle size distribution							
Sand fraction	%	10.89	3.35	3.89	4.34	4.42	14.84
Silt fraction	%	51.00	51.30	39.04	55.35	44.43	47.95
Clay fraction	%	38.06	45.35	56.98	40.31	51.15	37.21

Tab. 7.1 - Composition and physical-chemical properties of the samples of sediments used for the tests (preliminary phase, in situ options).

Metals	Unit	S4P	S8P	S9P	S11P	S16P	S17P
As	mg/kg ss	31.67	17.03	11.17	13.35	11.80	18.33
Cd	mg/kg ss	2.51	0.62	0.67	0.54	0.44	0.60
Be	mg/kg ss	0.79	2.05	1.39	1.09	0.73	1.15
Co	mg/kg ss	8.43	12.89	11.58	6.99	5.46	7.89
Cr	mg/kg ss	81.85	99.93	93.77	71.62	57.12	76.74
Hg	mg/kg ss	8.05	< LOD	< LOD	3.50	2.56	5.88
Ni	mg/kg ss	40.63	62.62	67.09	37.53	30.39	41.77
Pb	mg/kg ss	314.63	83.01	48.62	93.97	74.79	126.74
V	mg/kg ss	63.99	97.80	84.51	77.12	59.94	84.41
Cu	mg/kg ss	172.11	27.93	39.15	64.67	55.34	80.23
Zn	mg/kg ss	1541.51	100.18	1009.08	193.84	159.00	222.67

Tab. 7.2 - Concentration of heavy metals in untreated sediment samples (LOD = 0.01 mg/kg ss).

PAHs	Unit	S4P	S11P	S16P	S17P
Naphthalene	µg/kg ss	259	< LOD	< LOD	< LOD
Fluoranthene	µg/kg ss	969	2247	259	312
Anthracene	µg/kg ss	786	1058	130	140
Acenaphthene	µg/kg ss	135	51	< LOD	29
Acenaphthylene	µg/kg ss	43	43	< LOD	32
Fluorene	µg/kg ss	1021	60	< LOD	37
Phenanthrene	µg/kg ss	222	207	77	52
Pyrene	µg/kg ss	841	1999	225	267
Chrysene	µg/kg ss	654	1878	170	205
Benz[a]anthracene	µg/kg ss	650	1678	152	185
Benz[a]pyrene	µg/kg ss	758	1512	228	361
Benz[k]fluoranthene	µg/kg ss	1116	2211	329	447
Benz[b]fluoranthene	µg/kg ss	341	691	103	219
Benz[g,h,i]perylene	µg/kg ss	621	921	180	348
Dibenzo[a,h]anthracene	µg/kg ss	135	296	18	25
Indeno[1,2,3-cd]pyrene	µg/kg ss	681	1153	209	342
Total PAHs	µg/kg ss	9232	16004	2079	3002

Tab. 7.3 - Concentration of PAHs in untreated sediment samples (LOD = 20 µg/kg ss).

PCBs	Unit	S4P	S11P	S16P	S17P
PCB 28	µg/kg ss	< LOD	< LOD	< LOD	< LOD
PCB 52	µg/kg ss	< LOD	< LOD	< LOD	< LOD
PCB 81	µg/kg ss	< LOD	< LOD	< LOD	< LOD
PCB 95	µg/kg ss	< LOD	< LOD	< LOD	< LOD
PCB 101	µg/kg ss	< LOD	< LOD	116	148
PCB 99	µg/kg ss	608	< LOD	101	122
PCB 77	µg/kg ss	< LOD	< LOD	< LOD	< LOD
PCB 110	µg/kg ss	789	< LOD	83	134
PCB 128	µg/kg ss	428	< LOD	125	88
PCB 151	µg/kg ss	972	138	263	186
PCB 123	µg/kg ss	< LOD	< LOD	< LOD	< LOD
PCB 118	µg/kg ss	757	138	124	< LOD
PCB 114	µg/kg ss	< LOD	< LOD	< LOD	< LOD
PCB 149	µg/kg ss	303	< LOD	< LOD	70
PCB 146	µg/kg ss	2177	353	655	419
PCB 105	µg/kg ss	< LOD	< LOD	< LOD	< LOD
PCB 153	µg/kg ss	1793	285	481	416
PCB 126	µg/kg ss	< LOD	< LOD	< LOD	< LOD
PCB 183	µg/kg ss	1006	185	< LOD	205
PCB 187	µg/kg ss	302	< LOD	156	< LOD
PCB 138	µg/kg ss	251	< LOD	< LOD	< LOD
PCB 167	µg/kg ss	< LOD	< LOD	< LOD	< LOD
PCB 177	µg/kg ss	245	58	145	65
PCB 156	µg/kg ss	< LOD	< LOD	< LOD	< LOD
PCB 157	µg/kg ss	< LOD	< LOD	< LOD	< LOD
PCB 180	µg/kg ss	1713	< LOD	< LOD	364
PCB 169	µg/kg ss	< LOD	< LOD	< LOD	< LOD
PCB 170	µg/kg ss	662	< LOD	< LOD	< LOD
PCB 189	µg/kg ss	< LOD	< LOD	< LOD	< LOD
Total PCBs	µg/kg ss	12004	1157	2250	2216

Tab.7.4 - Concentration of PCBs in untreated sediment samples (LOD = 1 µg/kg ss).

Column experiments

Column tests were conducted to a first assessment of the effectiveness of reactive permeable mats (or Reactive Core Mat, RCM) for the remediation of contaminated sediments. The testing procedures and devices used for these tests have been described in section 6.4. In particular, 4 reactors were used to test two different solutions of RCM: samples S4P and S11P were treated with a RCM with organoclay (OC), while samples S16 and S17 were treated with a RCM with active carbon (AC).

In the static phase, water samples - before and after the placement of the capping layer - for the determination of heavy metals in solution were taken. Both for the pore water samples and for seawater, the As is the only metal detected in solution. All other heavy metals had a lower concentration than the Limit of Detection (LOD) of the analysis tool used (Tab. 7.5).

Metals	LOD [$\mu\text{g/l}$]	Methods of analysis
As	0.10 $\mu\text{g/l}$	UNI EN ISO 15587-1 2002 + UNI EN ISO 17294-2 2005
Be	0.40 $\mu\text{g/l}$	UNI EN ISO 15587-1 2002 + UNI EN ISO 17294-2 2005
Cd	0.15 $\mu\text{g/l}$	UNI EN ISO 15587-1 2002 + UNI EN ISO 17294-2 2005
Co	1.00 $\mu\text{g/l}$	UNI EN ISO 15587-1 2002 + UNI EN ISO 17294-2 2005
Cr	1.50 $\mu\text{g/l}$	UNI EN ISO 15587-1 2002 + UNI EN ISO 17294-2 2005
Hg	0.0019 $\mu\text{g/l}$	UNI EN ISO 15587-1 2002 + UNI EN ISO 17294-2 2005
Ni	2.00 $\mu\text{g/l}$	UNI EN ISO 15587-1 2002 + UNI EN ISO 17294-2 2005
Pb	1.00 $\mu\text{g/l}$	UNI EN ISO 15587-1 2002 + UNI EN ISO 17294-2 2005
Cu	1.00 $\mu\text{g/l}$	UNI EN ISO 15587-1 2002 + UNI EN ISO 17294-2 2005
V	2.00 $\mu\text{g/l}$	UNI EN ISO 15587-1 2002 + UNI EN ISO 17294-2 2005
Zn	25.0 $\mu\text{g/l}$	UNI EN ISO 15587-1 2002 + UNI EN ISO 17294-2 2005

Tab. 7.5 - Limit of Detection (LOD) for the determination of metals in liquid samples.

Fig. 7.1 shows the As concentrations both in pore-water and in seawater, before and after the placement of the capping layer when the equilibrium states were reached. The results show that environmental goals in seawater are always respected, according to the Directive 2008/105/CE (5 $\mu\text{g/l}$). In particular, for the sample S16P

(Fig. 7.1c), As concentrations in pore water increase after the placement of the cap; the contaminant tends to migrate into the overlying water due to the consolidation induced by capping, however the environmental standard in seawater is respected.

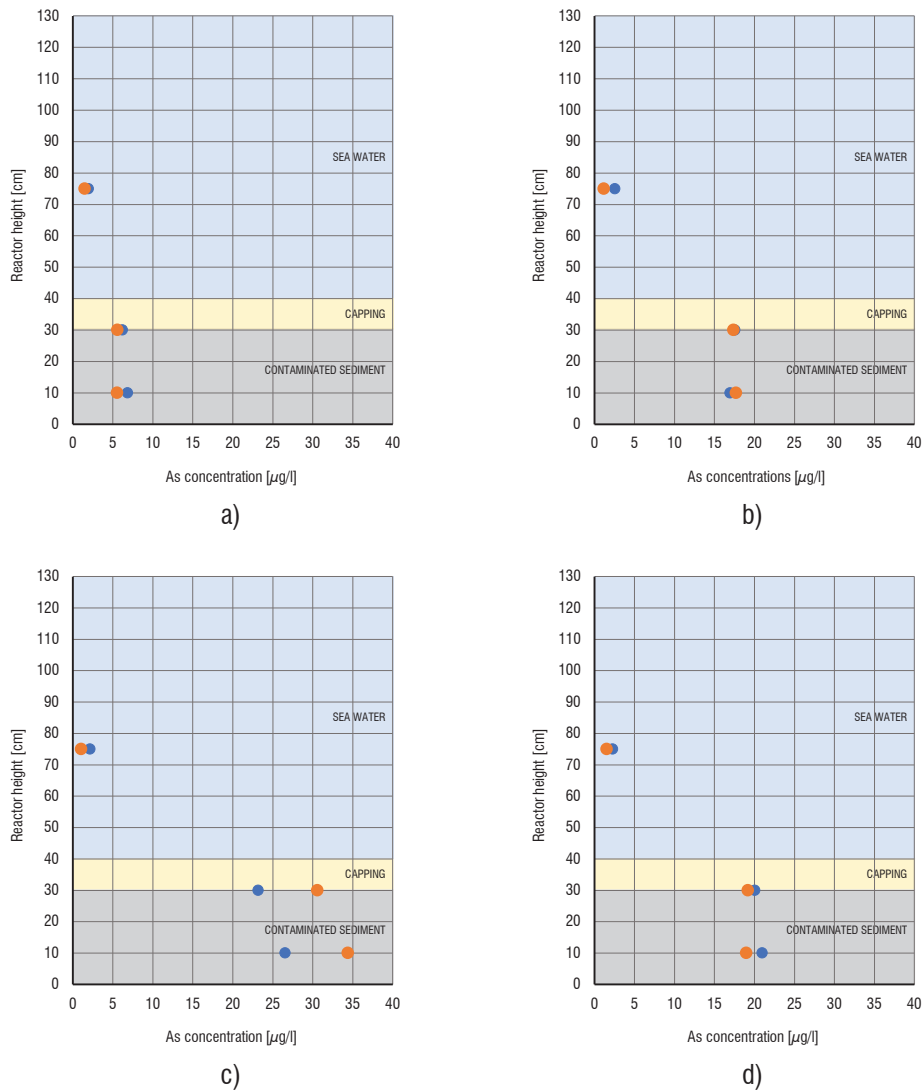


Fig. 7.1 - As concentrations in pore-water and seawater, before the placement of the capping (blue coloured dots) and after (orange coloured dots): a) sample S4P treated by RCM with OC; b) sample S11P treated by RCM with OC; c) sample S16P treated by RCM with AC; and d) sample S17P treated by RCM with AC.

It is worth to note that S16P is the sediment sampler characterized by highest clay fraction (51.15%). Moreover, it should be noted that the permeability of the capping (1×10^{-3} cm/s; CETCO, 2013) is always lower than the range of permeability values of the top sediments determined in the laboratory during oedometer tests ($1 \times 10^{-10} \div 1 \times 10^{-12}$ m/s; Sollecito et al., in prep.).

A moderate leaching was observed during the tests; however, the high concentrations of toxic metals present in the sediments represent a potential source for pollution. Metal-sulphides suspended in oxic seawater can be rapidly oxidised resulting in the release of metals in the water phase (Simpson et al., 1998). This suggests that one of the most important effect of the capping solution would be that of preventing re-suspension and oxidation and thereby keeping the metal mobility low.

At the end of the static phase, the reactive materials inside the cap were sampled and analysed. The results of the chemical analyses carried out post-treatment on the reactive materials are summarised in Tab. 7.6. They show adsorption of Be, Co, Cr, Ni, Pb, V, Cu and Zi for the organoclay and of Ni, Pb, Cu and Zi for the activated carbon. In general, OC seem to be more competitive than the AC (e.g. adsorption potential of Ni is 44.01 mg/kg for OC and 8.65 mg/kg for AC).

Exposure to seawater, with high ionic strength and content of divalent ions, can release a considerable amount of metals from the cap material into solution (e.g. Eek et al., 2007). The experimental data show that capping material tested with seawater, does not release metals but, as time passes (for the timeframe tested, i.e. 20 days), it absorbs metals at the interface sediment-cap.

PAHs were detected in seawater inside the reactor for each simulated scenario. Fig. 7.2 shows the PAHs concentrations without the capping, both for static and dynamic conditions, and after 5 days from the capping placement, both for static and dynamic conditions. The results show a release of contaminant without the capping, with higher concentrations in dynamic conditions. In the reactors without capping environmental standards in the water column are not met (Tab. 7.7); environmental goals are evaluated negatively because the PAHs concentrations are higher than the limit of law ($0.1 \mu\text{g/l}$). The reactive capping limits the flow of PAHs from sediments to

seawater: in static conditions of about 67% with OC (samples S4P and S11P) and of about 47% for AC (samples S16P and S17P); in dynamic conditions of about 89% with OC (samples S4P and S11P) and of 84% for the sample S16P and of 54% for the sample S17P (sediments treated with AC). After the treatment, the environmental standards are respected (Tab. 7.7).

Fig. 7.3 shows the PCBs concentrations in seawater for the four tested scenarios: without the capping and with capping, static and dynamic conditions. There is a flow of PCBs from the sediments, but, in this case, the concentrations do not increase significantly in the dynamic phase. The results show that limited diffusion of PCBs occurred during tests with cap regardless of the cap composition. Moreover, data show a reduction in the flow of PCBs due to capping (86.6% for RCM with OC and 71.6% for RCM with AC), however environmental standards are never respected (Tab. 7.8). These could also depend on: i) errors in the sampling phase (e.g. cross-contamination); ii) limit of detection of methods of analysis (LOD 0.1 $\mu\text{g/l}$).

Both in the present experimental phase and in previous work it has been demonstrated that capping of contaminated sediments efficiently decreases the flux of contaminants from sediments (especially As and PAHs) (Dixon and Knox, 2012; Eek et al., 2007 and 2008; Gidley et al., 2012; Meric et al., 2014). However, the limited laboratory test period did not allow for the interpretation of the real in situ rate of contaminants desorption from sediments.

Sediment sample	Parameter	Unit	Metals										
			As	Be	Cd	Co	Cr	Hg	Ni	Pb	V	Cu	Zn
S4P	Concentration in OC before the treatment	mg/kg	<LOD	0.09	<LOD	0.23	0.88	<LOD	0.65	4.95	0.83	1.13	6.78
	Concentration in OC after the treatment	mg/kg	<LOD	0.69	<LOD	2.94	8.04	<LOD	6.51	49.98	8.71	10.7	69.73
	Adsorption	mg/kg	-	0.60	-	2.71	7.16	-	5.86	45.03	7.88	9.57	62.95
S11P	Concentration in OC before the treatment	mg/kg	<LOD	0.09	<LOD	0.23	0.88	<LOD	0.65	4.95	0.83	1.13	6.78
	Concentration in OC after the treatment	mg/kg	<LOD	0.78	<LOD	2.41	10.54	<LOD	6.54	47.95	9.79	11.73	64.89
	Adsorption	mg/kg	-	0.69	-	2.18	9.66	-	5.89	43.00	8.96	10.60	58.11
S16P	Concentration AC before the treatment	mg/kg	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	4.43	<LOD	<LOD	18.15	5.58
	Concentration AC after the treatment	mg/kg	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	14.21	8.55	<LOD	20.38	13.68
	Adsorption	mg/kg	-	-	-	-	-	-	9.78	8.55	-	2.23	8.10
S17P	Concentration AC before the treatment	mg/kg	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	4.43	<LOD	<LOD	18.15	5.58
	Concentration AC after the treatment	mg/kg	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	10.74	8.76	<LOD	19.99	8.21
	Adsorption	mg/kg	-	-	-	-	-	-	6.31	8.76	-	1.84	2.63

Tab. 7.6 - Adsorption of metals in reactive materials after treatment. Adsorption potential is evaluated as the difference between the concentration before the treatment and concentration after the treatment (mg of metal per kg of reactive material) (LOD: 0.01 mg/kg).

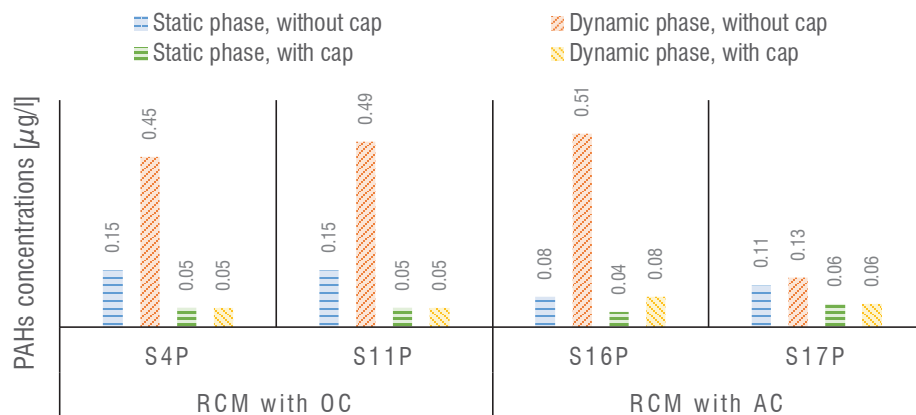


Fig. 7.2 - PAHs concentrations in seawater.

Sediment sample	Parameter	Unit	Scenario			
			Static		Dynamic	
			Without cap	With cap	Without cap	With cap
S4P	Concentration in sediment	µg/kg ss	9232	9232	9232	9232
	Concentration in seawater	µg/l	0.15	0.05	0.45	0.05
	Chemical isolation ^a	%	66.67		88.89	
	Environmental goals ^b	-	✗	✓	✗	✓
S11P	Concentration in sediment	µg/kg ss	16004	16004	16004	16004
	Concentration in seawater	µg/l	0.15	0.05	0.49	0.05
	Chemical isolation ^a	%	66.67		89.80	
	Environmental goals ^b	-	✗	✓	✗	✓
S16P	Concentration in sediment	µg/kg ss	2079	2079	2079	2079
	Concentration in seawater	µg/l	0.08	0.04	0.51	0.08
	Chemical isolation ^a	%	50.00		84.31	
	Environmental goals ^b	-	✗	✓	✗	✓
S17P	Concentration in sediment	µg/kg ss	3002	3002	3002	3002
	Concentration in seawater	µg/l	0.11	0.06	0.13	0.06
	Chemical isolation ^a	%	45.45		53.85	
	Environmental goals ^b	-	✗	✓	✗	✓

Tab. 7.7 - PAHs concentrations and capping performance. Symbols in table: a) Chemical isolation is evaluated as: $((C_{\text{Without cap}} - C_{\text{With cap}}) / C_{\text{Without cap}}) \times 100$; b) Environmental goals: positively (✓) and negatively (✗) if the PAHs concentrations are, respectively, lower and higher than law limit (according to the Directive 2013/39/CE).

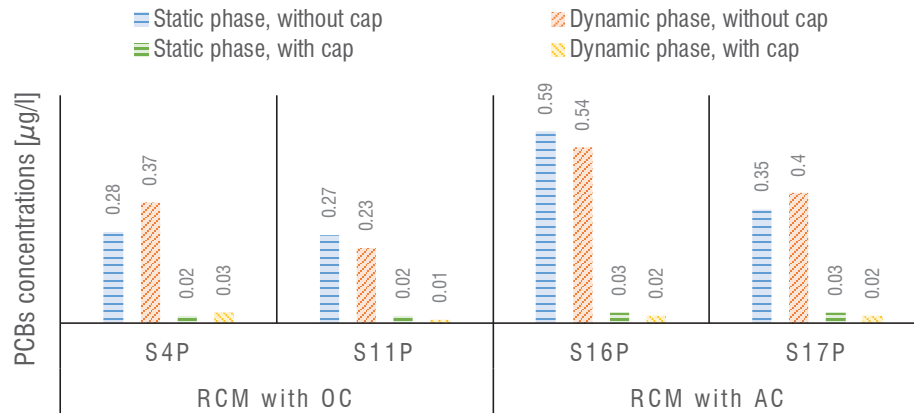


Fig. 7.3 - PCBs concentrations in seawater.

Sediment sample	Parameter	Unit	Scenario			
			Static		Dynamic	
			Without cap	With cap	Without cap	With cap
S4P	Concentration in sediment	μg/kg ss	12004	12004	12004	12004
	Concentration in seawater	μg/l	0.28	0.02	0.37	0.03
	Chemical isolation ^a	%	94.64		91.89	
	Environmental goals ^b	-	✗	✗	✗	✗
S11P	Concentration in sediment	μg/kg ss	1157	1157	1157	1157
	Concentration in seawater	μg/l	0.27	0.02	0.23	0.01
	Chemical isolation ^a	%	91.11		95.65	
	Environmental goals ^b	-	✗	✗	✗	✗
S16P	Concentration in sediment	μg/kg ss	2250	2250	2250	2250
	Concentration in seawater	μg/l	0.59	0.03	0.54	0.02
	Chemical isolation ^a	%	95.76		96.30	
	Environmental goals ^b	-	✗	✗	✗	✗
S17P	Concentration in sediment	μg/kg ss	2216	2216	2216	2216
	Concentration in seawater	μg/l	0.35	0.03	0.40	0.02
	Chemical isolation ^a	%	91.43		95.00	
	Environmental goals ^b	-	✗	✗	✗	✗

Tab. 7.8 - PCBs concentrations and capping performance. Symbols in table: a) Chemical isolation is evaluated as: $((C_{\text{Without cap}} - C_{\text{With cap}}) / C_{\text{Without cap}}) \times 100$; b) Environmental goals: positively (✓) and negatively (✗) if the PCBs concentrations are, respectively, lower and higher than law limit (according to the Directive 2013/39/CE).

Squeezing of contaminated sediments

In the present section, the results of the chemical analyses carried out on the samples S8P, S9P and S17P, which have been subjected to the test in the environmental consolidometer apparatus (Section 6.7.4) are reported.

Advection of pore water from capped sediment can be driven by two mechanisms: (1) submarine groundwater discharge, and (2) consolidation of the contaminated sediments. In many fine-grained contaminated sediments (as in the case in the Mar Piccolo basin), low permeability values suggest that submarine groundwater discharge have limited importance on transport of metals from capped sediments. Porewater advection from sediments can also be caused by compaction of the soil matrix (consolidation). A layer of materials placed at the top of the contaminated sediments results in an increased vertical effective stress in the significant volume of soil. In response to this stress the solid grains will seek a more compact configuration resulting in reduced porosity and dissipation of excess pore water. Therefore, consolidation can facilitate considerable advection of contaminated pore water. It is, therefore, important to discern how and if the occurrence of the consolidation process affects the metal concentration in the pore water released from contaminated sediments.

The specimens were compressed up to 100 kPa and the pore fluid squeezed out from the specimens during the consolidation processes - in the first loads and up to 12 kPa - has been collected in HDPE bottle.

Tab. 7.9 reports the total concentrations of heavy metals in the sediments before and after the consolidometer tests. The comparison between the metal concentration in the solids before and after the tests allows to notice that the concentration of As, Be, Cd, Co, Pb, Cu and V reduces after the consolidation process. All of them were also found in the pore fluid extracted during the consolidation process, suggesting the possible migration of these contaminants due to loading process.

Metal concentrations in the squeezed fluid comply with environmental quality standards for loads equal to 12 kPa (Directive 2013/39/CE); however, it has to be noted that the data suggest that the mobility of metals increases as the applied load increases.

Sediment sample	Measurements of metal concentrations	Units	Metals						
			As	Be	Cd	Co	Pb	V	Cu
S8P	Sediments before consolidation	mg/kg ss	17.03	2.05	0.62	12.89	83.01	27.93	97.80
	Sediments after consolidation	mg/kg ss	8.79	1.27	0.27	10.78	30.14	9.25	53.14
	Squeezed fluid (12 kPa)	mg/l	< LOD	< LOD	0.44	0.67	0.39	< LOD	0.11
S9P	Sediments before consolidation	mg/kg ss	11.17	1.39	0.67	11.58	48.62	39.15	84.51
	Sediments after consolidation	mg/kg ss	9.04	1.05	0.48	10.31	25.11	14.94	59.38
	Squeezed fluid (12 kPa)	mg/l	0.01	< LOD	0.06	< LOD	0.01	< LOD	1.15
S17P	Sediments before consolidation	mg/kg ss	13.35	5.83	13.35	5.83	13.35	5.83	13.35
	Sediments after consolidation	mg/kg ss	1.97	1.18	1.97	1.18	1.97	1.18	1.97
	Squeezed fluid (12 kPa)	mg/l	< LOD	< LOD	0.01	0.03	0.03	< LOD	0.5

Tab. 7.9 - Metal concentrations in the solid phase and in the squeezed fluid.

7.2.2 Ex situ options

Contaminated sediments

The sediments used for the tests were characterised by the composition and physical-chemical properties reported in Tab. 7.10.

They are essentially fine-grained soils, for which clay fraction, CF, varies between 40.25% (S6P sample) and 51.66% (S9P sample), sand fraction, SF, between 4.12% (S14P sample) and 14.26% (S16P sample) and silt fraction, MF, ranges from 41.26% of the S7P sample to 45.49% of the S6P sample.

The chemical characterisation (Tabb. 7.11 – 7.13) showed that they were polluted by heavy metals, PAHs and PCBs. The contents of contaminants in the Tables are compared with the corresponding limits defined by both site-specific law (ICRAM, 2004, in yellow in the Tables), and Italian National Law (D.Lgs. 152/2006, in red in the Tables)

Parameter	Unit	S6P	S7P	S14P
pH	u. pH	9.10	9.20	8.85
Eh	mV	-106.5	-115.8	-100.9
Conductivity	mS/cm	3.24	3.29	4.78
Moisture content	%	53.33	44.95	64.57
Ashes at 550°C	%	80.00	79.81	76.28
Organic matter content	%	20.00	20.19	23.72
Grain size distribution				
Sand fraction, SF	%	14.26	7.08	4.12
Silt fraction, MF	%	45.49	41.26	45.09
Clay fraction, CF	%	40.25	51.66	50.79

Tab. 7.10 - Physical-chemical properties and composition of the samples of sediments used for the tests (Preliminary phase, in situ options).

Metals	Unit	S6P	S7P	S14P
As	mg/kg ss	48.42	65.19	18.99
Cd	mg/kg ss	0.90	0.95	1.26
Be	mg/kg ss	1.17	0.99	0.82
Co	mg/kg ss	9.85	11.14	7.09
Cr	mg/kg ss	80.58	77.96	65.31
Hg	mg/kg ss	14.25	23.97	2.55
Ni	mg/kg ss	50.10	57.17	44.24
Pb	mg/kg ss	241.27	392.02	106.72
V	mg/kg ss	105.75	74.98	103.22
Cu	mg/kg ss	121.21	131.93	117.77
Zn	mg/kg ss	430.82	464.19	423.82

Tab. 7.11 - Concentration of heavy metals in untreated sediment samples (LOD = 0.01 mg/kg ss).

PAHs	Unit	S6P	S7P	S14P
Naphthalene	µg/kg ss	< LOD	< LOD	< LOD
Fluoranthene	µg/kg ss	667	727	337
Anthracene	µg/kg ss	444	306	204
Acenaphthene	µg/kg ss	< LOD	29	< LOD
Acenaphthylene	µg/kg ss	< LOD	< LOD	< LOD
Fluorene	µg/kg ss	49	39	< LOD
Phenanthrene	µg/kg ss	71	62	61
Pyrene	µg/kg ss	670	683	391
Chrysene	µg/kg ss	541	525	260
Benz[a]anthracene	µg/kg ss	477	480	232
Benz[a]pyrene	µg/kg ss	728	708	309
Benz[k]fluoranthene	µg/kg ss	1186	671	577
Benz[b]fluoranthene	µg/kg ss	373	459	190
Benz[g,h,i]perylene	µg/kg ss	481	293	209
Dibenzo[a,h]anthracene	µg/kg ss	170	125	40
Indeno[1,2,3-cd]pyrene	µg/kg ss	695	703	362
Total PAHs	µg/kg ss	6552	5810	3172

Tab. 7.12 - Concentration of PAHs in untreated sediment samples (LOD = 20 µg/kg ss).

PCBs	Unit	S6P	S7P	S14P
PCB 28	µg/kg ss	< LOD	< LOD	< LOD
PCB 52	µg/kg ss	< LOD	< LOD	< LOD
PCB 81	µg/kg ss	< LOD	< LOD	< LOD
PCB 95	µg/kg ss	< LOD	< LOD	< LOD
PCB 101	µg/kg ss	787	< LOD	48
PCB 99	µg/kg ss	445	< LOD	42
PCB 77	µg/kg ss	< LOD	< LOD	< LOD
PCB 110	µg/kg ss	716	53	< LOD
PCB 128	µg/kg ss	343	< LOD	< LOD
PCB 151	µg/kg ss	800	55	52
PCB 123	µg/kg ss	< LOD	< LOD	< LOD
PCB 118	µg/kg ss	729	< LOD	< LOD
PCB 114	µg/kg ss	< LOD	< LOD	< LOD
PCB 149	µg/kg ss	220	< LOD	< LOD
PCB 146	µg/kg ss	1612	131	120
PCB 105	µg/kg ss	< LOD	< LOD	< LOD
PCB 153	µg/kg ss	< LOD	124	< LOD
PCB 126	µg/kg ss	< LOD	< LOD	< LOD
PCB 183	µg/kg ss	< LOD	55	61
PCB 187	µg/kg ss	241	< LOD	< LOD
PCB 138	µg/kg ss	< LOD	< LOD	< LOD
PCB 167	µg/kg ss	< LOD	< LOD	< LOD
PCB 177	µg/kg ss	239	< LOD	< LOD
PCB 156	µg/kg ss	< LOD	< LOD	< LOD
PCB 157	µg/kg ss	< LOD	< LOD	< LOD
PCB 180	µg/kg ss	1511	116	70
PCB 169	µg/kg ss	< LOD	< LOD	< LOD
PCB 170	µg/kg ss	< LOD	< LOD	< LOD
PCB 189	µg/kg ss	< LOD	< LOD	< LOD
Total PCBs	µg/kg ss	7643	533	393

Tab. 7.13 - Concentration of PCBs in untreated sediment samples (LOD = 1 µg/kg ss).

Leaching tests

Following the procedures described in section 6.5, stabilization and solidification procedures have been carried out on samples of sediments characterised by different contamination. In particular, for different curing time (i.e. 1, 7, 14, 21 and 28 days), the leached heavy metal concentrations of As, Co, Cr, Hg, Ni, Pb, V and Zn, and that of the organic substances PAHs and PCBs, have been determined.

A first consideration emerging from the analysis of the results is the totally absence of organic contaminants in the liquid samples: PAHs and PCBs concentrations in all the leached samples were not detectable (LOD is approximately 0.001 mg/l). However, these contaminants may have a detrimental effect on the properties of treated materials slowing down the hydration process of the binders (Hasegawa et al., 2016; Kogbara, 2014).

Focusing on the heavy metals, the most important processes are sorption and precipitation, both strongly depending on the pH conditions. Fig. 7.4 shows the effect of the binders on the pH of the specimens, after different curing time. When binders are added, there is a substantial pH increase with respect to that of the natural sediments. After 24 hours (execution of the first leaching test), the pH of the mixtures is equal to approximately 13: the pH values varying between 12.2 (MIX A, sediment sample S14P) and 13.1 (MIX C, sediment samples S6P). Longer curing times tends to reduce the pH of the eluates, however the values are still higher than those of the untreated sediment: the pH values varying between 10.3 (MIX A, sample S14) and 12.6 (MIX C, sample S7P). It can be observed that the addition of cement (MIX A) involves the lower increase in pH with the respect to lime.

The solubility of silica and alumina greatly increase at elevated pH levels (12–13), which can lead to an increase in pozzolanic reactions. Under the attack of OH^- in such a high pH solution, a mineralogical breakdown takes place in the matrix. Silicate or aluminosilicate network formers (from the sediment) are also depolymerized and dissolve into solution, producing two primary cementing agents, C-S-H and C-A-H, which have important roles in improving the mechanical properties of the specimens

(Silitonga et al., 2010). However, high pH values may increase the leaching of some metals (Desogus et al., 2012; Stegemann and Zhou, 2009; Cao et al., 2008).

In Figs. 7.5 - 7.12 the concentrations detected into the leached fluid of the chosen heavy metals respect to the different binder/sediment relationship are reported for the three sediment samples investigated. The concentrations of Hg are not reported because they always resulted to be lower than the instrumental detection limit, (about 0.001 mg/l).

With respect to As, the pattern of release varies with the sediment sample: for S6P, As shows its lowest solubility at low pH values (except for the MIX A); for S7P, its solubility remains almost constant with curing time; for S14P there is an increase of solubility with the reduction of pH (i.e. increase of curing time).

The increasing release of Co with the decrease of the pH (i.e. with the increase of the curing time) can be observed in Fig. 7.6. A similar behaviour is found for Ni, V, Cu, and Zn concentrations. However, the higher concentrations in the leached fluid of Co, V and Cu are found after 28 days; for Ni and Zn the maximum of the release curves is 14 days, this shows a positive effect of the curing time that blocks, at least, reduces the mobility of metals.

The concentrations of Cr and Pb are reduced with curing time (i.e. with the reduction of pH values).

It could be noted that, in general, the addition of binders is found to highly increase the leaching characteristics of the mixture, which decrease with curing time only for some metals. For almost all the metals, except for the As, V and Zn, the leached concentrations increase after the treatment. In particular, an enhanced leaching has been obtained for As (exceptions: MIX A sample S6P and MIX C sample S14P) and Zn (exceptions: mixtures of sample S6P).

It is possible to calculate the rate of leaching of metals as a ratio of the content of an element in eluate after 28 days to its total content in the untreated sediments. This coefficient provides information about both the amount and rate of leaching of a given element from the treated sediment. The data indicate that the highest amount of As, Co, Cr, Ni and V are released from sample S14P, whereas the highest amount of Cr and Pb

are released from sample S7P and highest amount of Cu is released from sample S6P. According to the literature (Peakall and Burger, 2003; Trojanowski et al., 2007), the main factors affecting mobility of metals from bottom sediments include pH and organic matter content. Moreover, the rate of solution permeating through sediments is also connected with their grain size distribution. Permeability of solutions seeping through sediments is connected with the finest fraction, which seals the spaces between coarser fractions, and favours reduction and therefore element leaching. It follows that, the relatively high mobility of metals from S14P (sample with the highest value of organic matter content and the minimum values of sand fraction), despite the low total content of metals, can depend on its composition.

For the beneficial reuse of contaminated marine sediments, the leaching of each metal has to be lower than law limits. In Italy, the chemical parameters must be under the threshold levels defined by the Italian Ministerial Decree 5/2/1998. Tab. 7.14 shows the compliance of metal concentrations with legal limits after 28 days of curing time. In general, the addition of binders to the contaminated marine sediments shows a negative effect on decreasing the mobility of heavy metals. However, only Ni, Pb (MIX B and MIX C for sample S7P) and Cu are released with concentrations higher than the law limits.

The results of this experimental phase indicate that, for untreated sediments, the release of contaminants after contact with deionized water is very limited. This is due to the low metals' solubility and to the stability of their solid phases under slightly basic conditions. The adding of cement and lime increases the pH of the mixtures and appears to increase the leaching of different metals; in particular, mobility of the metals appears to be mainly governed by pH and curing time. However, it has to be underlined that, the performance of the mixtures is also conditioned by the presence of organic contaminants (i.e., organic matter, PAHs and PCBs) that interfered with the hydration of binders, compromising the effectiveness of metal stabilization and development of hardening (Wang et al., 2015). Furthermore, even seawater may have interfered with the chemistry of the binders.

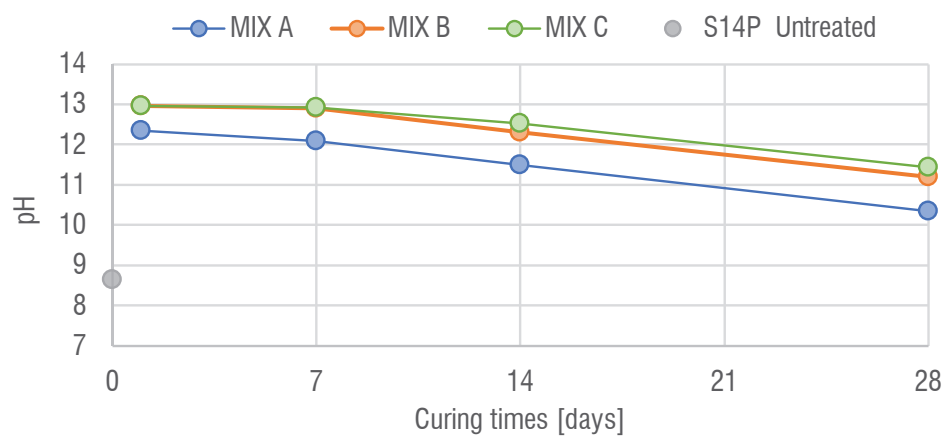
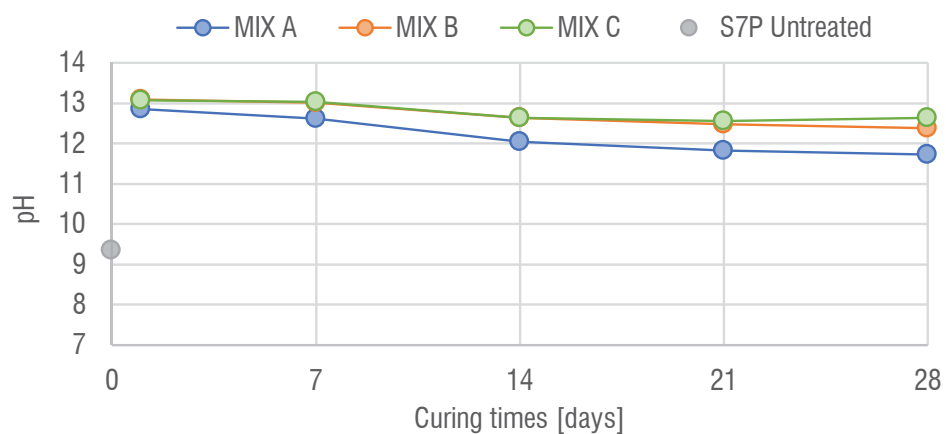
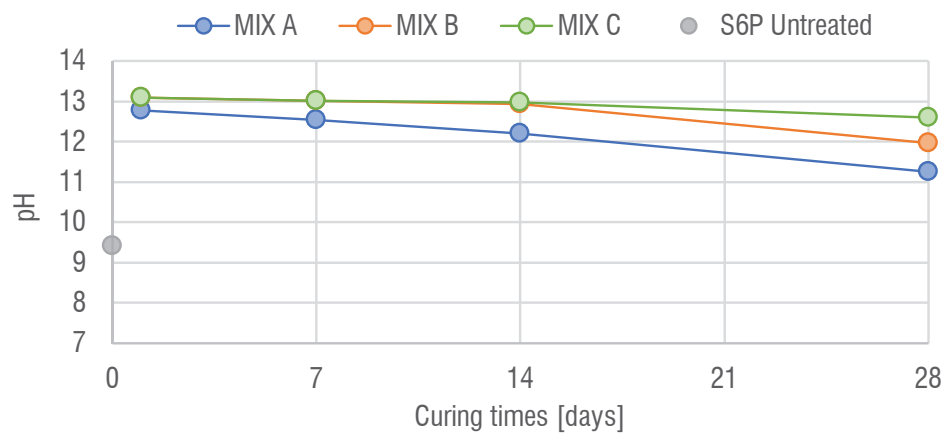


Fig. 7.4 - Variation of pH with curing time for different sediment samples (MIX A, sediment with 15% of cement; MIX, sediment with 7.5% of cement and 7.5% of lime; MIC C, sediment with 15% of lime).

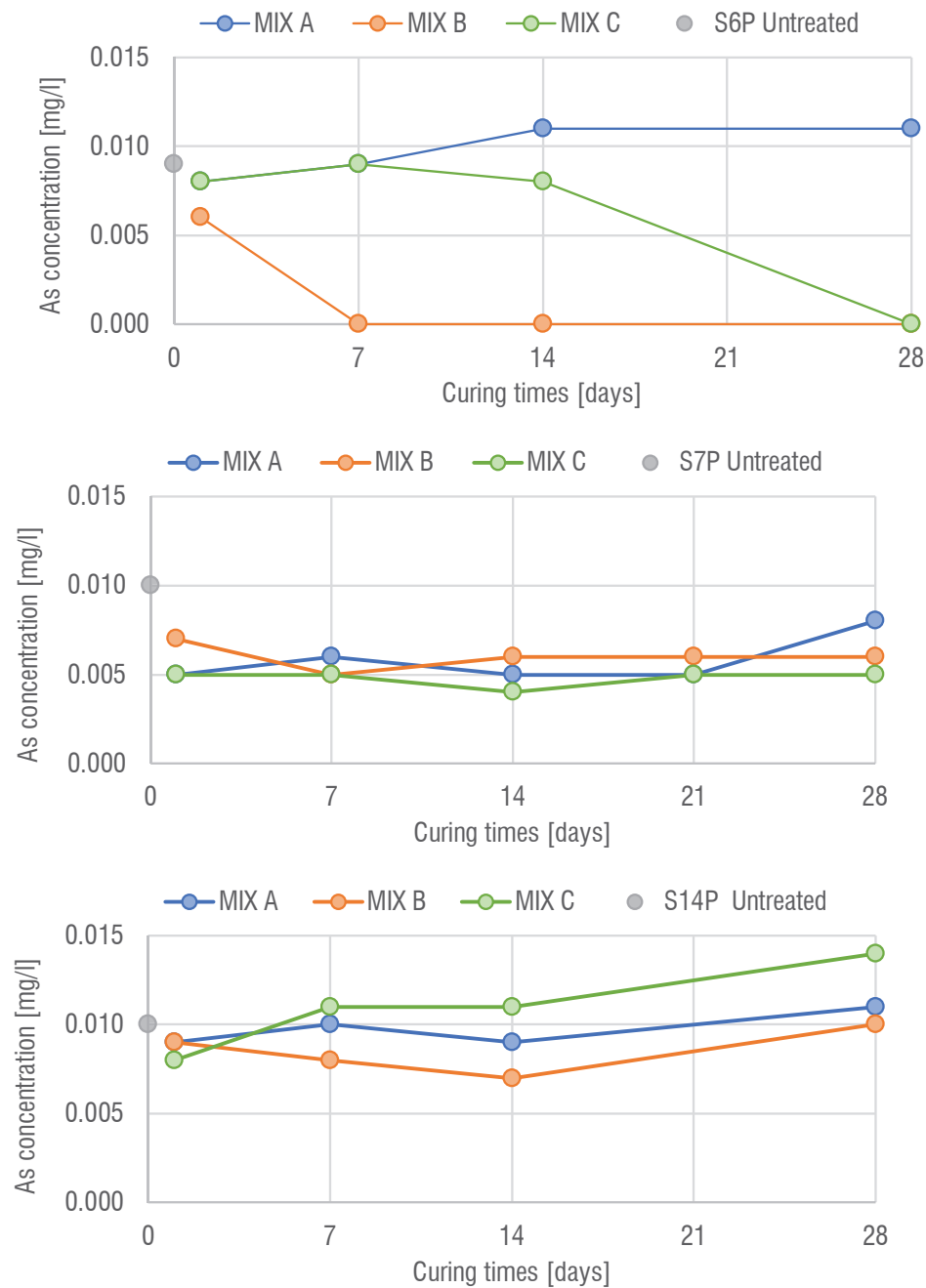


Fig. 7.5 - Variation of As concentrations after different curing time (MIX A, sediment with 15% of cement; MIX B, sediment with 7.5% of cement and 7.5% of lime; MIX C, sediment with 15% of lime. (Regulatory standards 0.05 mg/l).

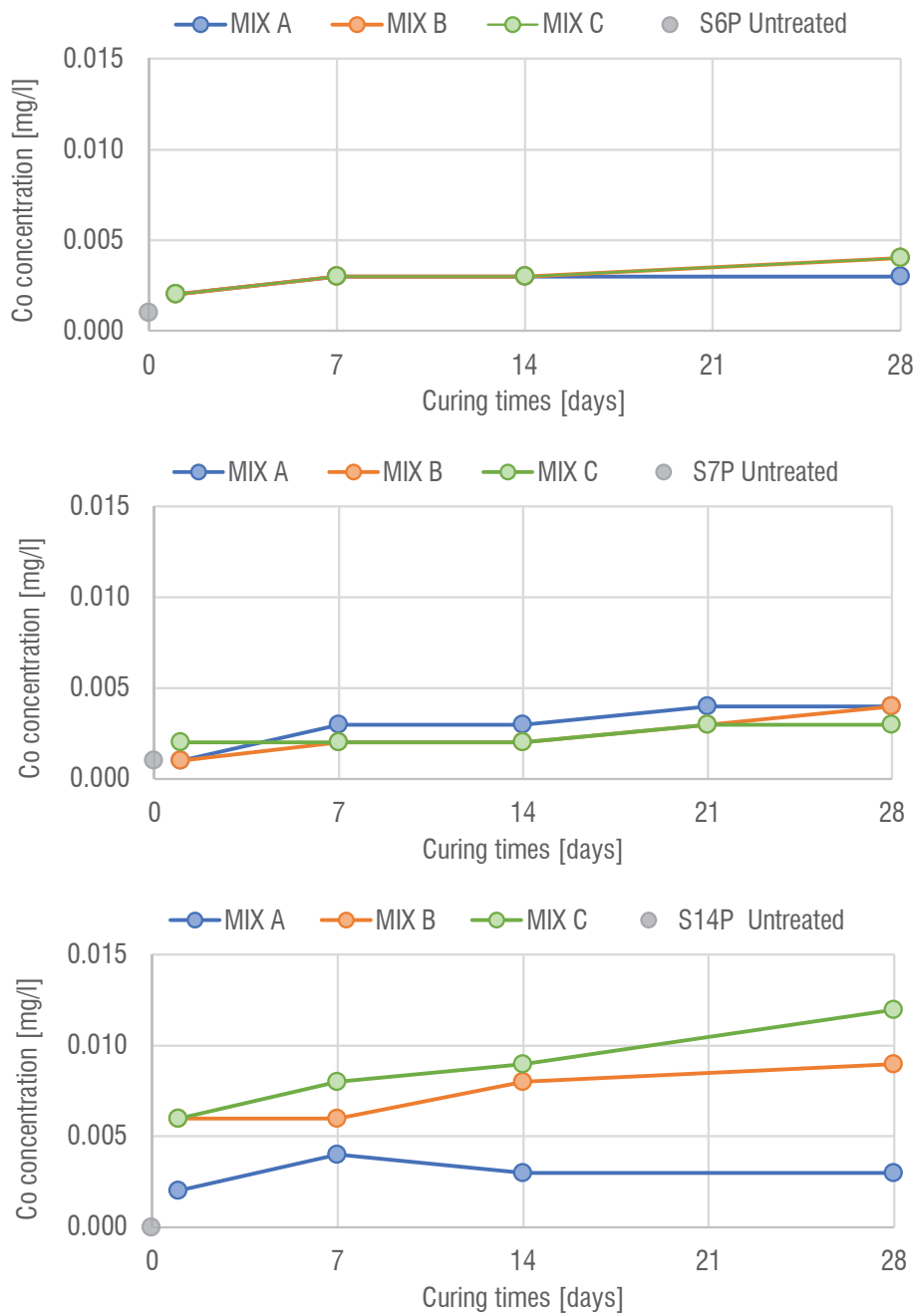


Fig. 7.6 - Variation of Co concentrations after different curing time (MIX A, sediment with 15% of cement; MIX B, sediment with 7.5% of cement and 7.5% of lime; MIX C, sediment with 15% of lime). (Regulatory standards 0.25 mg/l).

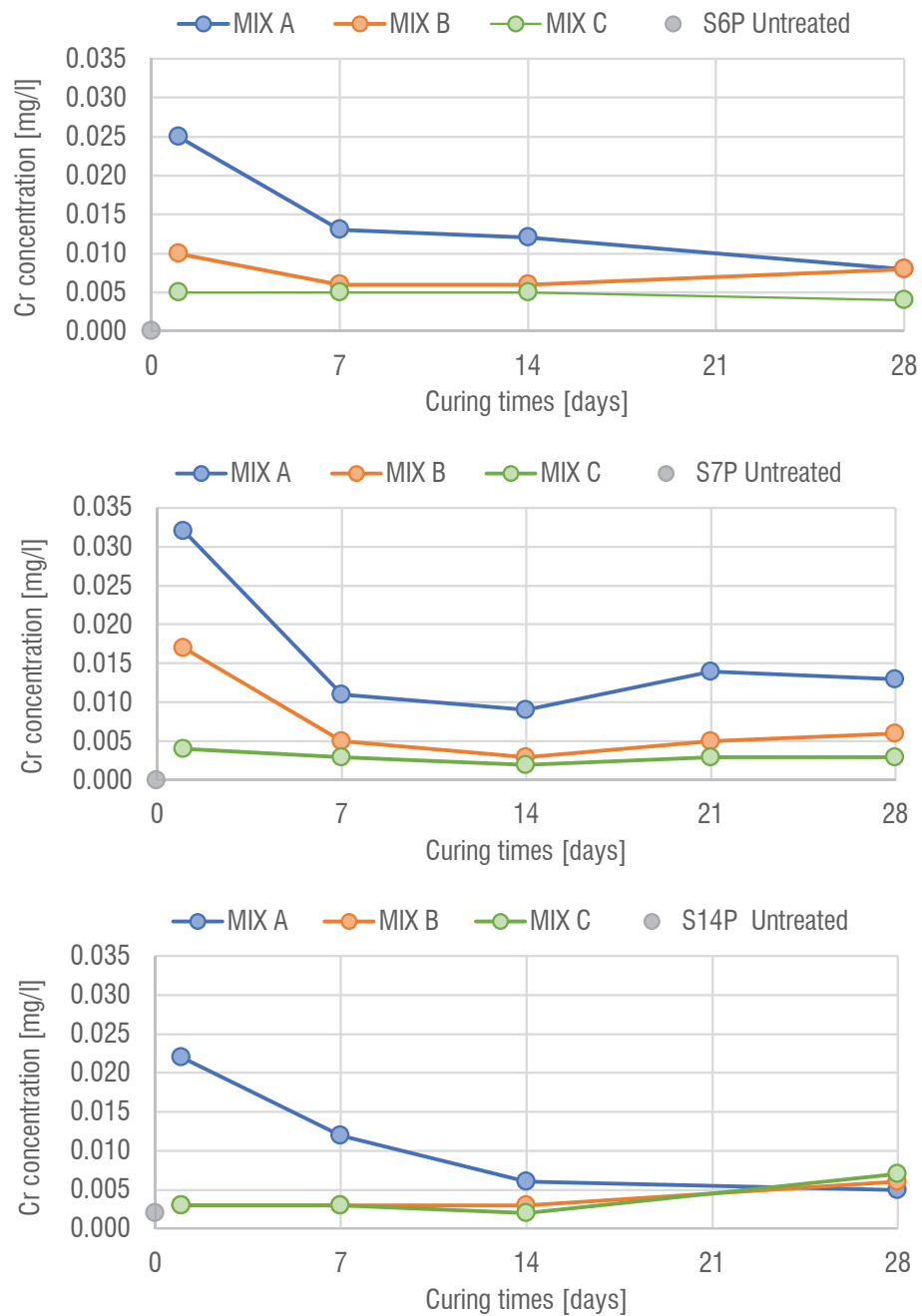


Fig. 7.7 - Variation of Cr concentrations after different curing time (MIX A, sediment with 15% of cement; MIX B, sediment with 7.5% of cement and 7.5% of lime; MIX C, sediment with 15% of lime). (Regulatory standards 0.05 mg/l).

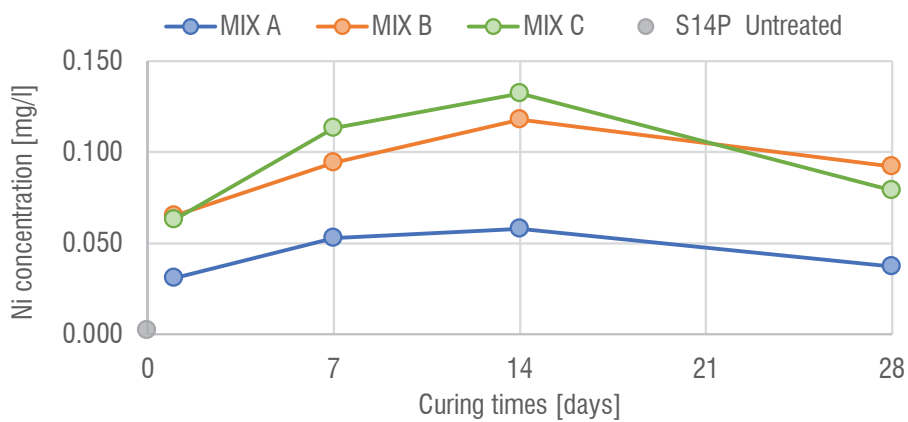
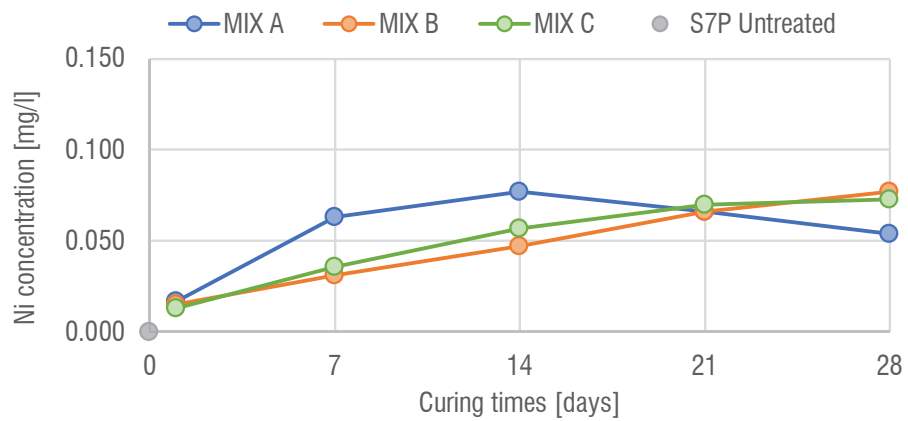
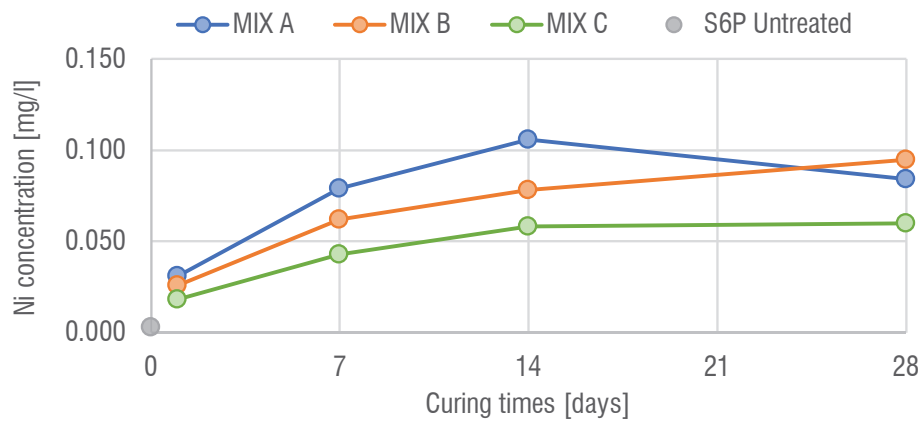


Fig. 7.8 - Variation of Ni concentrations after different curing time (MIX A, sediment with 15% of cement; MIX B, sediment with 7.5% of cement and 7.5% of lime; MIX C, sediment with 15% of lime). (Regulatory standards 0.01 mg/l).

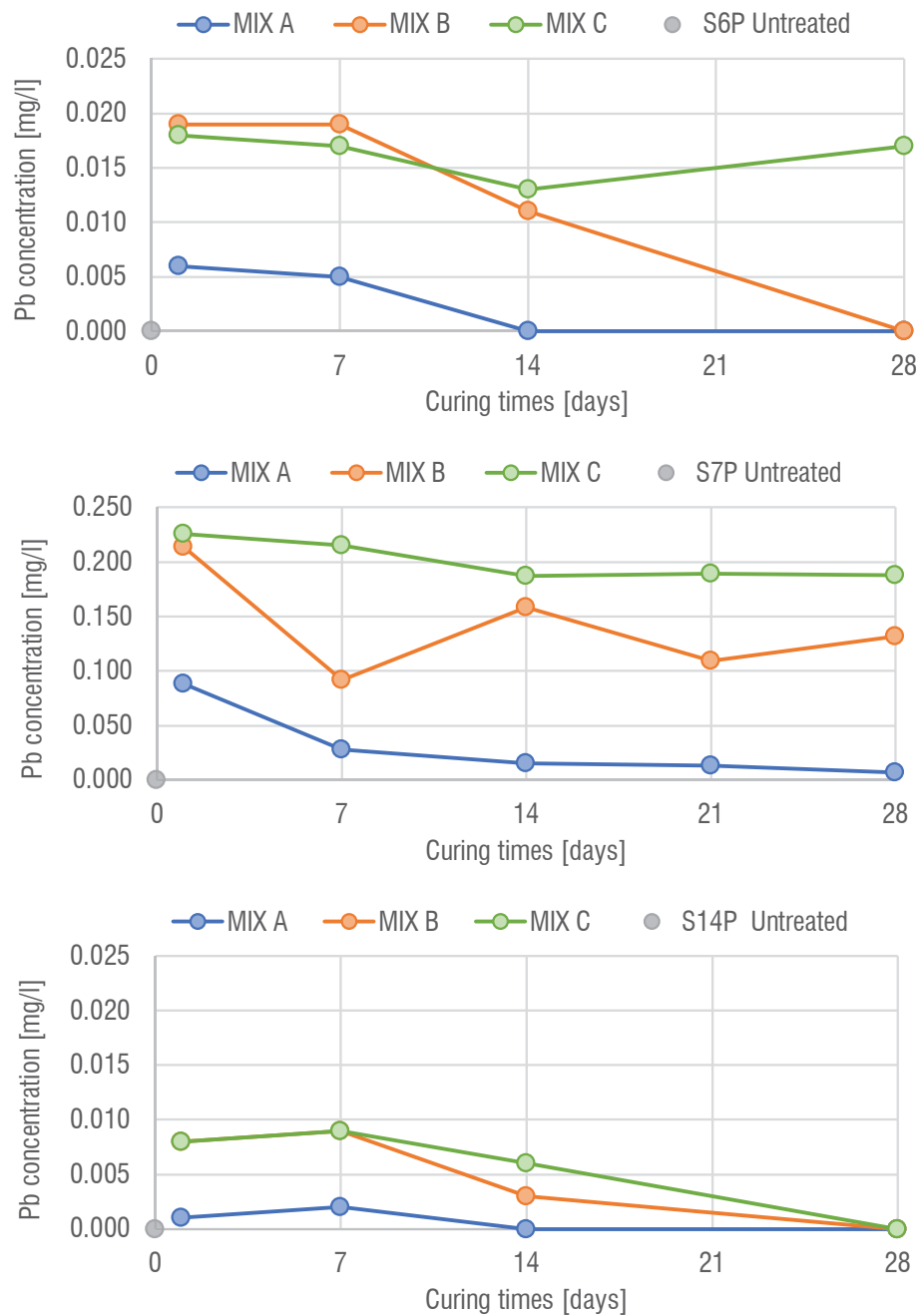


Fig. 7.9 - Variation of Pb concentrations after different curing time (MIX A, sediment with 15% of cement; MIX B, sediment with 7.5% of cement and 7.5% of lime; MIX C, sediment with 15% of lime). (Regulatory standards 0.05 mg/l).

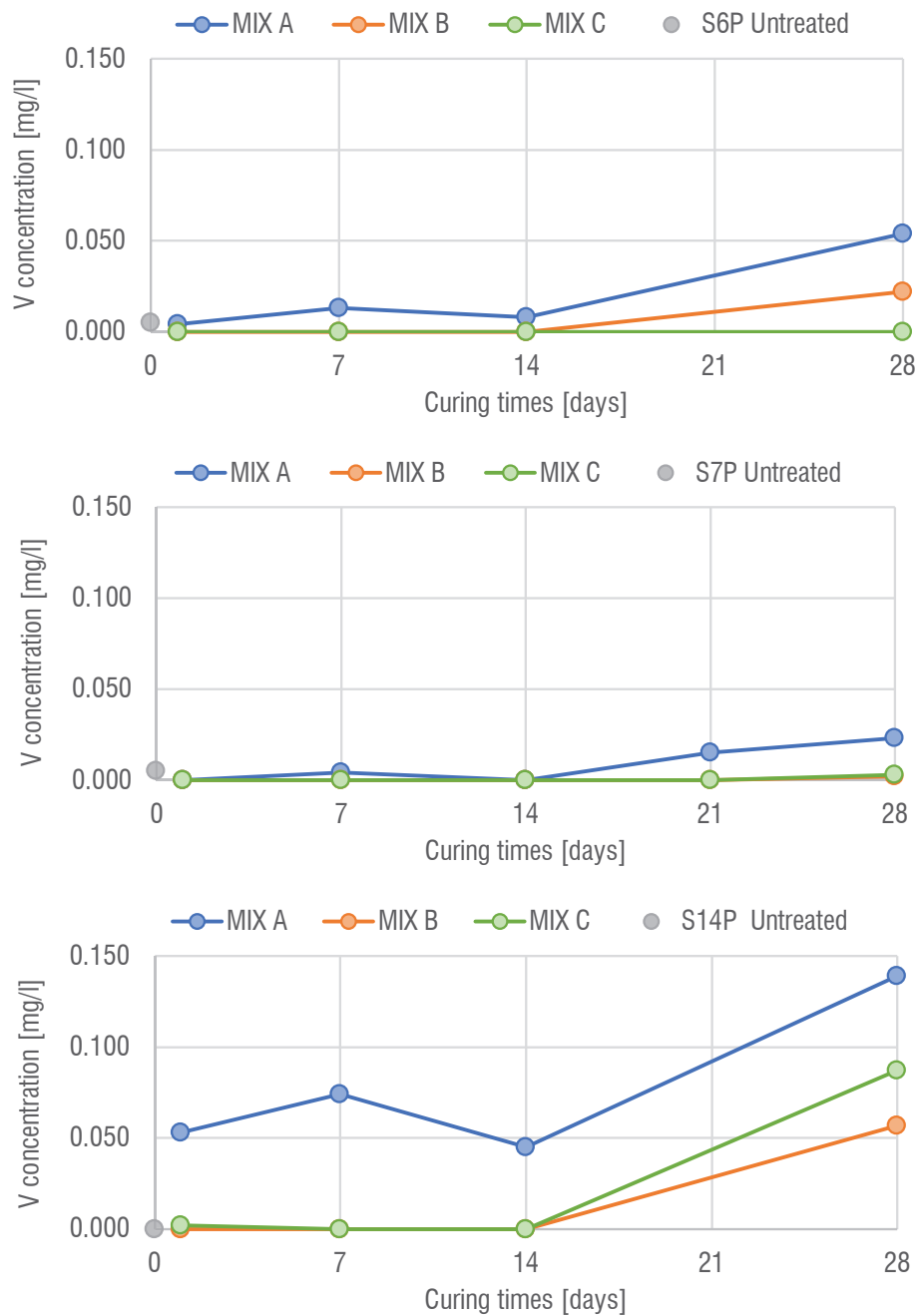


Fig. 7.10 - Variation of V concentrations after different curing time (MIX A, sediment with 15% of cement; MIX B, sediment with 7.5% of cement and 7.5% of lime; MIX C, sediment with 15% of lime). (Regulatory standards 0.25 mg/l).

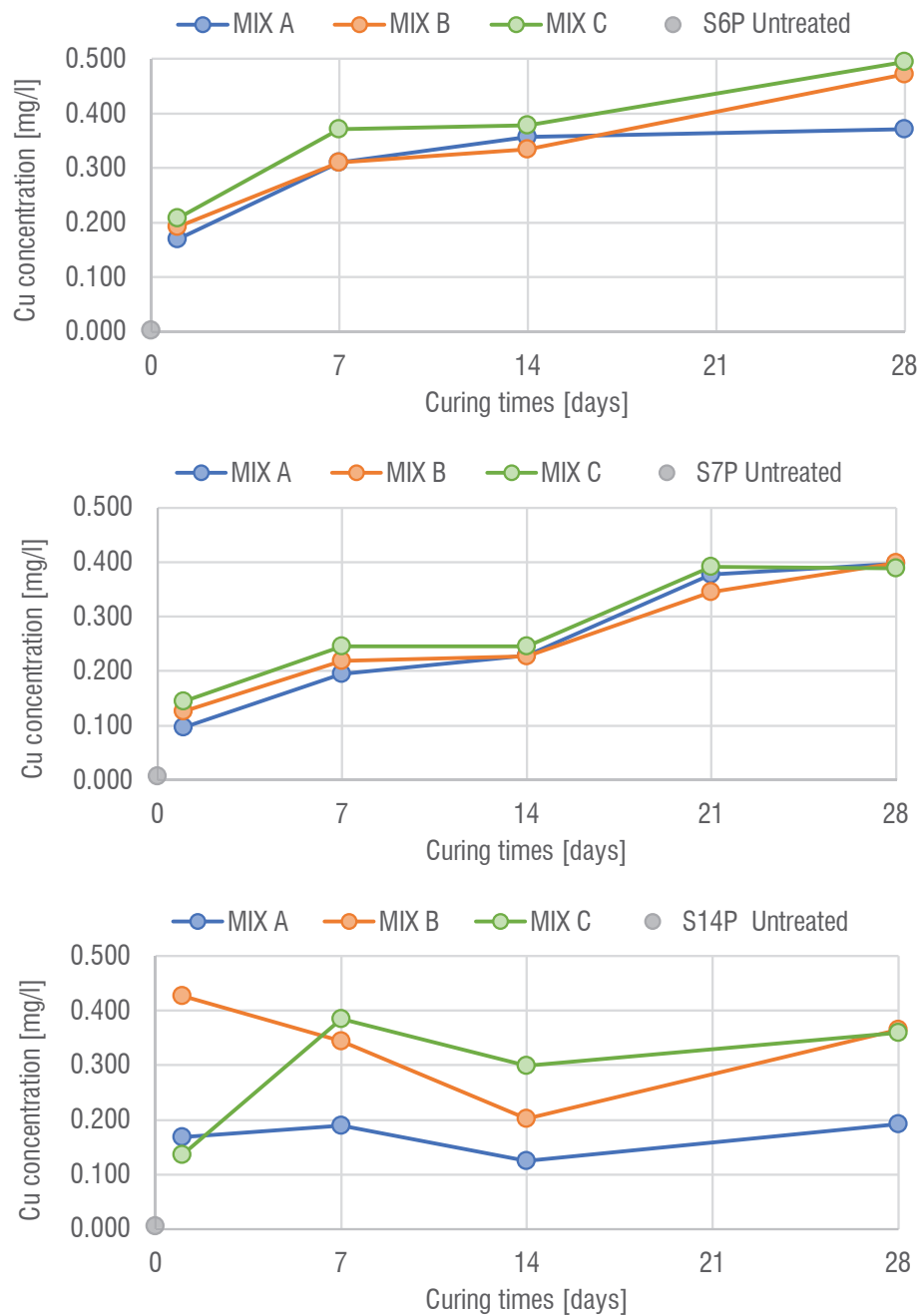


Fig. 7.11 - Variation of Cu concentrations after different curing time (MIX A, sediment with 15% of cement; MIX B, sediment with 7.5% of cement and 7.5% of lime; MIX C, sediment with 15% of lime). (Regulatory standards 0.05 mg/l).

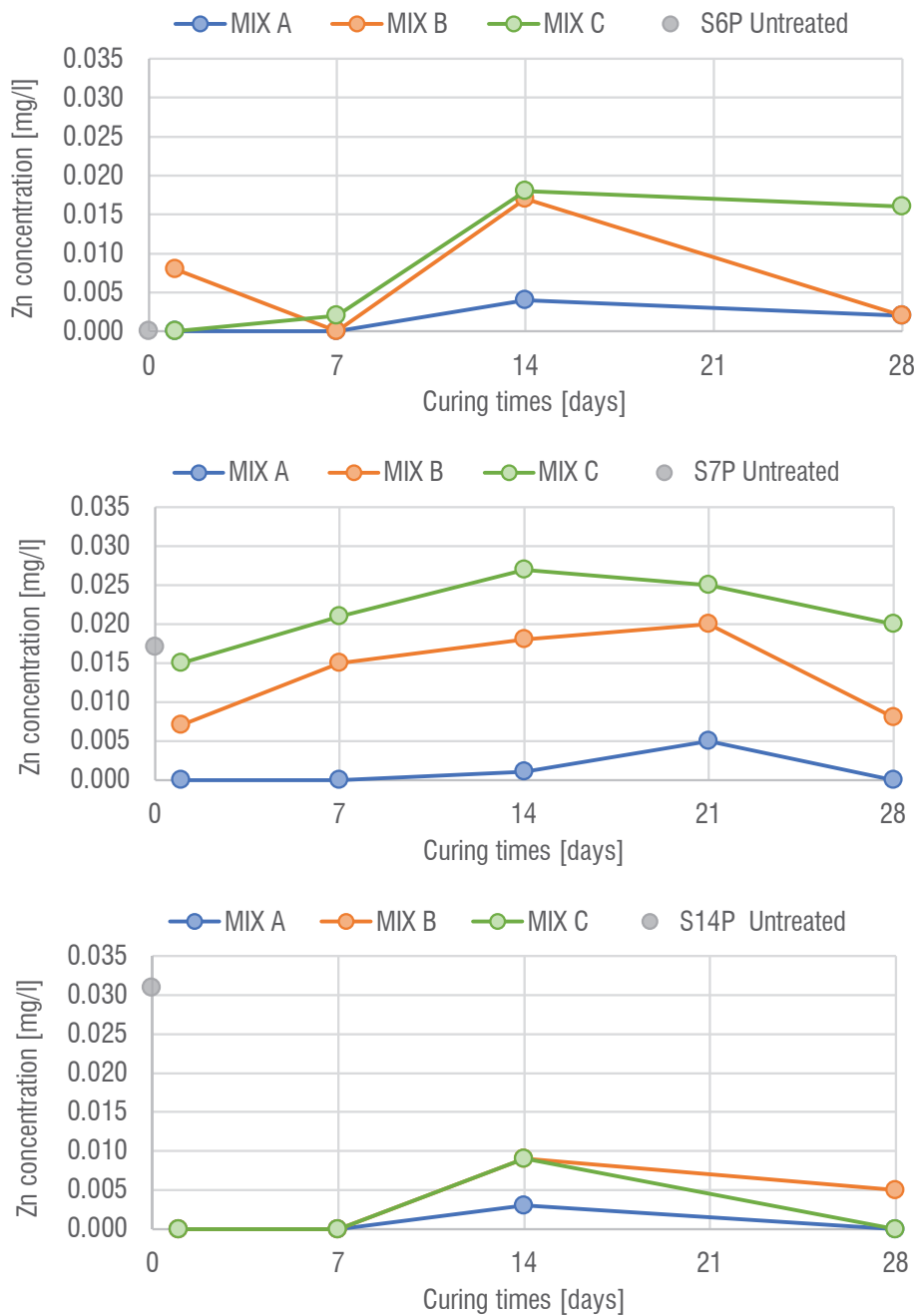


Fig. 7.12 - Variation of Zn concentrations after different curing time (MIX A, sediment with 15% of cement; MIX B, sediment with 7.5% of cement and 7.5% of lime; MIX C, sediment with 15% of lime). (Regulatory standards 3 mg/l).

Sediment sample	Mix	Parameter	Unit	Metals							
				As	Co	Cr	Ni	Pb	V	Cu	Zn
S6P	A	Leachate concentration	mg/l	0.011	0.003	0.008	0.084	< LOD	0.054	0.371	0.002
		Environmental goals	-	✓	✓	✓	✗	✓	✓	✗	✓
	B	Leachate concentration	mg/l	< LOD	0.004	0.008	0.095	< LOD	0.022	0.472	0.002
		Environmental goals	-	✓	✓	✓	✗	✓	✓	✗	✓
	C	Leachate concentration	mg/l	< LOD	0.004	0.004	0.060	0.017	< LOD	0.495	0.016
		Environmental goals	-	✓	✓	✓	✗	✓	✓	✗	✓
S7P	A	Leachate concentration	mg/l	0.008	0.004	0.013	0.054	0.007	0.023	0.397	0.000
		Environmental goals	-	✓	✓	✓	✗	✓	✓	✗	✓
	B	Leachate concentration	mg/l	0.006	0.004	0.006	0.077	0.132	0.002	0.398	0.008
		Environmental goals	-	✓	✓	✓	✗	✗	✓	✗	✓
	C	Leachate concentration	mg/l	0.005	< LOD	0.003	0.073	0.188	0.003	0.388	0.020
		Environmental goals	-	✓	✓	✓	✗	✗	✓	✗	✓
S14P	A	Leachate concentration	mg/l	0.011	< LOD	0.005	0.037	< LOD	0.139	0.192	< LOD
		Environmental goals	-		✓	✓	✗	✓	✓	✗	✓
	B	Leachate concentration	mg/l	0.010	0.009	0.006	0.092	< LOD	0.057	0.365	0.005
		Environmental goals	-		✓	✓	✗	✓	✓	✗	✓
	C	Leachate concentration	mg/l	0.014	0.012	0.007	0.079	< LOD	0.087	0.360	< LOD
		Environmental goals	-		✓	✓	✗	✓	✓	✗	✓

Tab. 7.14 - Environmental performance of the mixtures in terms of metal stabilization. Environmental goals: positive (✓) and negative (✗) if metal concentrations are, respectively, lower and higher than law limits (according to the Directive 2013/39/CE).

7.3 Advanced phase

7.3.1 In situ options

Contaminated sediments

As already discussed in Section 7.2.1, in this experimental phase, the tests have been performed on a prototype-marine sediment, made by mixing several samples of the official campaign. This allowed to test different capping technologies on the same prototype-sample. The physical-chemical properties and the grain size distribution of the sediment prototype-sample are reported in Tab. 7.15.

Parameter	Unit	MIX_2
pH	u. pH	8.82
Eh	mV	-100.7
Conductivity	mS/cm	4.78
Moisture content	%	44.63
Ashes at 550°C	%	89.14
Organic matter content	%	10.86
Particle size distribution		
Sand fraction	%	19.44
Silt fraction	%	43.18
Clay fraction	%	37.38

Tab. 7.15 - Physical-chemical properties of the prototype-sample used for the tests carried out in the Advanced phase (in situ options).

The chemical characterisation (Tabb. 7.16 - 7.18) showed that the sample was polluted by heavy metals, PAHs (5732 µg/kg ss), PCBs (1513 µg/kg ss). The Hg concentration was 1.99 mg/kg ss; the Pb level was 91.45 mg/kg ss, Cu were 59.00 mg/kg ss and Zn were 172.73 mg/kg ss.

Metals	Unit	MIX_2
As	mg/kg ss	12.71
Cd	mg/kg ss	0.47
Be	mg/kg ss	0.80
Co	mg/kg ss	7.20
Cr	mg/kg ss	50.58
Hg	mg/kg ss	1.99
Ni	mg/kg ss	37.70
Pb	mg/kg ss	91.45
V	mg/kg ss	49.28
Cu	mg/kg ss	59.00
Zn	mg/kg ss	172.73

Tab. 7.16 - Concentration of heavy metals in the untreated prototyped-sample of sediments (LOD = 0.01 mg/kg ss).

PAHs	Unit	MIX_2
Naphthalene	µg/kg ss	74
Fluoranthene	µg/kg ss	995
Anthracene	µg/kg ss	695
Acenaphthene	µg/kg ss	127
Acenaphthylene	µg/kg ss	87
Fluorene	µg/kg ss	134
Phenanthrene	µg/kg ss	175
Pyrene	µg/kg ss	898
Chrysene	µg/kg ss	559
Benz[a]anthracene	µg/kg ss	528
Benz[a]pyrene	µg/kg ss	519
Benz[k]fluoranthene	µg/kg ss	773
Benz[b]fluoranthene	µg/kg ss	< LOD
Benz[g,h,i]perylene	µg/kg ss	< LOD
Dibenzo[a,h]anthracene	µg/kg ss	< LOD
Indeno[1,2,3-cd]pyrene	µg/kg ss	168
Total PAHs	µg/kg ss	5732

Tab. 7.17- PAHs concentration in the untreated prototyped-sample of sediments (LOD= 20 µg/kg ss).

PCBs	Unit	MIX_2
PCB 28	$\mu\text{g/kg ss}$	< LOD
PCB 52	$\mu\text{g/kg ss}$	43
PCB 81	$\mu\text{g/kg ss}$	15
PCB 95	$\mu\text{g/kg ss}$	21
PCB 101	$\mu\text{g/kg ss}$	106
PCB 99	$\mu\text{g/kg ss}$	62
PCB 77	$\mu\text{g/kg ss}$	< LOD
PCB 110	$\mu\text{g/kg ss}$	97
PCB 128	$\mu\text{g/kg ss}$	44
PCB 151	$\mu\text{g/kg ss}$	121
PCB 123	$\mu\text{g/kg ss}$	< LOD
PCB 118	$\mu\text{g/kg ss}$	94
PCB 114	$\mu\text{g/kg ss}$	< LOD
PCB 149	$\mu\text{g/kg ss}$	29
PCB 146	$\mu\text{g/kg ss}$	258
PCB 105	$\mu\text{g/kg ss}$	24
PCB 153	$\mu\text{g/kg ss}$	125
PCB 126	$\mu\text{g/kg ss}$	< LOD
PCB 183	$\mu\text{g/kg ss}$	100
PCB 187	$\mu\text{g/kg ss}$	34
PCB 138	$\mu\text{g/kg ss}$	25
PCB 167	$\mu\text{g/kg ss}$	5
PCB 177	$\mu\text{g/kg ss}$	26
PCB 156	$\mu\text{g/kg ss}$	< LOD
PCB 157	$\mu\text{g/kg ss}$	< LOD
PCB 180	$\mu\text{g/kg ss}$	205
PCB 169	$\mu\text{g/kg ss}$	< LOD
PCB 170	$\mu\text{g/kg ss}$	79
PCB 189	$\mu\text{g/kg ss}$	< LOD
Total PCBs	$\mu\text{g/kg ss}$	1513

Tab. 7.18 - PCBs concentration in the untreated prototyped-sample of sediments (LOD = 1 $\mu\text{g/kg ss}$).

In the Tables 7.16 -7.18, the values of contaminants are compared with both the site-specific limits (ICRAM, 2004; yellow values) and Italian law (D.Lgs. 152/2006; red values).

Column tests

Column tests were conducted to assess the effectiveness of different capping technologies in the sequestration of various metals and organic contaminants. The experimental layout aimed to study the performance of two different system of reactive capping was:

SCENARIO 0: contaminated sediment without capping;

SCENARIO 1: contaminated sediment capped by RCM with AC);

SCENARIO 2: contaminated sediment capped by RCM with OC;

SCENARIO 3: contaminated sediment capped by RCM with OC and AC;

SCENARIO 4: contaminated sediment capped by granular materials with CH₄ and AC;

SCENARIO 5: contaminated sediment capped by granular materials with CH₄ and ZVI;

SCENARIO 6: contaminated sediment capped by granular materials with CH₄, ZVI, AC.

Columns monitoring was performed for 20 days in static condition and for 24 hours after the shaking of the water in the column (shaking occurred with two different ways). The samples were chemically analysed for 11 metals (i.e. As, Be, Cd, Co, Cr, Hg, Ni, Pb, Cu, V, and Zn), PCBs and PAHs.

Metals were detected in seawater samples, but some of these values were statistically equal to those measured for pre-capping conditions (Tabb. 7.19 - 7.23). Be, Cd, Co, Hg, Pb and V concentrations were always found to be lower than the instrumental detection limit (LOD = 0.5 µg/l). Capping retarded Cr, Ni and Cu fluxes from contaminated sediment while appeared to have no significant effect in retarding As flux. In the Scenarios 2, 4 and 5, the Pb is released in water in concentrations between 1 µg/l and 2 µg/l (the increase of Pb flux is not significant). Zn concentration, in static condition, increases with time without the capping or with RCM with OC or AC; however, the concentrations comply with environmental standards. Negative Zn fluxes (Scenarios 3, 4, 5 and 6) suggest that metal in the overlying water is adsorbed by the

capping material. In the absence of simulated groundwater flow, the consolidation process may transport the pore water and cause high initial fluxes from uncapped sediment to the overlying water (Liu et al., 2001). However, though the monitoring of columns showed a slight consolidation (a few mm) during the first week after the placement of capping, no significant flow of metals was observed. Probably, this effect has been successfully mitigated by the chemical isolation effect of capping materials.

The release of metals from the sediments is not influenced by the agitation of the water in the column. In general, the literature reports that the disturbance of sediment and exposure of anoxic sediment to an oxic environment may increase the metal mobility and cause high pore-water concentrations in the sediments (Forstner et al., 1988). In the present case, even for the column without capping, there is not increase of the metal concentrations following the disturbance of seawater. This may indicate both that the release and absorption phenomena are very fast so that they were not observed in the laboratory time interval (1 hr) and that metals in the sediments are very stable under both in anoxic and oxic conditions.

Metals	Unit	SCENARIO 0 (contaminated sediment without capping)							
		Static				Dynamic 1		Dynamic 2	
		0 days	5 days	10 days	20 days	1 hr	6 hrs	1 hr	6 hrs
As	µg/l	< LOD	1	1	1	1	1	1	1
Be	µg/l	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Cd	µg/l	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Co	µg/l	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Cr	µg/l	< LOD	1	1	1	< LOD	< LOD	< LOD	< LOD
Hg	µg/l	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Ni	µg/l	< LOD	2	2	2	< LOD	< LOD	< LOD	< LOD
Pb	µg/l	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Cu	µg/l	< LOD	1	1	1	< LOD	< LOD	< LOD	< LOD
V	µg/l	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Zn	µg/l	7	12	13	57	3	3	2	2

Tab. 7.19 - Scenario 0: concentrations of metals in the seawater (LOD = 0.5 µg/l).

Metals	Unit	SCENARIO 1 (contaminated sediment + RCM with OC)							
		Static				Dynamic 1		Dynamic 2	
		0 days	5 days	10 days	20 days	1 hr	6 hrs	1 hr	6 hrs
As	µg/l	< LOD	1	1	1	1	1	1	1
Be	µg/l	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Cd	µg/l	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Co	µg/l	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Cr	µg/l	< LOD	< LOD	1	1	< LOD	< LOD	< LOD	< LOD
Hg	µg/l	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Ni	µg/l	< LOD	< LOD	1	1	< LOD	< LOD	< LOD	< LOD
Pb	µg/l	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Cu	µg/l	< LOD	< LOD	< LOD	1	< LOD	< LOD	< LOD	< LOD
V	µg/l	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Zn	µg/l	7	8	12	44	1	1	1	1

Tab. 7.20 - Scenario 1: concentrations of metals in the seawater (LOD = 0.5 µg/l).

Metals	Unit	SCENARIO 2 (contaminated sediment + RCM with AC)							
		Static				Dynamic 1		Dynamic 2	
		0 days	5 days	10 days	20 days	1 hr	6 hrs	1 hr	6 hrs
As	µg/l	< LOD	1	1	1	1	1	1	1
Be	µg/l	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Cd	µg/l	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Co	µg/l	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Cr	µg/l	< LOD	1	1	1	< LOD	< LOD	< LOD	< LOD
Hg	µg/l	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Ni	µg/l	< LOD	< LOD	1	1	< LOD	< LOD	< LOD	< LOD
Pb	µg/l	< LOD	< LOD	< LOD	1	< LOD	< LOD	< LOD	< LOD
Cu	µg/l	< LOD	< LOD	< LOD	1	< LOD	< LOD	< LOD	< LOD
V	µg/l	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Zn	µg/l	7	7	21	41	3	3	1	1

Tab. 7.21 - Scenario 2: concentrations of metals in the seawater (LOD 0.5 µg/l).

Metals	Unit	SCENARIO 3 (contaminated sediment + RCM with OC and AC)							
		Static				Dynamic 1		Dynamic 2	
		0 days	5 days	10 days	20 days	1 hr	6 hrs	1 hr	6 hrs
As	µg/l	< LOD	1	1	1	1	1	1	1
Be	µg/l	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Cd	µg/l	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Co	µg/l	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Cr	µg/l	< LOD	< LOD	< LOD	1	< LOD	< LOD	< LOD	< LOD
Hg	µg/l	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Ni	µg/l	< LOD	< LOD	< LOD	1	< LOD	< LOD	< LOD	< LOD
Pb	µg/l	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Cu	µg/l	< LOD	< LOD	< LOD	1	< LOD	< LOD	< LOD	< LOD
V	µg/l	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Zn	µg/l	7	7	1	1	1	1	1	1

Tab. 7.22 - Scenario 3: concentrations of metals in the seawater (LOD = 0.5 µg/l).

Metals	Unit	SCENARIO 4 (contaminated sediment + granular materials CH4 and AC)							
		Static				Dynamic 1		Dynamic 2	
		0 days	5 days	10 days	20 days	1 hr	6 hrs	1 hr	6 hrs
As	µg/l	< LOD	1	1	1	1	1	1	1
Be	µg/l	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Cd	µg/l	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Co	µg/l	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Cr	µg/l	< LOD	< LOD	< LOD	1	< LOD	< LOD	< LOD	< LOD
Hg	µg/l	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Ni	µg/l	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Pb	µg/l	< LOD	< LOD	< LOD	2	< LOD	< LOD	< LOD	< LOD
Cu	µg/l	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
V	µg/l	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Zn	µg/l	7	7	3	1	1	1	2	2

Tab. 7.23 - Scenario 4: concentrations of metals in the seawater (LOD 0.5 µg/l).

Metals	Unit	SCENARIO 5 (contaminated sediment + granular materials CH4 and ZVI)							
		Static				Dynamic 1		Dynamic 2	
		0 days	5 days	10 days	20 days	1 hr	6 hrs	1 hr	6 hrs
As	µg/l	< LOD	1	1	1	1	1	1	1
Be	µg/l	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Cd	µg/l	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Co	µg/l	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Cr	µg/l	< LOD	< LOD	< LOD	1	< LOD	< LOD	< LOD	< LOD
Hg	µg/l	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Ni	µg/l	< LOD	< LOD	1	2	< LOD	< LOD	< LOD	< LOD
Pb	µg/l	< LOD	< LOD	< LOD	1	< LOD	< LOD	< LOD	< LOD
Cu	µg/l	< LOD	< LOD	< LOD	1	< LOD	< LOD	< LOD	< LOD
V	µg/l	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Zn	µg/l	7	15	3	1	4	4	6	6

Tab. 7.24 - Scenario 5: concentrations of metals in the seawater (LOD = 0.5 µg/l).

Metals	Unit	SCENARIO 6 (contaminated sediment without capping)							
		Static				Dynamic 1		Dynamic 2	
		0 days	5 days	10 days	20 days	1 hr	6 hrs	1 hr	6 hrs
As	µg/l	< LOD	1	1	1	1	1	1	1
Be	µg/l	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Cd	µg/l	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Co	µg/l	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Cr	µg/l	< LOD	< LOD	< LOD	1	< LOD	< LOD	< LOD	< LOD
Hg	µg/l	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Ni	µg/l	< LOD	< LOD	< LOD	1	< LOD	< LOD	< LOD	< LOD
Pb	µg/l	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Cu	µg/l	< LOD	< LOD	1	1	< LOD	< LOD	< LOD	< LOD
V	µg/l	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Zn	µg/l	7	6	2	1	1	1	3	3

Tab. 7.25 - Scenario 6: concentrations of metals in the seawater (LOD = 0.5 µg/l).

Tab. 7.26 shows an evaluation of the different technologies tested for the detected metals in static condition (i.e. As, Cr, Ni, Pb, Cu and Zn). Although the environmental standards are always respected, the best performance is achieved when granular materials are used. It could be noted that the permeability of RCMs (1×10^{-3} cm/s; CETCO, 2015) is higher than that of granular reactive materials (Tab. 6.4); then composite-aggregate technology has a considerable effect in retarding fluxes of metals.

At the end of the static phase, the reactive materials inside the cap were sampled and analysed; the results are reported in Fig. 7.13. Adsorption potential is evaluated as the difference between the concentration before the treatment and concentration after the treatment (mg of metal per kg of reactive material). The chemical analyses of reactive material post-treatment show adsorption of As, Be, Cd, Co, Cr, Ni, Pb, V, Cu and Zi in variable concentrations. The higher adsorption levels are obtained for advanced solutions that make use of multiple reactive materials simultaneously (Scenario 3: RCM with OC and AC and Scenario 6: granular materials with CH₄, ZVI and PAC).

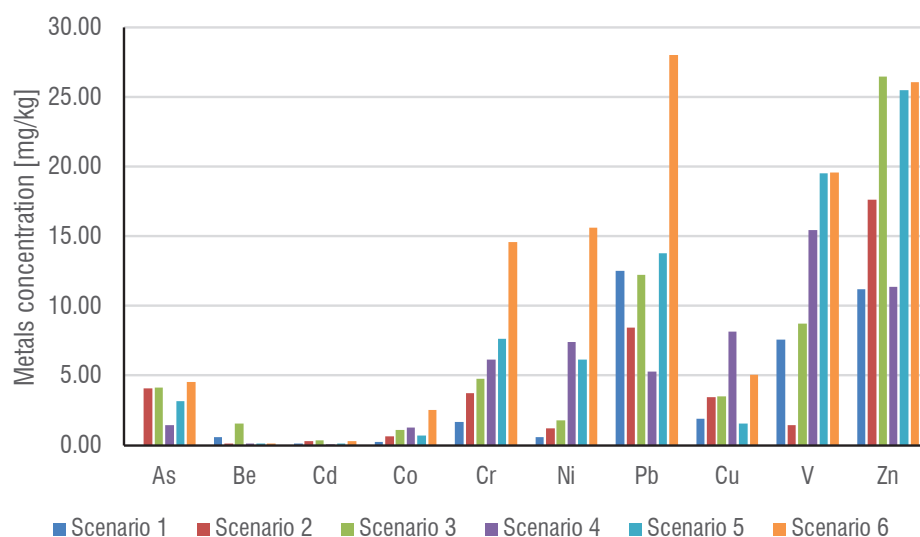


Fig. 7.13 - Adsorption of metals in reactive materials after treatment (concentrations expressed in mg of metal per kg of reactive material).

Metals	Parameters	Unit	Scenario						
			0	1	2	3	4	5	6
As	Efficiency	%	-	0.0	0.0	0.0	0.0	0.0	0.0
	Concentration	µg/l	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	Environmental goals	-	✓	✓	✓	✓	✓	✓	✓
Cr	Efficiency	%	-	0.0	0.0	0.0	0.0	0.0	0.0
	Concentration	µg/l	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	Environmental goals	-	✓	✓	✓	✓	✓	✓	✓
Ni	Efficiency	%	-	50.0	50.0	50.0	100.0	0.0	50.0
	Concentration	µg/l	2.0	2.0	1.0	1.0	0.0	2.0	1.0
	Environmental goals	-	✓	✓	✓	✓	✓	✓	✓
Pb	Efficiency	%	-	0.0	-50.0	0.0	-100.0	-50.0	0.0
	Concentration	µg/l	0.0	0.0	1.0	1.0	2.0	1.0	0.0
	Environmental goals	-	✓	✓	✓	✓	✓	✓	✓
Cu	Efficiency	%	-	0.0	0.0	0.0	100.0	0.0	0.0
	Concentration	µg/l	1.0	1.0	1.0	1.0	0.0	1.0	1.0
	Environmental goals	-	✓	✓	✓	✓	✓	✓	✓
Zn	Efficiency	%	-	22.8	28.1	98.2	98.2	98.2	98.2
	Concentration	µg/l	57.0	44.0	41.0	1.0	1.0	1.0	1.0
	Environmental goals	-	✓	✓	✓	✓	✓	✓	✓

Tab. 7.26 - Performance evaluation of metals isolation in static condition. Environmental goals: positive (✓) and negative (✗) if metal concentrations are, respectively, lower and higher than the limit (according to the Directive 2013/39/CE).

PAHs were detected in water inside the reactor, both for static and dynamic conditions. Seawater used for the tests showed an initial PAHs concentration due to real contamination of site (the samples were taken from the north coast of Mar Piccolo). PAHs concentrations of the no-flow column studies with various capping application scenarios are shown in Fig. 7.14. Without capping (Scenario 0) is possible evaluate migration of PAHs during advective conditions: concentrations of contaminant in the seawater increase in the time up to a value of $0.214 \mu\text{g/l}$. It can be seen that reactive

capping greatly reduced the PAHs concentrations in seawater. In particular, technology reduces the transport of PAHs from sediment to seawater and also involves a negative flux that suggest as the contaminant in the overlying water is adsorbed by the capping material. PAHs concentrations in seawater decreased from 0.100 $\mu\text{g/l}$ to near 0.050 $\mu\text{g/l}$ for column apparatus with reactive capping (Scenario 1 - Scenario 6). In Fig. 7.14 the environmental standard (according to the Directive 2013/39/CE) is indicated with a dashed red line.

Tab. 7.27 shows a performance evaluation of PAHs isolation in static condition. The reactive solution can be considered feasible because the efficiency of the treatment, observed in the laboratory, allows compliance with environmental standards.

After 20 days of monitoring, the contaminated sediment has been sampled. Capping solutions seem to provide a reduction from the 16.5% (RCM with AC) to 60.9% (RCM with OC) of the original PAH contamination (Tab. 7.28). This phenomenon is mainly attributable to the environmental conditions favourable to autochthonous microbial populations which, as demonstrated by several authors (i.e. Matturro et al., 2016; Yan and Reible, 2015; Kim et al., 2013; Sun et al., 2010), may have an important role of in situ remediation. To encourage biodegradation of organics contaminants is necessary to maintain conducive conditions, e.g., nutrient-sufficient conditions, redox potentials, electron donor or acceptor levels (Yan and Reible, 2015). Reactive materials cannot only remove target pollutants from the water phase quickly, but they can also provide an interface for biotic and abiotic processes (Zimmerman et al., 2004). Sorbents materials, such as activated carbon, have been confirmed to yield much higher levels of substrate biodegradation and higher specific microbial growth rates when used as a bio-support matrix compared to non-adsorbing or weakly adsorbing media, such as sand (Sun et al., 2010). The results of PAHs concentration show that the biodegradation rates were greater for solution with OC; the performance of capping with ZVI did not reach the expected results. Since the products of Fe(0) reduction often pose greater biodegradability, the combination of Fe(0) and microbial cells was proposed as a means to thoroughly remove organic contaminants. For capping solutions

based on AC the degradation of PAHs is lower end environmental standards are not achieved.

The purpose of this phase was to demonstrate that reactive capping technique can produce favourable conditions for (bio)degradation of organic contaminants and evaluate the kinetics of degradation for sediment remediation.

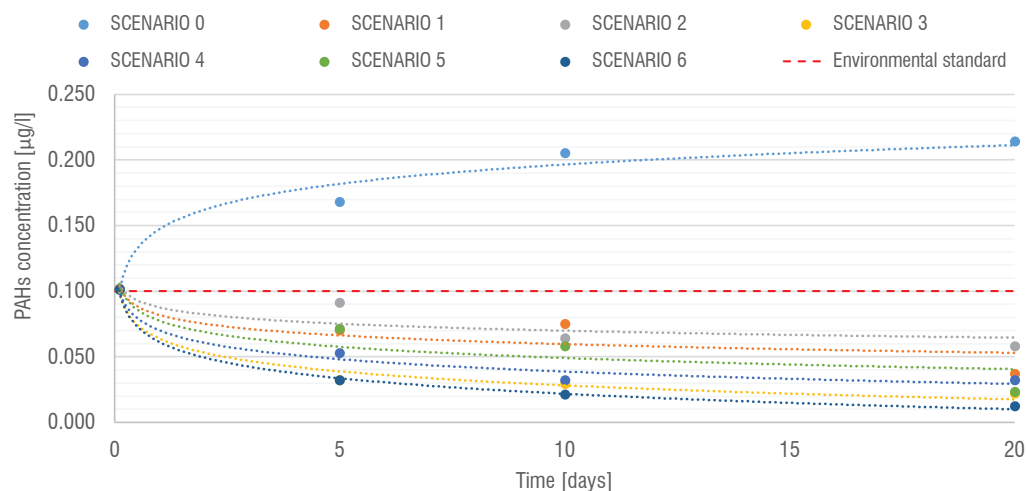


Fig. 7.14 - Concentrations of PAHs in the seawater: static conditions.

	Parameters	Unit	Scenario						
			0	1	2	3	4	5	6
Σ PAHs	Efficiency	%	-	63.4	42.6	78.2	68.3	77.2	88.1
	Concentration	µg/l	0.214	0.037	0.058	0.022	0.032	0.023	0.012
	Environmental goals	-	✗	✓	✓	✓	✓	✓	✓

Tab. 7.27 - Performance evaluation of PAHs isolation in static condition. Environmental goals: positive (✓) and negative (✗) if PAHs concentrations are, respectively, lower and higher than the limit (according to the Directive 2013/39/CE).

	Parameters	Unit	Scenario						
			0	1	2	3	4	5	6
Σ PAHs	Efficiency	%	-	16.5	60.8	60.9	25.3	48.1	49.4
	Concentration	$\mu\text{g/kg}$	5484	4579	2149	2146	4095	2845	2776
	Environmental goals	-	✗	✗	✓	✓	✗	✓	✓

Tab. 7.28 - Performance evaluation of PAHs degradation in static condition. Environmental goals: positive (✓) and negative (✗) if PAHs concentrations are, respectively, lower and higher than the limit (according to ICRAM, 2004).

The treatment efficiencies, with reference to PAHs, are shown in Fig. 7.15. Granular material with CH₄, ZVI and AC is the is the best solution for chemical isolation of PAHs (with an efficiency of 88.1%). Good performances are also obtained with RCM with OC and AC (efficiency of 78.2%) which also offers the greatest degradation efficiency (60.9%).

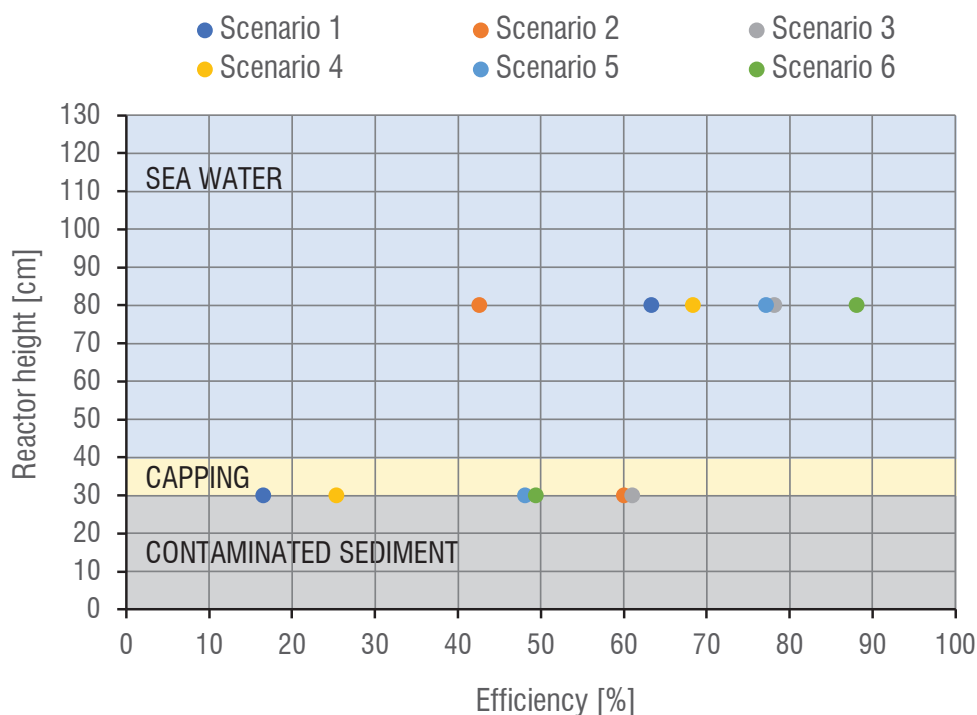


Fig. 7.15 - Assessment of capping efficiency for PAHs: static condition.

Figs. 7.15 and 6.16 show the PAHs concentrations after the dynamic condition in columns. The first sampling occurred one hour after the end of the agitation of the water in the column; PAHs concentrations in the water increase without the cap (Scenario 0) from $0.074 \mu\text{g/l}$ (i.e. real contamination of seawater sampled from Mar Piccolo) to a value of $0.09 \mu\text{g/l}$. This concentration tends to decrease over time, until the initial conditions are reached after 24 hrs. For capping scenarios, the results show that PAHs concentrations in water decreased from $0.074 \mu\text{g/l}$ to near $0.010 \mu\text{g/l}$ for column apparatus with reactive capping. The effects seem independent of the type of applied agitation. There is no different behaviour of contaminant migration depending on the type of forcing: the results of dynamics conditions type 1 (100 rpm for 30 minutes) are similar to the results of dynamics conditions type 2 (300 rpm for 10 minutes).

In Figs. 7.16 and 7.17 the environmental standard (according to the Directive 2013/39/CE) is indicated with a dashed red line. For all the scenarios environmental standards are respected (Tables 7.29 and 7.30).

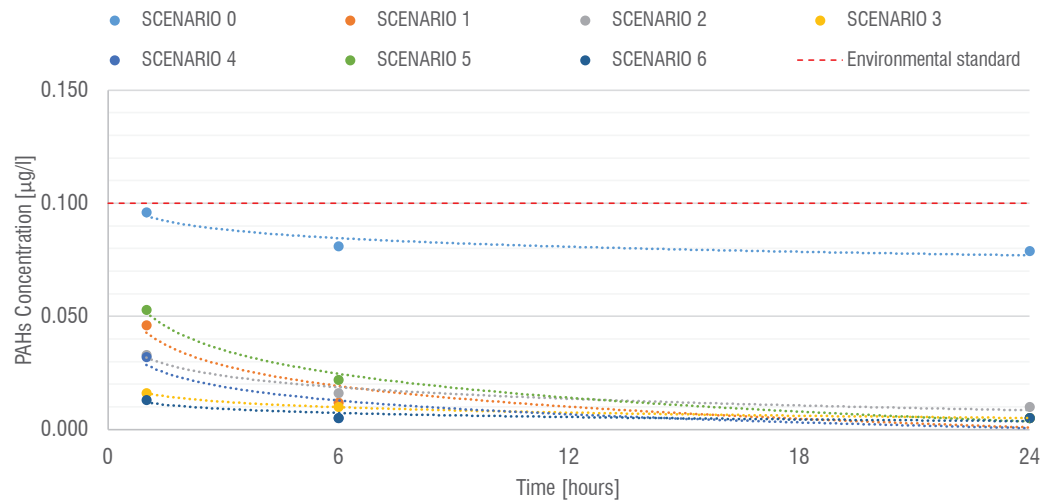


Fig. 7.16 - PAHs concentrations in the water: dynamic conditions type 1 (the time scale starts from the end of the dynamical event, PAHs concentration in water before the forcing was of $0.074 \mu\text{g/l}$).

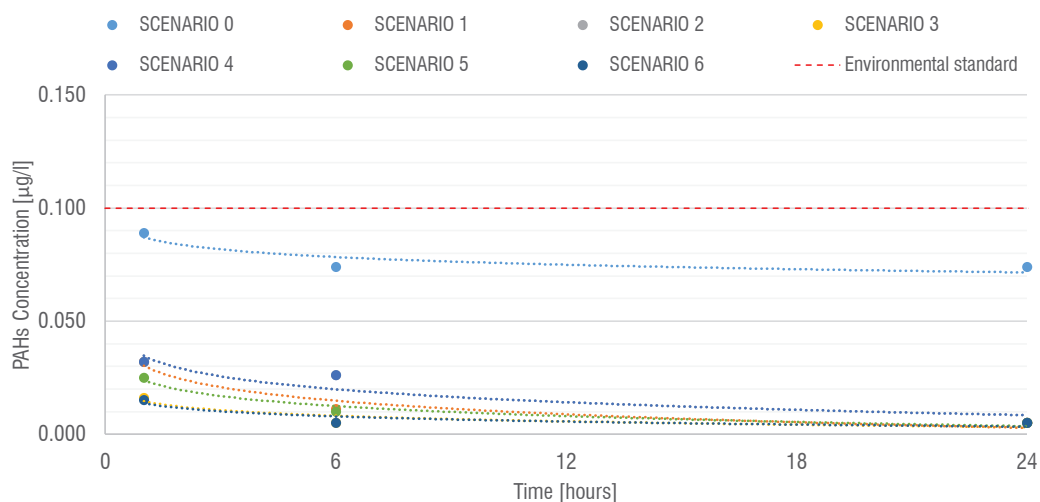


Fig. 7.17 - PAHs concentrations in the water: dynamic conditions type 2 (the time scale starts from the end of the dynamical event, PAHs concentration in water before the forcing was of 0.074 µg/l).

	Parameters	Unit	Scenario						
			0	1	2	3	4	5	6
Σ PAHs	Efficiency	%	-	93.7	87.3	93.7	93.7	93.7	93.7
	Concentration	µg/l	0.079	0.005	0.010	0.005	0.005	0.005	0.005
	Environmental goals	-	✓	✓	✓	✓	✓	✓	✓

Tab. 7.29 - Performance evaluation of PAHs isolation in dynamic conditions type 1. Environmental goals: positive (✓) and negative (✗) if PAHs concentrations are, respectively, lower and higher than the limit (according to the Directive 2013/39/CE).

	Parameters	Unit	Scenario						
			0	1	2	3	4	5	6
Σ PAHs	Efficiency	%	-	93.2	93.2	93.2	93.2	93.2	93.2
	Concentration	µg/l	0.074	0.005	0.005	0.005	0.005	0.005	0.005
	Environmental goals	-	✓	✓	✓	✓	✓	✓	✓

Tab. 7.30 - Performance evaluation of PAHs isolation in dynamic conditions type 2. Environmental goals: positive (✓) and negative (✗) if PAHs concentrations are, respectively, lower and higher than the limit (according to the Directive 2013/39/CE).

PCB congeners concentrations in seawater samples were not detectable (LOD is approximately $0.001 \mu\text{g/L}$), both in static conditions and in dynamic conditions. This could be a possible effect of the method used for the analysis. In water samples, humic substances are major components of dissolved organic matter (Botero et al., 2011), and humic acids significantly reduce the retention of PCBs and might cause insufficient recoveries attained (Rodriguez et al., 2011). Moreover, concentration levels of PCBs in contaminated environment are typically low in complex matrices like sea water (Botero et al., 2011; Wang et al., 2009). Di Leo et al. (2014) studied the effects of resuspension in sediments (collected in Mar Piccolo) on the fate of PCBs in seawater. The Authors, show PCB levels in water, calculated as the sum of the dissolved fractions, varied after sediment resuspension, from 0.00082 to $0.0048 \mu\text{g/l}$, values that are noticeably detectable with the method used.

Following the monitoring for 20 days a reduction of the PCBs concentrations in the sediment was observed (Tab. 7.31). Capping solutions seem to provide a reduction from the 1.7% (RCM with AC) to 30.5% (granular materials with CH₄, ZVI and AC) of the original PAH contamination. The presence of congeners with a low degree of chlorination indicates that some reductive processes are likely to have occurred. Results from microcosm studies for Mar Piccolo sediments (Matturro et al., 2016) showed that the biodegradation of PCBs occurred rapidly under strictly anaerobic conditions, confirmed the involvement of the autochthonous microbial community, including PCB-degrading bacteria (*Dehalococcoides mccartyi*). However, in all the studied scenarios, after 20 days, environmental standards are not complied (Tab. 7.31).

	Parameters	Unit	Scenario						
			0	1	2	3	4	5	6
Σ PCBs	Efficiency	%	-	1.7	13.3	18.6	20.8	22.7	30.5
	Concentration	$\mu\text{g/l}$	1504	1479	1304	1225	1191	1163	1045
	Environmental goals	-	✖	✖	✖	✖	✖	✖	✖

Tab. 7.31 - Performance evaluation of PCBs degradation in static condition. Environmental goals: positive (✓) and negative (✖) if PCBs concentrations are, respectively, lower and higher than the limit (according to ICRAM, 2004).

The treatment efficiencies, with reference to PCBs, are shown in Fig. 7.18.

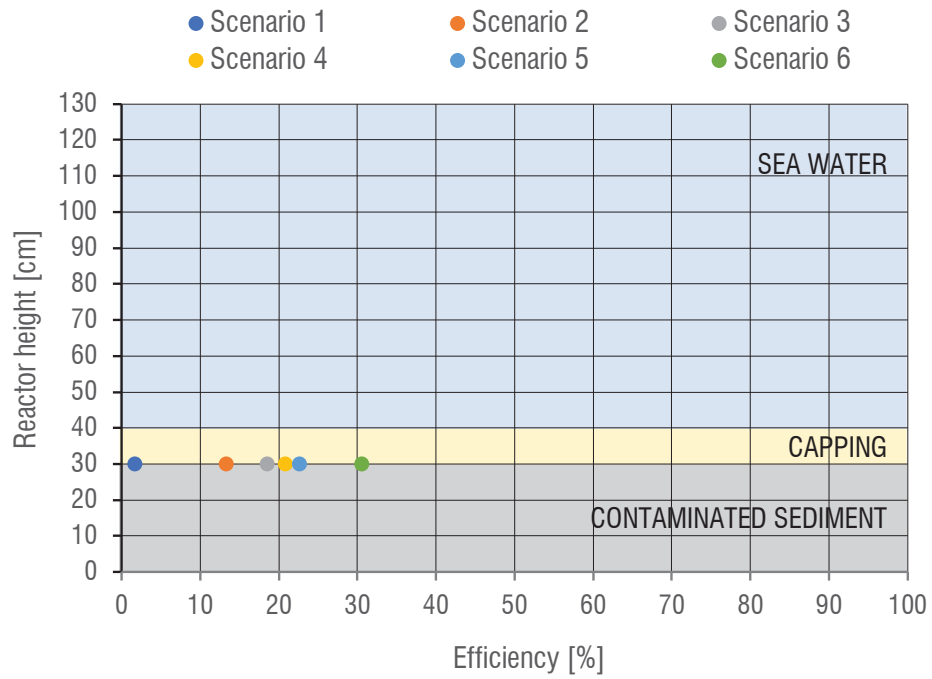


Fig. 7.18 - Assessment of capping efficiency PCBs: static condition.

Geotechnical investigation

The data discussed in the following are the results of an experimental geomechanical investigation carried out on sediment samples mixed with adsorbent materials (i.e. 5% of Activated Carbon, Organoclay or Biochar). The objective of the experiments was to explore in situ alternatives for the sustainable management of contaminated marine sediments. In situ amendment to contaminated sediments effectively reduces organic contaminant bioavailability and has provided a new direction in contaminated sediment management (Silvani et al., 2017; Zhang et al., 2016; Samuelsson et al., 2015). Major unknowns are currently whether the materials have effects on geomechanical properties of sediments (Todaro et al., 2018b). Moreover, in this section the the geotechnical properties of the prototyped-untreated sediments sample (named MIX 2) are presented.

Fig. 7.19 shows the grain-size distributions of both untreated and treated sediments. In general, it can be observed that the treated sediments have a slight increase of sand fraction. This is due to the addition of the absorbent material, characterized by equivalent diameter sizes from 2.36 mm to 0.08 mm (Tab. 6.3).

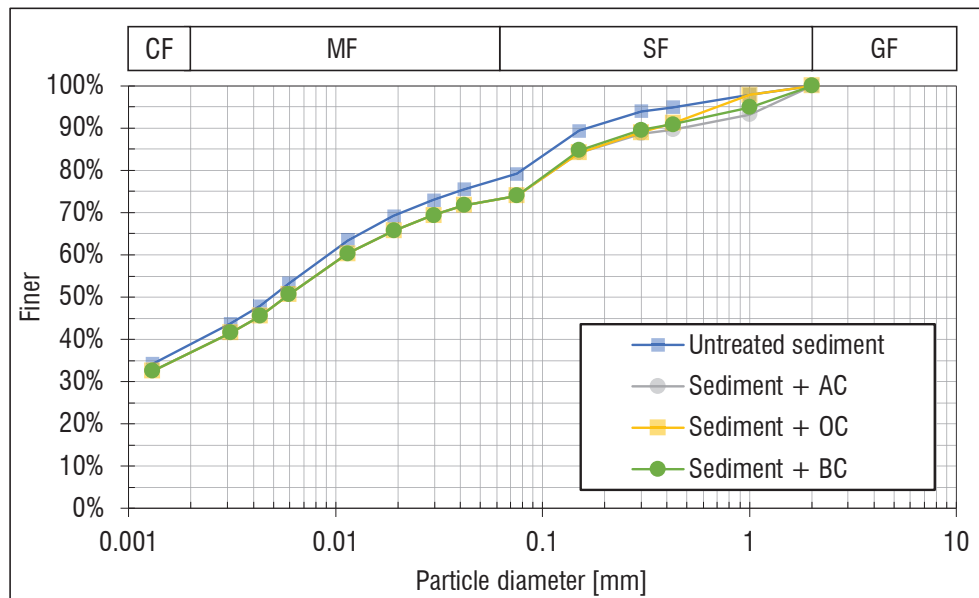


Fig. 7.19 - Grading curves of the untreated and treated sediments.

The Casagrande's plasticity chart in Fig. 7.20a shows the effects of the treatments on the Atterberg limits. For the treatments with OC and AC a reduction in Plasticity index (PI) is recorded. The sediments treated with biochar show the minimum effect on the soil plasticity indices. The Activity index chart, reported in Fig. 7.20b, displays a moderate variability of the values, which confirms the trends observed in Fig. 7.20a. OC treated sediment exhibits the maximum IP variation, whereas the sediment treated with BC does not present significant changes.

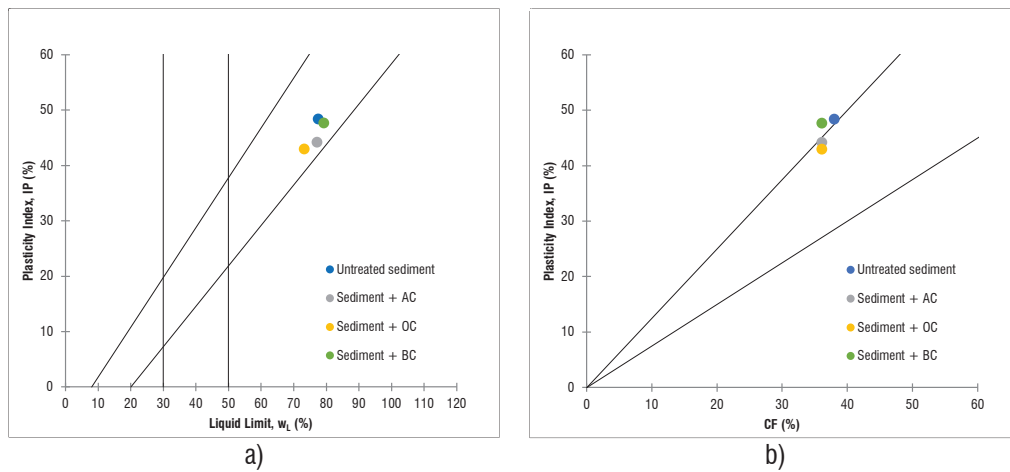


Fig. 7.20 - Plasticity chart (a) and Activity (b) of the untreated and treated sediments.

Fig. 7.21a-b show the results of the oedometer tests carried out on the untreated sediments and on the specimens with reagents AC, OC and BC, respectively. The figures also compare the data obtained by using tap water and seawater. The specimens did not exhibit any recompression branch during loading. It is important to note how the test curves obtained using tap water are located below those with seawater in the void ratio, e , vertical effective stress (σ'_v) logarithmic plot. Specimens in seawater have generally lower compressibility with the exception of the sediment treated with OC.

In Fig. 7.22a-b all the loading-unloading oedometer compression curves when using tap water and seawater are reported, respectively. The results show that the sediment compressibility seem to be not significantly influenced by the use of the reagents.

A reduction in the initial void ratio is recorded when BC and OC are used, irrespective of the water salinity. Sediments treated with OC and BC are less understandable. In tap water the average compressibility reduces when using 5% BC. The results obtained by the OED tests carried out on the untreated prototyped-sediment and the sediment treated with AC, OC and BC (5% compared to the weight of dry solid) are summarised in Tab. 7.32.

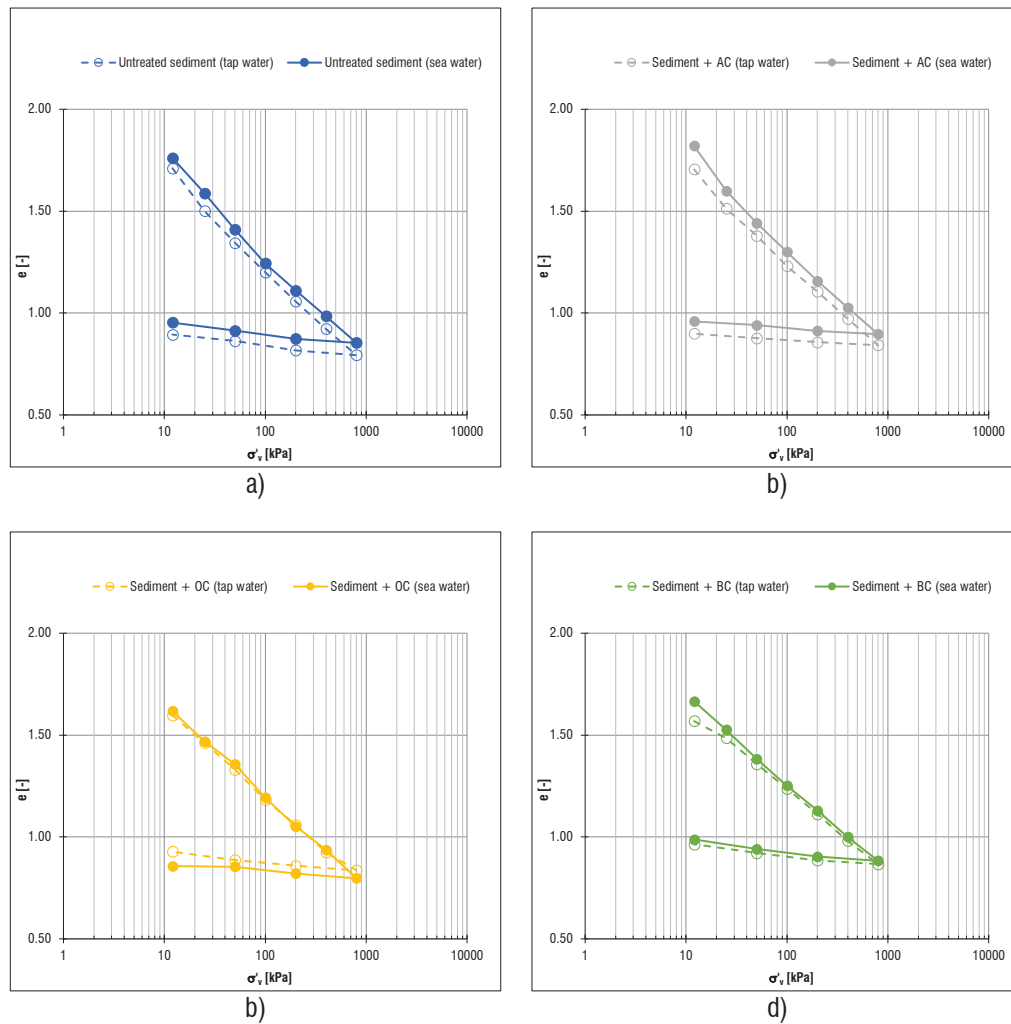


Fig. 7.21 - Loading-unloading oedometer compression curves of the sediment samples: a) untreated sediment; b) AC treated sediment; c) OC treated sediment; d) BC treated sediment.

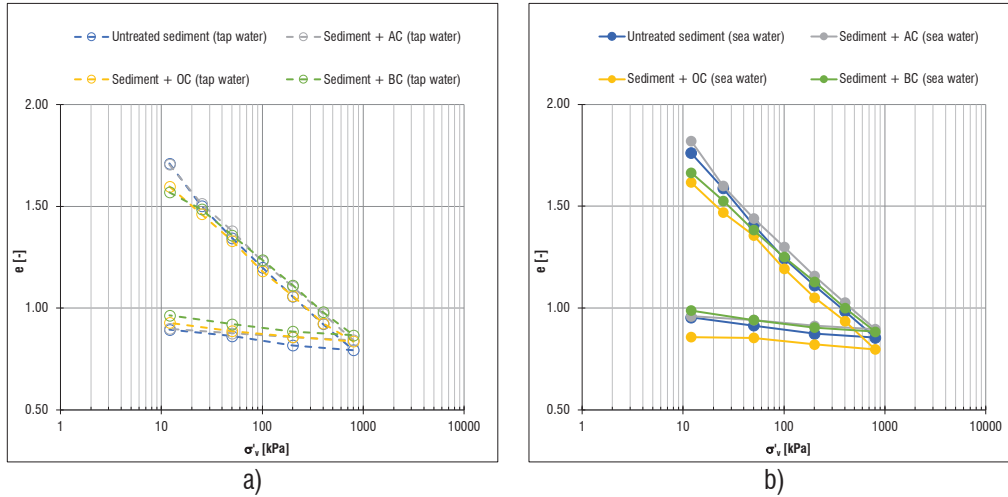


Fig. 7.22 - Loading-unloading oedometer compression curves of the untreated sediment samples and the sediment samples treated with the different reagents in (a) tap water and (b) seawater.

Fig. 7.23a-b report the compression index, c_c , computed by the total displacement followed during each loading step, plotted against the average value of the vertical effective stress, when using tap water and seawater, respectively. With tap water, c_c values of the untreated specimen vary between 0.43 and 0.66, those of the treated samples seem to decrease as the vertical effective stress increases (except for BC-added specimens). In particular, for the specimen treated with AC they vary between 0.43-0.60, for that treated with OC they are between 0.29-0.49 and in the range 0.26-0.43 for the specimen treated with BC. With seawater the trends are similar, but the ranges are: 0.43-0.69 (AC); 0.37-0.54 (OC); 0.39-0.47 (BC) (Fig. 7.23b). As a reference, typical values of compression index of clay minerals are $c_c=0.19$ to 0.26 for kaolinite, $c_c=0.50$ to 1.10 for illite, and $C_c=1.0$ to 3.6 for montmorillonite (Terzaghi et al., 1996; Sridharan & Nagaraj, 2000). The larger content of organic matter in the top soil could confer a more open structure to the soil skeleton, and a consequent higher compressibility. Similar trend was found in the literature (Coutinho & Lacerda, 1987, Levesque et al., 2007). On the contrary, an increase of salt in the pore fluid tends to reduce the compressibility, especially in active clays as the sediments under study (e.g. Di Maio 1996; Di Maio et al., 2004).

The swelling index, c_s , values are plotted against the vertical effective stress, σ'_v , for each unloading step in Fig. 7.24a-b when using tap water and seawater, respectively.

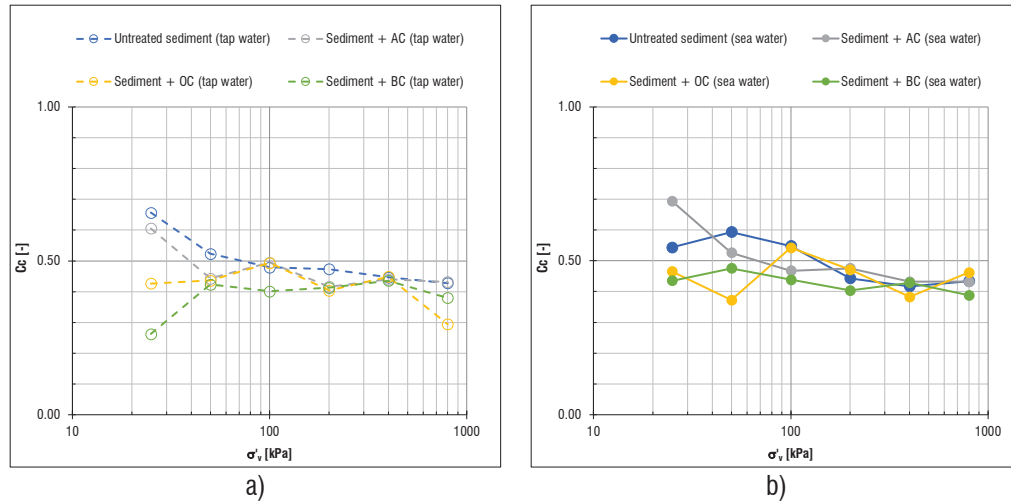


Fig. 7.23 - Compression index versus vertical effective stress: tap water (a) and seawater (b).

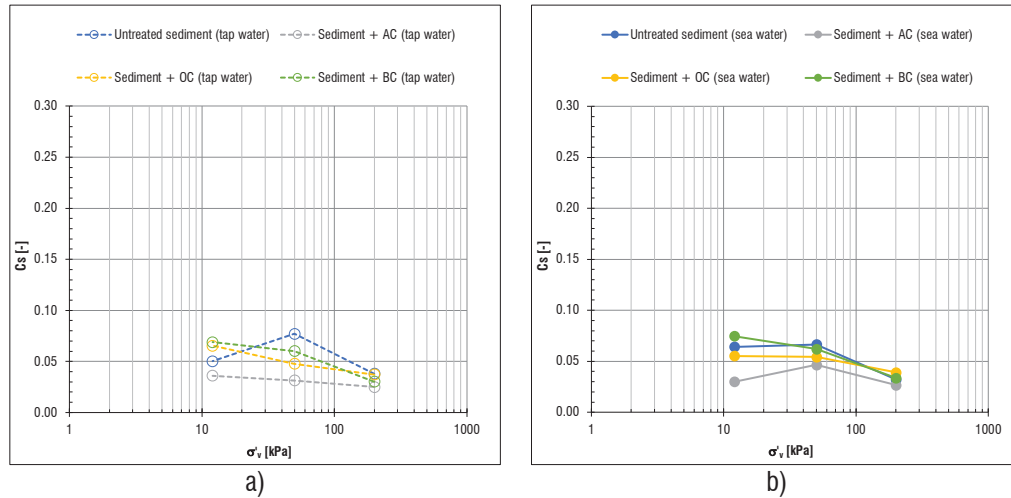


Fig. 7.24 - Swelling index versus vertical effective stress: tap water (a) and seawater (b).

The values of the coefficient of permeability, k , are plotted in Figures 7.25a (tap water)-b (seawater) and 7.26a (tap water)-b (seawater) against vertical effective stress

and void ratio, respectively. They have been computed according to the consolidation theory by Terzaghi (1923), in both oedometer loading and unloading phases. For all the specimens, k in loading varies between $8.0 \cdot 10^{-12}$ and $4.7 \cdot 10^{-10}$ m/s and, in general, it decreases with void ratio (Fig. 7.26). In unloading, k is always lower than that in loading and it seems not to vary with the unloading phase (tap water, $k_{unl} = 1 \cdot 10^{-12} \div 1.6 \cdot 10^{-12}$ m/s; seawater, $k_{unl} = 1 \cdot 10^{-12} \div 2.0 \cdot 10^{-13}$ m/s). Moreover, k decreases for those specimens in contact with seawater. Based on these figures, the following considerations can be made: i) the e - $\log(k)$ relationship is nearly linear, which implies that Taylor's (1948) e - $\log(k)$ relationship can be extended to treated sediments.; ii) in unloading the k values reduce considerably and seem to not depend on the vertical effective stress.

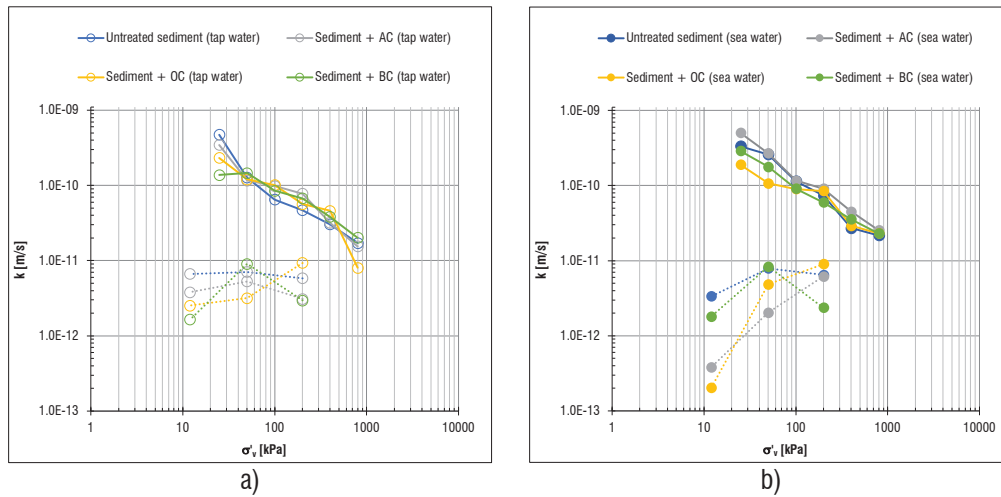


Fig. 7.25 - Coefficient of permeability versus vertical effective stress (data in loading and unloading): tap water (a) and seawater (b).

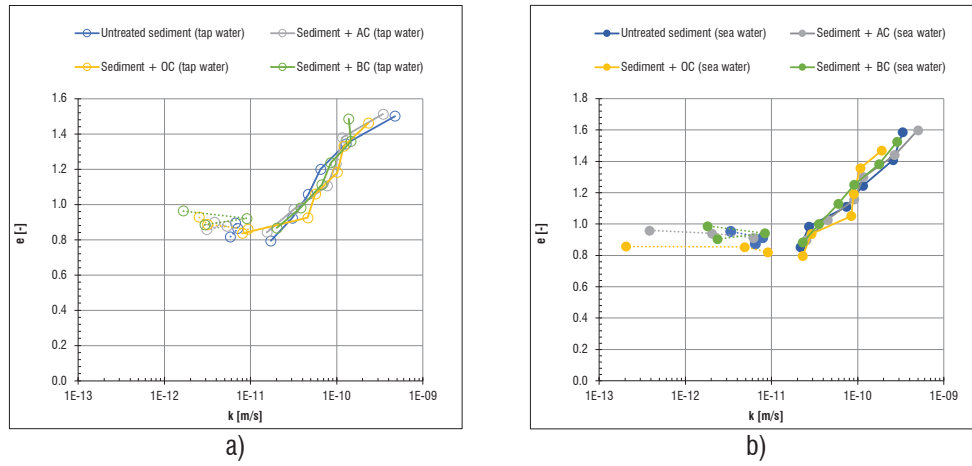


Fig. 7.26 - Coefficient of permeability versus void ratio (data in loading and unloading): tap water (a) and seawater (b).

Specimen	G_s [-]	w_i [%]	e_0 [-]	γ [kN/m ³]	w_f [%]	e_f [-]	c_c^{AV} [-]	c_s^{AV} [-]	M_L^{AV} [kPa]	M_U^{AV} [kPa]	k_L^{AV} [m/s]	k_U^{AV} [m/s]
Untreated sediment (tap water)	2.537	80.9	2.053	15.12	37.8	0.948	0.501	0.055	2485	31246	1.2E ⁻¹⁰	6.5E ⁻¹²
Untreated sediment (seawater)	2.537	80.9	2.032	15.33	36.9	0.937	0.497	0.054	2991	36067	1.4E ⁻¹⁰	5.9E ⁻¹²
Sediment + 5% AC (tap water)	2.500	86.6	2.144	15.02	36.9	0.923	0.472	0.031	3133	52078	1.1E ⁻¹⁰	4.7E ⁻¹²
Sediment + 5% AC (seawater)	2.500	86.6	2.149	14.97	36.7	0.917	0.504	0.034	3087	47103	1.8E ⁻¹⁰	2.9E ⁻¹²
Sediment + 5% OC (tap water)	2.505	85.6	2.119	15.13	35.6	0.893	0.417	0.050	3868	34301	9.4E ⁻¹¹	5.0E ⁻¹²
Sediment + 5% OC (seawater)	2.505	85.6	2.146	14.86	32.9	0.823	0.449	0.050	3113	33120	8.7E ⁻¹¹	4.7E ⁻¹²
Sediment + 5% BC (tap water)	2.460	78.4	1.928	15.08	41.3	1.015	0.386	0.053	3217	37138	8.2E ⁻¹¹	4.5E ⁻¹²
Sediment + 5% BC (seawater)	2.460	78.4	1.943	14.94	41.5	1.022	0.428	0.057	3157	33714	1.1E ⁻¹⁰	4.2E ⁻¹²

Tab. 7.32 - Results of oedometer tests carried out on the sediment amendment with AC, OC or BC.

Key: G_s soil specific gravity, w_i initial water content, e_0 initial void ratio, γ bulk unit weight, w_f final water content, e_f final void ratio, c_c^{AV} average compression index, c_s^{AV} average swelling index, M_L^{AV} average oedometric stiffness in loading, M_U^{AV} average oedometric stiffness in unloading, k_L^{AV} average coefficient of hydraulic conductivity in loading, k_U^{AV} average coefficient of hydraulic conductivity in unloading, blue values: tests with tap water, red values: tests with seawater.

Direct shear tests (DST) have been carried out on two specimens for each sample. They were sheared after consolidation at vertical effective stresses, σ'_v , of 12 and 50 kPa. In Figs. 7.27a-b and 7.28a-b, the state paths followed by untreated and treated specimens during consolidation before shearing in both tap water and seawater are reported together with the oedometer (OED) compression curve of the same samples. The data show that the DST specimens' consolidation states lie always either close or just in correspondence of the normal compression line of the OED specimens.

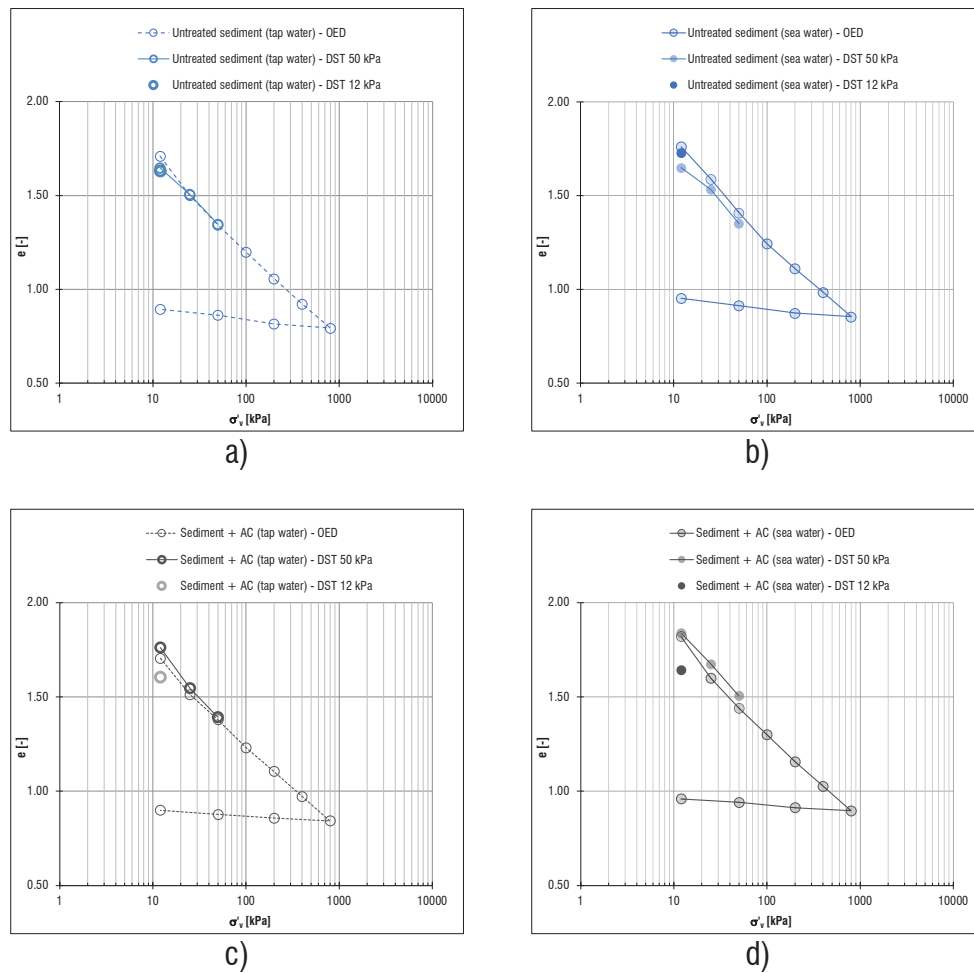


Fig. 7.27 - Consolidation states during compression in oedometer (OED) and direct shear tests (DST): of untreated sediment with a) tap water and b) seawater, and AC treated sediment with c) tap water and d) seawater. Dashed lines are used for tap water and continuous lines for seawater.

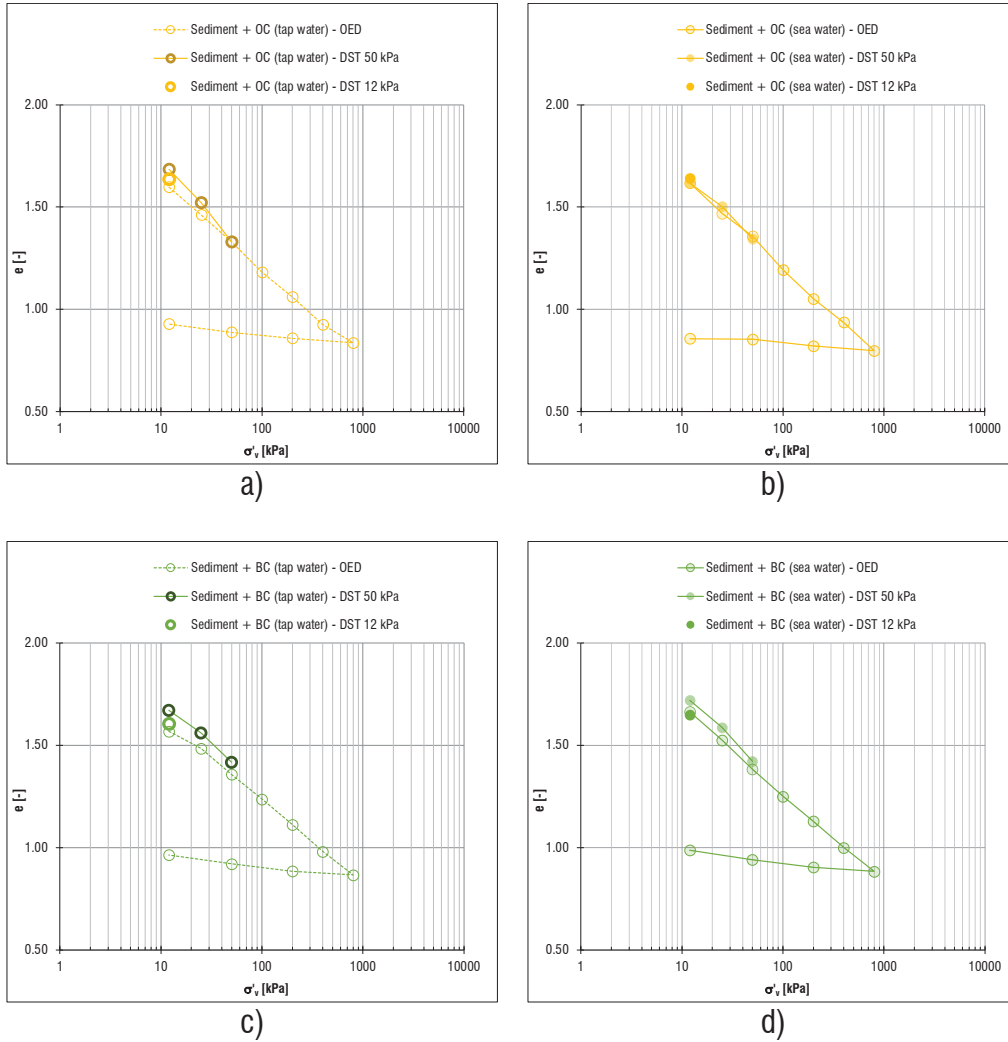


Fig. 7.28 - Consolidation states during compression in oedometer (OED) and direct shear tests (DST): of OC treated sediment with a) tap water and b) seawater, and BC treated sediment with c) tap water and d) seawater. Dashed lines are used for tap water and continuous lines for seawater.

During shearing, the specimens, as expected, harden and contract up to large strains, following the so-called wet behaviour according to Critical State Soil Mechanics (CSSM) (Roscoe et al., 1958; Schofield and Wroth, 1968). Fig. 7.29a-b and Fig. 7.30a-b show the results of all direct shear tests performed on the untreated sediment samples and on the specimens treated with OC, AC and BC, in the shear stress - horizontal

displacement, Δ plot and in the vertical displacement, ΔH - horizontal displacement, Δ plot, respectively.

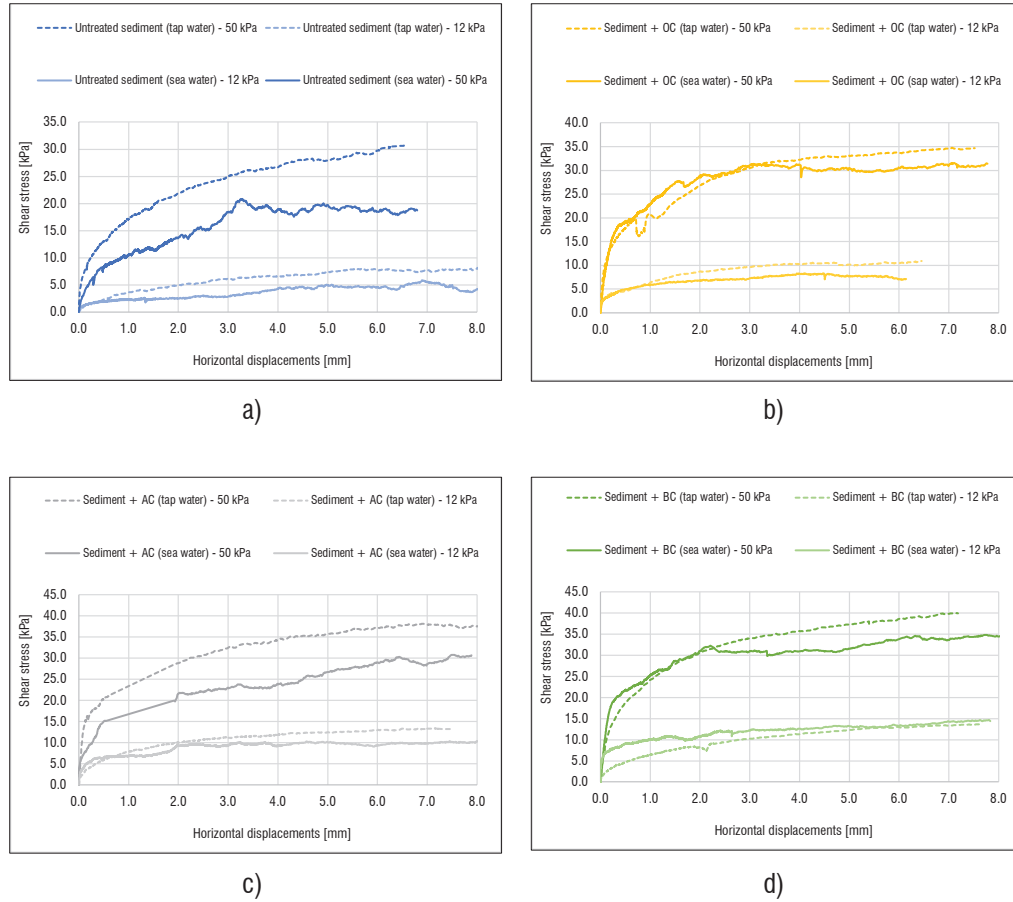
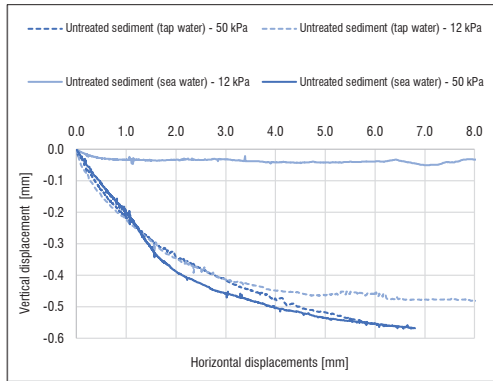
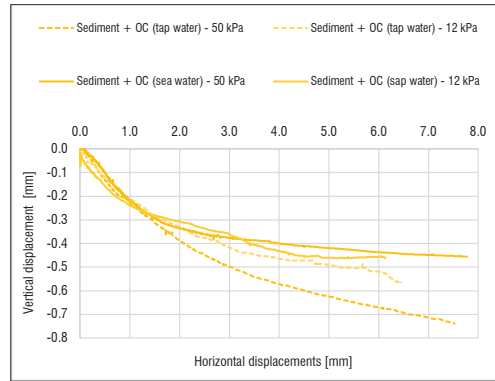


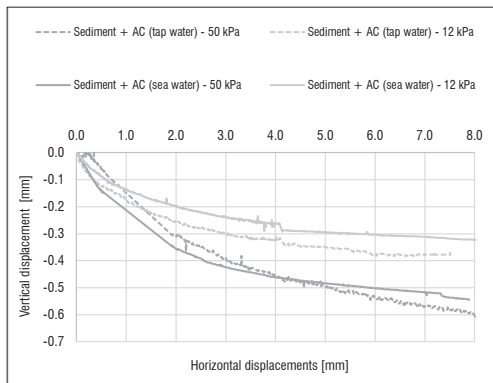
Fig. 7.29 - Direct Shear test results: shear stress, τ , vs horizontal displacements, Δ . a) untreated prototype sediment; b) AC treated sediment; c) OC treated sediment; d) BC treated sediment. Dashed lines are used for tap water and continuous lines for seawater.



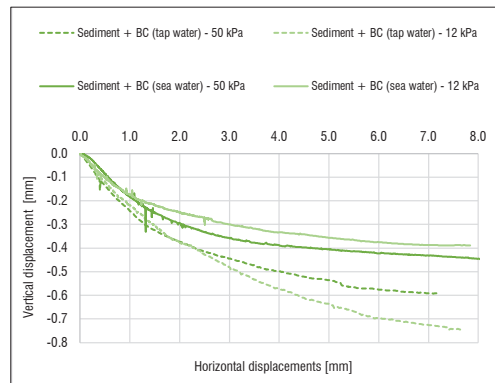
a)



b)



c)



d)

Fig. 7.30 - Direct Shear test results: vertical displacement, ΔH - horizontal displacements Δ . a) untreated prototype sediment; b) AC treated sediment; c) OC treated sediment; d) BC treated sediment. Dashed lines are used for tap water and continuous lines for seawater.

Specimens reach a pseudo-critical state, characterised by the effective strength parameters summarised in Tab.7.32.

Specimen	$\sigma'_{V \text{ MAX}}$ [kPa]	$\tau_{\text{ MAX}}$ [kPa]	$\delta_{\text{ MAX}}$ [mm]	ϕ'_{CS} [°]	$\phi'_{\text{CS}}^{\text{AV}}$ [°]	R^2 [-]
Untreated sediment (tap water)	12	8.14	8.02	34.15	31.72	0.9978
	50	30.73	6.56	31.57		
Untreated sediment (seawater)	12	5.88	6.9	26.10	22.78	0.9933
	50	20.80	3.25	22.59		
Sediment + 5% AC (tap water)	12	13.37	7.16	48.09	38.06	0.9457
	50	38.19	6.92	37.37		
Sediment + 5% AC (seawater)	12	10.48	8.85	41.13	32.21	0.9563
	50	30.80	7.55	31.63		
Sediment + 5% OC (tap water)	12	10.91	6.45	42.28	35.25	0.9780
	50	34.75	7.52	34.80		
Sediment + 5% OC (seawater)	12	8.22	4.37	34.41	32.38	0.9986
	50	31.56	7.1	32.26		
Sediment + 5% BC (tap water)	12	13.66	7.65	48.70	39.25	0.8923
	50	39.99	7.2	38.65		
Sediment + 5% BC (seawater)	12	14.65	7.81	50.68	35.96	0.9345
	50	34.85	8.77	34.88		

Tab. 7.33 - Strength parameters from direct shear tests performed on the prototyped untreated sediment and the samples of sediments treated with AC, OC and BC.

Key: $\sigma'_{V \text{ MAX}}$ maximum vertical effective stress, $\tau_{\text{ MAX}}$ maximum shear stress, $\delta_{\text{ MAX}}$ maximum horizontal displacements, ϕ'_{CS} critical state friction angle, $\phi'_{\text{CS}}^{\text{AV}}$ average critical state friction angle, R^2 coefficient of determination, blue values: tests with tap water, red values: tests with seawater.

In Fig. 7.31a-b the effective strength envelopes are reported for the untreated specimens and the specimens treated with AC, OC and BC, respectively. The figures also show the sediments tested with both tap water and seawater. In the graphs, the data for the treated sediment samples are comparison with those of the untreated prototyped-sediment sample. In tap water, the friction angles vary between 31.7° (untreated sediment) and 39.25° (BC treated sediment). While, in seawater, the effective friction angles vary between 22.8° (untreated sediment) and 35.9° (BC treated sediment). The results show that: i) the use of reagents can significantly influence the

effective strength of the soil and ii) interestingly, lower effective friction angles are recorded for specimens put in contact with seawater. Despite the contract volumetric behaviour of all the treated specimens, those consolidated at vertical effective stress equal to 12 kPa exhibit maximum friction angles higher than those of specimens consolidated at $\sigma'_v = 50$ kPa.

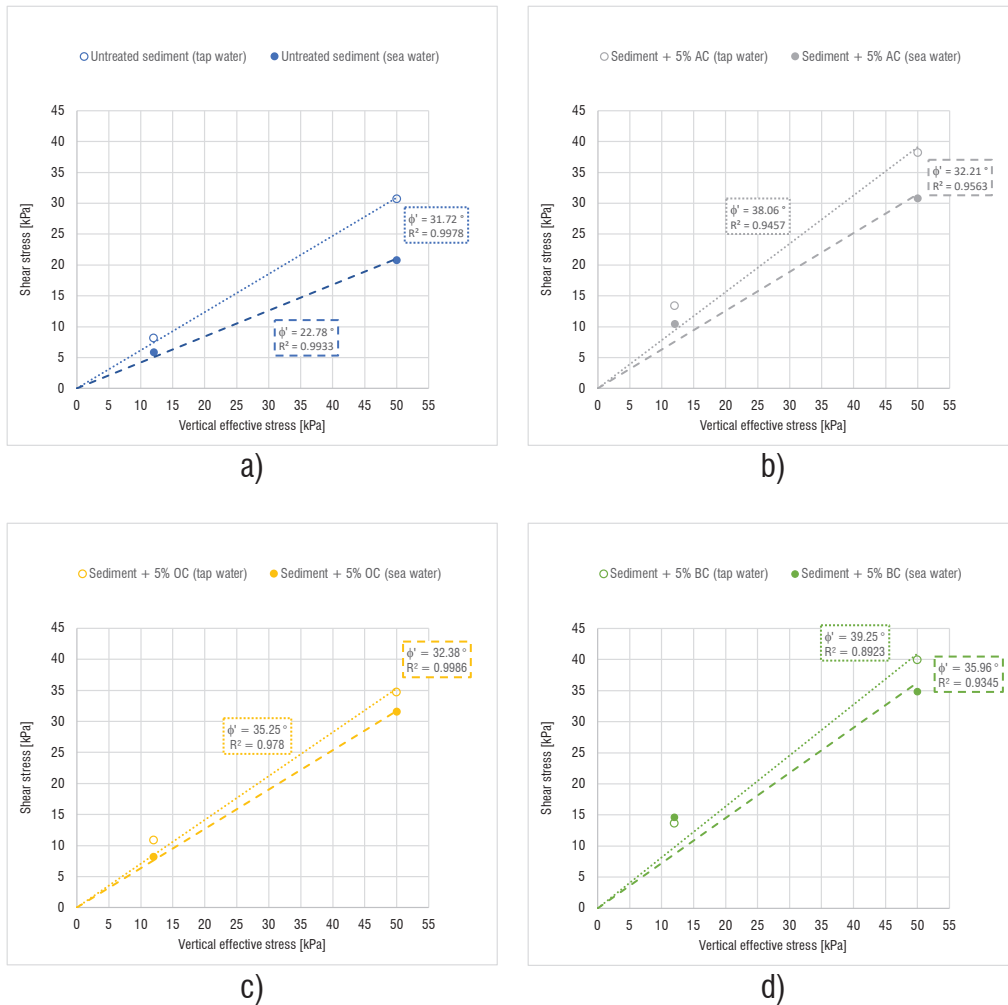


Fig. 7.31 - Effective strength envelopes of the specimens: a) untreated prototyped sediment; b) AC treated sediment; c) OC treated sediment; d) BC treated sediment. Dashed lines are used for tap water and continuous lines for seawater.

Fig. 7.32 and Fig. 7.32 show the effective strength envelopes of the specimens of both untreated and treated sediments tested with tap water and seawater, respectively. It seems that, despite the water used. The best performances are always obtained with the treatment based on BC.

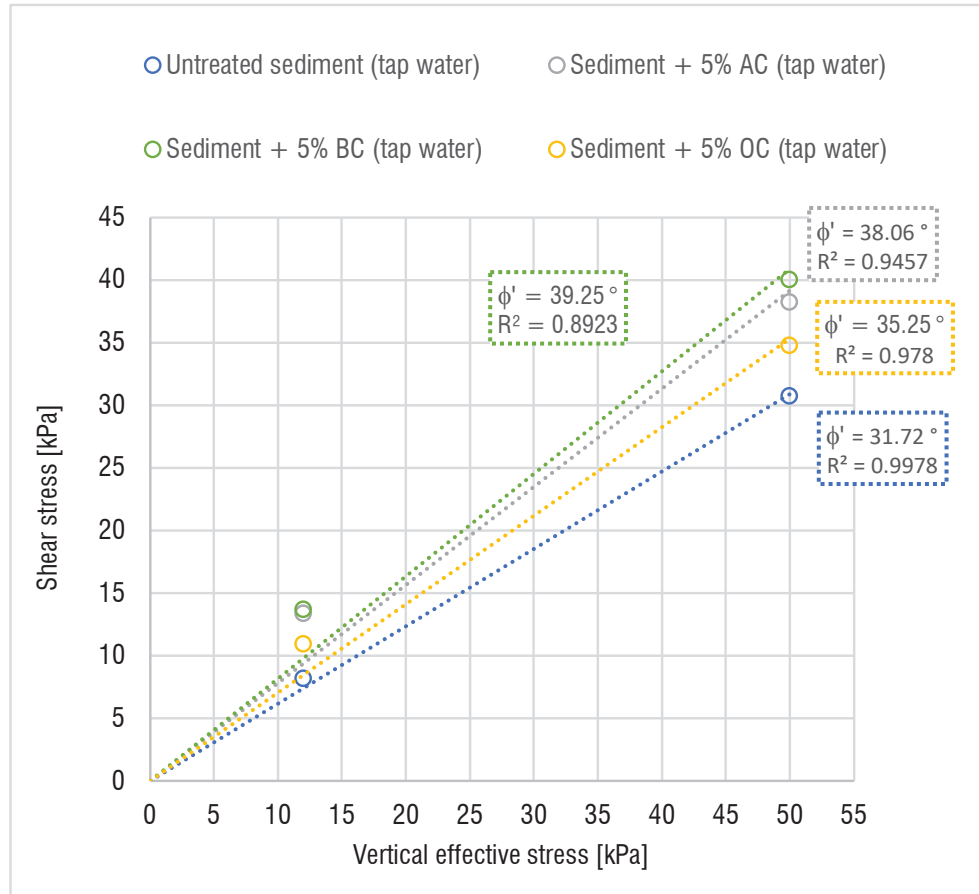


Fig. 7.32 - Effective strength envelopes of the specimens of both untreated and treated sediments tested with tap water.

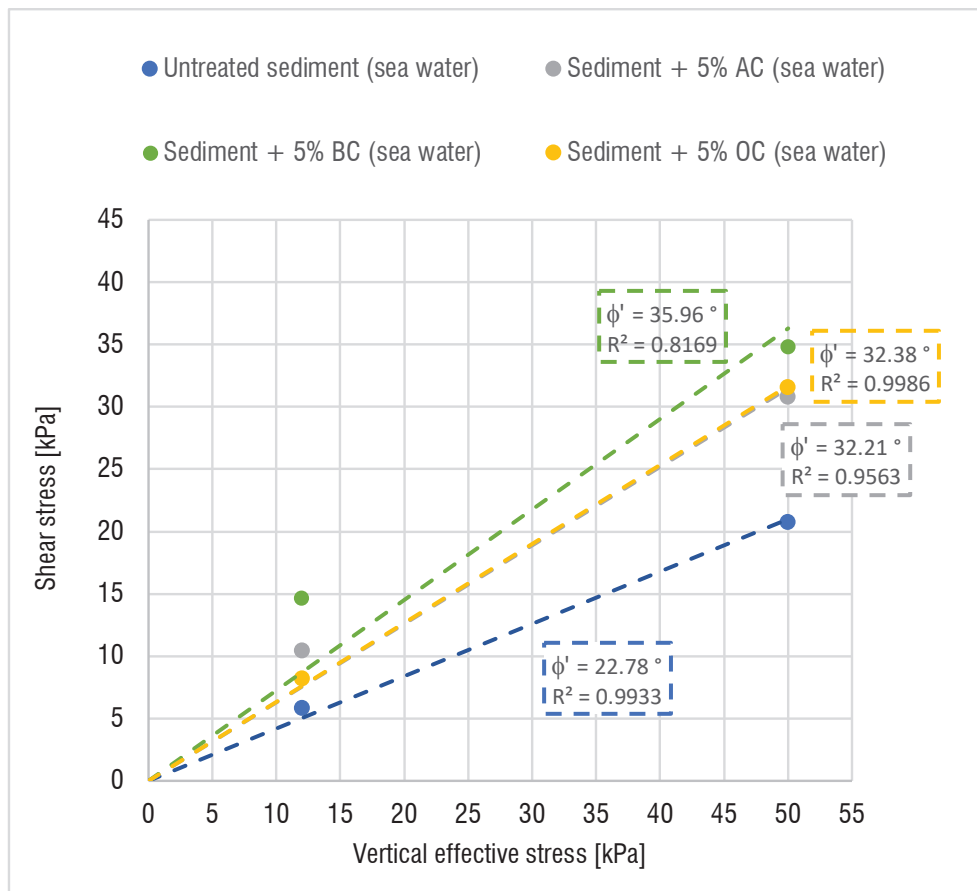


Fig. 7.33 - Effective strength envelopes of the specimens of both untreated and treated sediments tested with seawater.

7.3.2 Ex situ options

Contaminated sediments

In this experimental phase, the tests have been performed on two types of marine sediments made by mixing several samples of the official campaign, to test different S/S treatment on a sediment sample contaminated only by heavy metal (named MIX_1) and a sediment sample contaminated by inorganic and organic pollutants (named MIX_2, the same sediment used for testing in situ technologies in the advanced phase). In particular, the sediment samples used for the tests were characterised by physical-chemical properties and composition reported in Tab. 7.34.

Parameter	Unit	MIX_1	MIX_2
pH	u. pH	8.93	8.82
Eh	mV	-110.0	-100.7
Conductivity	mS/cm	3.05	4.78
Moisture content	%	49.79	44.63
Ashes at 550°C	%	79.47	89.14
Organic matter content	%	21.53	10.86
Grain size distribution			
Sand fraction, SF	%	18.86	19.44
Silt fraction, MF	%	45.32	43.18
Clay fraction, CF	%	35.82	37.38

Tab. 7.34 - Physical-chemical properties and composition of the samples of sediments used for the tests advanced phase (ex situ options).

The chemical characterisation of the samples is reported in Tab. 7.34 - 7.36. In the tables, the values of contaminants are compared with both site-specific limits (ICRAM, 2004; yellow values), and Italian law limits (D.Lgs. 152/2006; red values).

The samples exhibit similar contamination by heavy metals (i.e. Hg, Pb, Cu and Zn); however, the MIX 1 does not show any significant concentration of organic contaminants (i.e. PAHs=101 µg/kg ss and PCBs = 23 µg/kg ss).

Metals	Unit	MIX_1	MIX_2
As	mg/kg ss	18.91	12.71
Cd	mg/kg ss	0.71	0.47
Be	mg/kg ss	1.29	0.80
Co	mg/kg ss	8.93	7.20
Cr	mg/kg ss	68.74	50.58
Hg	mg/kg ss	3.68	1.99
Ni	mg/kg ss	48.28	37.70
Pb	mg/kg ss	82.11	91.45
V	mg/kg ss	68.34	49.28
Cu	mg/kg ss	64.59	59.00
Zn	mg/kg ss	135.32	172.73

Tab. 7.35 - Concentration of heavy metals in untreated sediment samples (LOD = 0.01 mg/kg ss).

PAHs	Unit	MIX_1	MIX_2
Naphthalene	µg/kg ss	< LOD	74
Fluoranthene	µg/kg ss	< LOD	995
Anthracene	µg/kg ss	< LOD	695
Acenaphthene	µg/kg ss	< LOD	127
Acenaphthylene	µg/kg ss	< LOD	87
Fluorene	µg/kg ss	< LOD	134
Phenanthrene	µg/kg ss	< LOD	175
Pyrene	µg/kg ss	< LOD	898
Chrysene	µg/kg ss	< LOD	559
Benz[a]anthracene	µg/kg ss	< LOD	528
Benz[a]pyrene	µg/kg ss	< LOD	519
Benz[k]fluoranthene	µg/kg ss	101	773
Benz[b]fluoranthene	µg/kg ss	< LOD	< LOD
Benz[g,h,i]perylene	µg/kg ss	< LOD	< LOD
Dibenzo[a,h]anthracene	µg/kg ss	< LOD	< LOD
Indeno[1,2,3-cd]pyrene	µg/kg ss	< LOD	168
Total PAHs	µg/kg ss	101	5732

Tab. 7.36 - Concentration of PAHs in untreated sediment samples (LOD= 20 µg/kg ss).

PCBs	Unit	MIX_1	MIX_2
PCB 28	$\mu\text{g/kg ss}$	< LOD	< LOD
PCB 52	$\mu\text{g/kg ss}$	< LOD	43
PCB 81	$\mu\text{g/kg ss}$	< LOD	15
PCB 95	$\mu\text{g/kg ss}$	< LOD	21
PCB 101	$\mu\text{g/kg ss}$	< LOD	106
PCB 99	$\mu\text{g/kg ss}$	< LOD	62
PCB 77	$\mu\text{g/kg ss}$	< LOD	< LOD
PCB 110	$\mu\text{g/kg ss}$	< LOD	97
PCB 128	$\mu\text{g/kg ss}$	< LOD	44
PCB 151	$\mu\text{g/kg ss}$	< LOD	121
PCB 123	$\mu\text{g/kg ss}$	< LOD	< LOD
PCB 118	$\mu\text{g/kg ss}$	< LOD	94
PCB 114	$\mu\text{g/kg ss}$	< LOD	< LOD
PCB 149	$\mu\text{g/kg ss}$	< LOD	29
PCB 146	$\mu\text{g/kg ss}$	< LOD	258
PCB 105	$\mu\text{g/kg ss}$	11	24
PCB 153	$\mu\text{g/kg ss}$	< LOD	125
PCB 126	$\mu\text{g/kg ss}$	< LOD	< LOD
PCB 183	$\mu\text{g/kg ss}$	< LOD	100
PCB 187	$\mu\text{g/kg ss}$	< LOD	34
PCB 138	$\mu\text{g/kg ss}$	12	25
PCB 167	$\mu\text{g/kg ss}$	< LOD	5
PCB 177	$\mu\text{g/kg ss}$	< LOD	26
PCB 156	$\mu\text{g/kg ss}$	< LOD	< LOD
PCB 157	$\mu\text{g/kg ss}$	< LOD	< LOD
PCB 180	$\mu\text{g/kg ss}$	< LOD	205
PCB 169	$\mu\text{g/kg ss}$	< LOD	< LOD
PCB 170	$\mu\text{g/kg ss}$	< LOD	79
PCB 189	$\mu\text{g/kg ss}$	< LOD	< LOD
Total PCBs	$\mu\text{g/kg ss}$	23	1513

Tab. 7.37 - Concentration of PCBs in untreated sediment samples (LOD = 1 $\mu\text{g/kg ss}$).

Leaching tests

For the two types of sediment (named MIX_1 and MIX_2), 8 mixtures have been prepared (Tab. 5.7). Leaching tests have been carried out at different periods (i.e. 1, 7, 14, 21, 28 and 56 days) to assess the release of heavy metals and organic pollutants.

The pH trend shows that basicity decreases with time and reaches values close to the initial conditions (untreated sediment) after 56 days of curing (Figs. 7.34 and 7.35). After 24 hours (execution of the first leaching test) the pH of the mixtures is equal to approximately 13 (i.e. pH values vary between 12.2 for mixtures with cement and 12.7 for mixtures with lime).

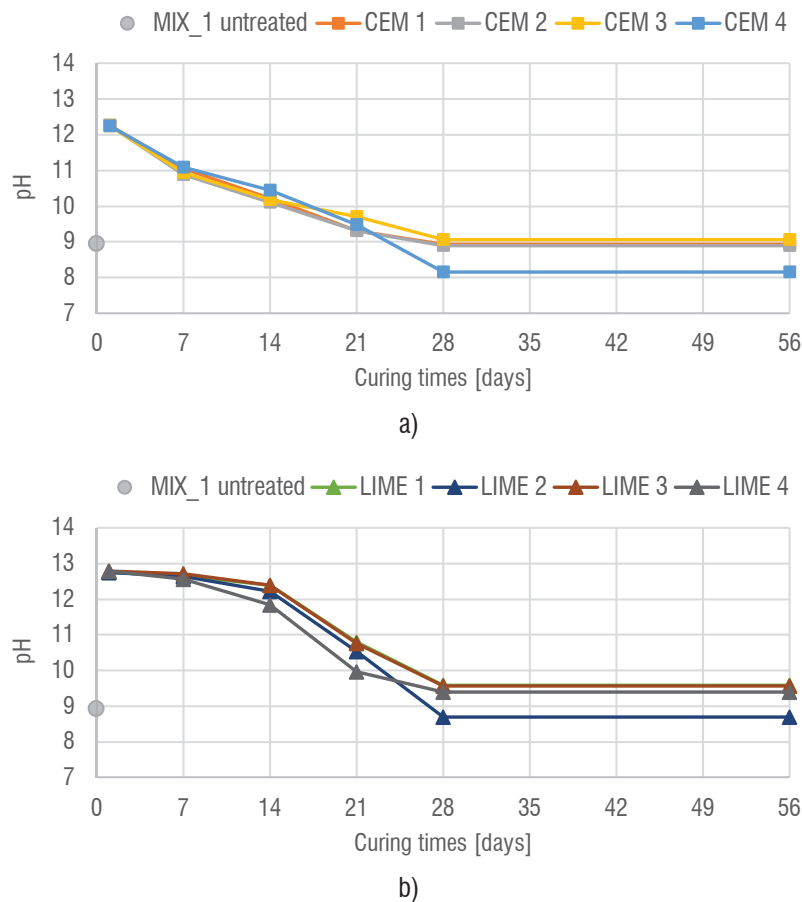


Fig. 7.34 - pH trend with the curing time: a) MIX_1 treated with cement; b) MIX_1 treated with lime.

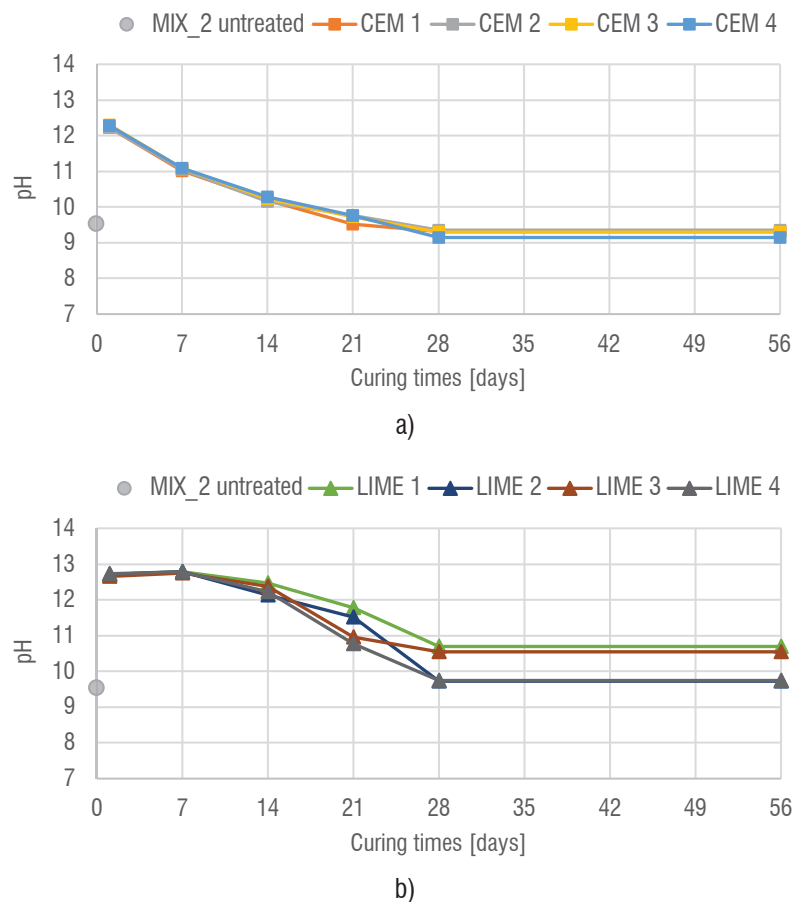


Fig. 7.35 - pH trend with curing time: a) MIX_2 treated with cement; b) MIX_2 treated with lime.

Longer curing times tends to reduce the pH of the eluates; from 28 to 56 days of curing no important changes are observed. After 28 days of curing there may be changes in release rates of contaminants because of cement hydration continues (Paria and Yuet, 2006). However, there are no significant changes in pH for curing times longer than 28 days. Specifically, both after 28 days and 56 days the cement mixtures are characterised by pH values about 9 (only the MIX_1 - CEM 4 have a pH of 8.2), lime mixtures between 8.7 and 9.4 for MIX_1 and between 9.7 and 10.5 for MIX_2. These observations are due to the well-known solubility behaviour of metals as a function of pH. As shown in the preliminary experimental phase, the solubility of metals in the sediment

decreases with pH. The main results indicate that, despite the total concentrations of heavy metals in the marine sediments under study, the release of contaminants after contact with deionized water is very limited. This is likely due to both the low metals' solubility and to the stability of their solid phases under slightly basic conditions (Chatain et al., 2013).

In Figs. 7.36-7.40 the concentrations detected into the eluted of the heavy metals respect to the different reagents/sediment relationship are reported. In general, the addition of binders and reagents to the contaminated marine sediments resulting shows positive effects on decreasing the mobility of heavy metals.

The concentrations of Hg, Co, Pb and Zn are not reported because they were always found to be lower than the instrumental detection limit (LOD is approximately 0.001 mg/l). These low concentrations show the good performance of the designed mixtures, also for short curing times (i.e. 1 day). The low solubility of Co, Pb and Zn is related to pH values between 13 and 8, which can be reached with a lower percentage of binders. In particular, Pb concentration in leachate becomes undetectable for pH values between 9 and 11, for the formation of insoluble hydroxide (Paria and Yuet, 2006). Moreover, it was suggested that the mechanism of Pb immobilization involves not only a physical encapsulation mechanism, but also the formation of a new phase with Al and Si species (Halim et al., 2004). Zn may form hydrated complexes such as $\text{CaZn}_2(\text{OH})_6$ (Mollah et al., 1992) and hemimorphite ($\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2$) (Ziegler et al., 2001), which may interact with and adsorb onto C-S-H.

As concentrations in the eluates, compared to the untreated sediments, show an initial reduction and an increase with the curing time. As values tend to stabilize at 56 days, except for CEM 1 mixture (sediment with 10% of cement). Bothe and Brown (1999) suggested that lime treatment reduces As mobility in contaminated slurries due to the formation of low-solubility Ca-As precipitates such as $\text{Ca}_4(\text{OH})_2(\text{AsO}_4)_2$ and $\text{Ca}_5(\text{AsO}_4)_3(\text{OH})$.

With respect to Cr (only mixtures with cement), Ni and Cu the release decreases, in a monotonous way, with the curing time; metals show lowest solubility at low values of pH. For the mixtures with lime, in the first 3 weeks, there is an increase

of Cr solubility with the reduction of pH (i.e. increase of curing time). After 21 days the concentrations decrease. Roy et al. (1992) observed that hydration of Portland cement was retarded by Ni-containing sludge, but the hydration products are the same as those formed without Ni. They suggested that physical encapsulation of metal hydroxide by the cement is the principal mechanism of stabilization. The solidification of chromium can be related to the formation of Ca–Cr aluminates and the formation of phases such as $\text{Ca}_4\text{Al}_6\text{O}_{12}\text{CrO}_4$ and $\text{Ca}_6\text{Al}_4\text{Cr}_2\text{O}_5$ (Stephan et al., 1999a; Stephan et al., 1999b).

V show a similar the pattern of release to that of Cr for lime mixtures. Initially, the release increases with curing time, maximum values are reached after 14 days for MIX_1 treated with cement, 28 days for MI_2 treated with lime, and around 28 days for the lime-treated sediment. The enhanced leaching observed can be depend to solidification process; with longer maturation times, the metals are encapsulated in the sediment into a solid monolithic structure with high structural integrity (Desogus et al., 2012; Wang et al., 2018). However, the adding of cement appears to increase the leaching of vanadium; whereas the adding of lime appears to increase the leaching of copper.

As indicated by results, the efficiency of S/S treatment has been improved using adsorbent materials (i.e. activated carbon and organoclay). In particular, for Ni and Cu the release curves for the mixtures with AC (i.e. CEM 2, CEM 4, LIME 1 and LIME 4) are translated downwards (Figs. 7.37 and 7.39). Ac and OC improve treatment. However, it has to be noted that there could be effects of the organic contaminants (i.e. PAHs and PCBs), that can interfere with the chemistry of binder's hydration, compromising the effectiveness of metal stabilization and development of hardening (Wang et al., 2015). There are not significant differences between the curves of MIX_1 (sediments contaminated by heavy metals) and others of MIX_2 (sediments contaminated by heavy metals, PAHs and PCBs).

For the beneficial reuse of contaminated marine sediments, the leaching of each metal has to be lower than law limits. In Italy, the chemical parameters must be under the threshold levels defined by the Italian Ministerial Decree 5/2/1998. The leaching tests results of S/S treated marine sediments after 28 days are given in Tab. 7.38 and

7.39. For MIX_1 samples, i.e. sediments mixed with either 10% cement alone (CEM 1) or 10% cement in combination with 2.5% AC and 2.5% OC (CEM 4) are found to be not effective for the stabilization of vanadium (regulatory standard is 0.025 mg/l). However, after 56 days of curing time the concentrations decrease (CEM 1, 0.095 mg/l; CEM 4, 0.087) up to comply with the standards. After 28 days of curing, MIX_2 samples, i.e. sediment mixed with either 10% lime alone (LIME 1) or 10% lime with 5% AC (LIME 2) or with 2.5% AC and 2.5% OC (LIME 4) is effective such that all metal concentrations meet the regulatory standards. In particular, the Vanadium from mixtures with cement (CEM 1, CEM 2, CEM 3 and CEM 4) and the Copper from CEM 1, LIME 5 and LIME 7 are released with concentrations exceeding the law limits. However, after longer curing times (i.e., 56 days) the leaching of these metals was less than 0.02 mg/l (i.e. compliant with the standards).

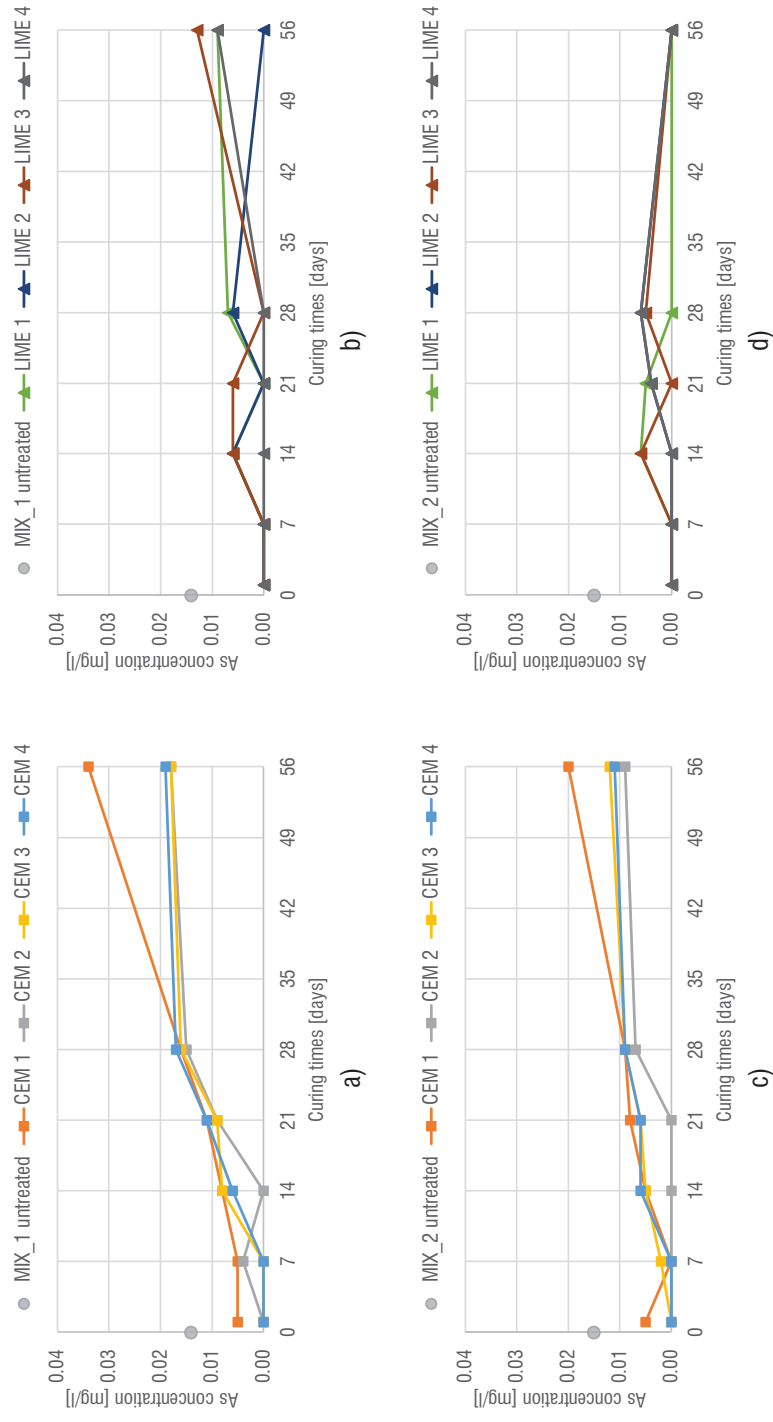


Fig.7.36 - Variations of As concentrations after different curing time: a) MIX_1 treated with cement; b) MIX_1 treated with lime; c) MIX_2 treated with cement; d) MIX_2 treated with lime. (Regulatory standards 0.05 mg/l).

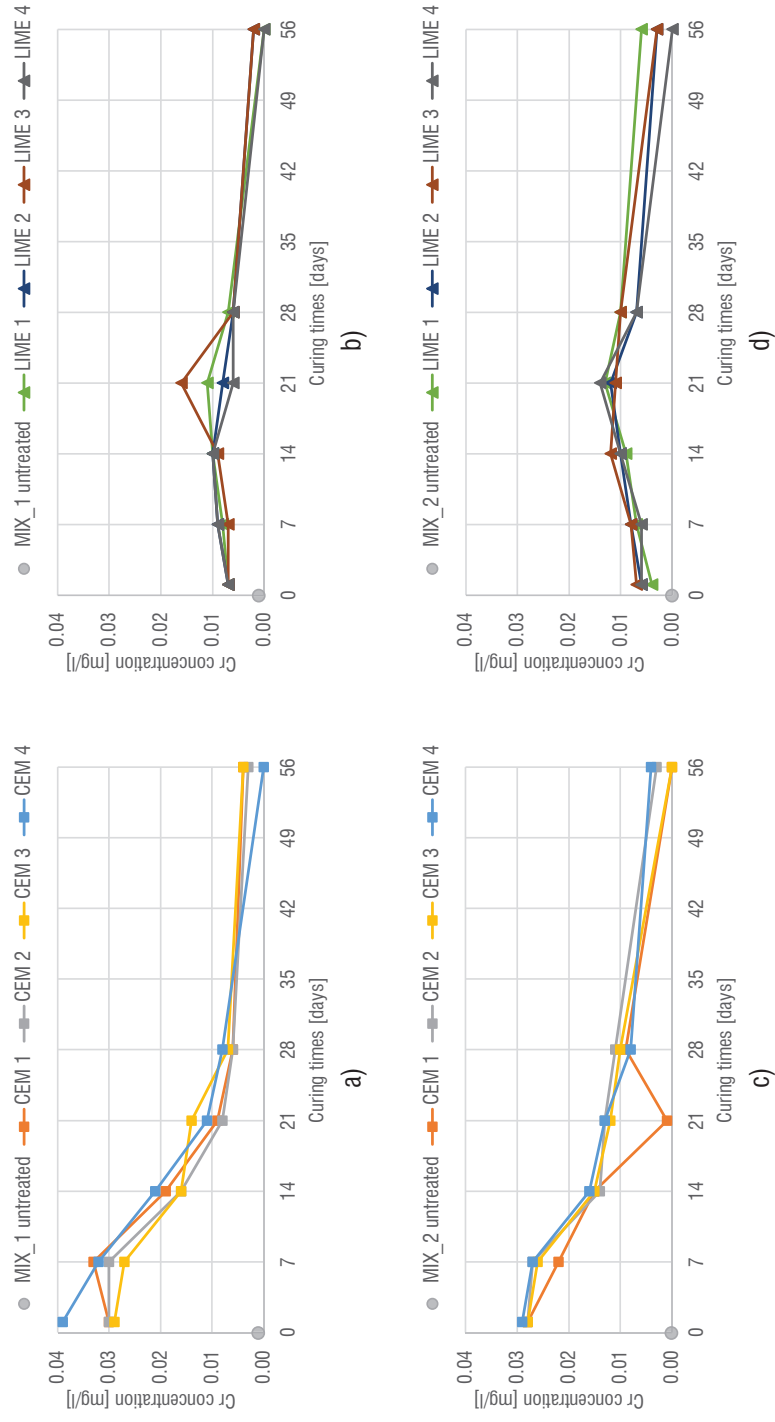


Fig. 7.37 - Variations of Cr concentrations after different curing time: a) MIX_1 treated with cement; b) MIX_1 treated with lime; c) MIX_2 treated with cement; d) MIX_2 treated with lime. (Regulatory standards 0.05 mg/l).

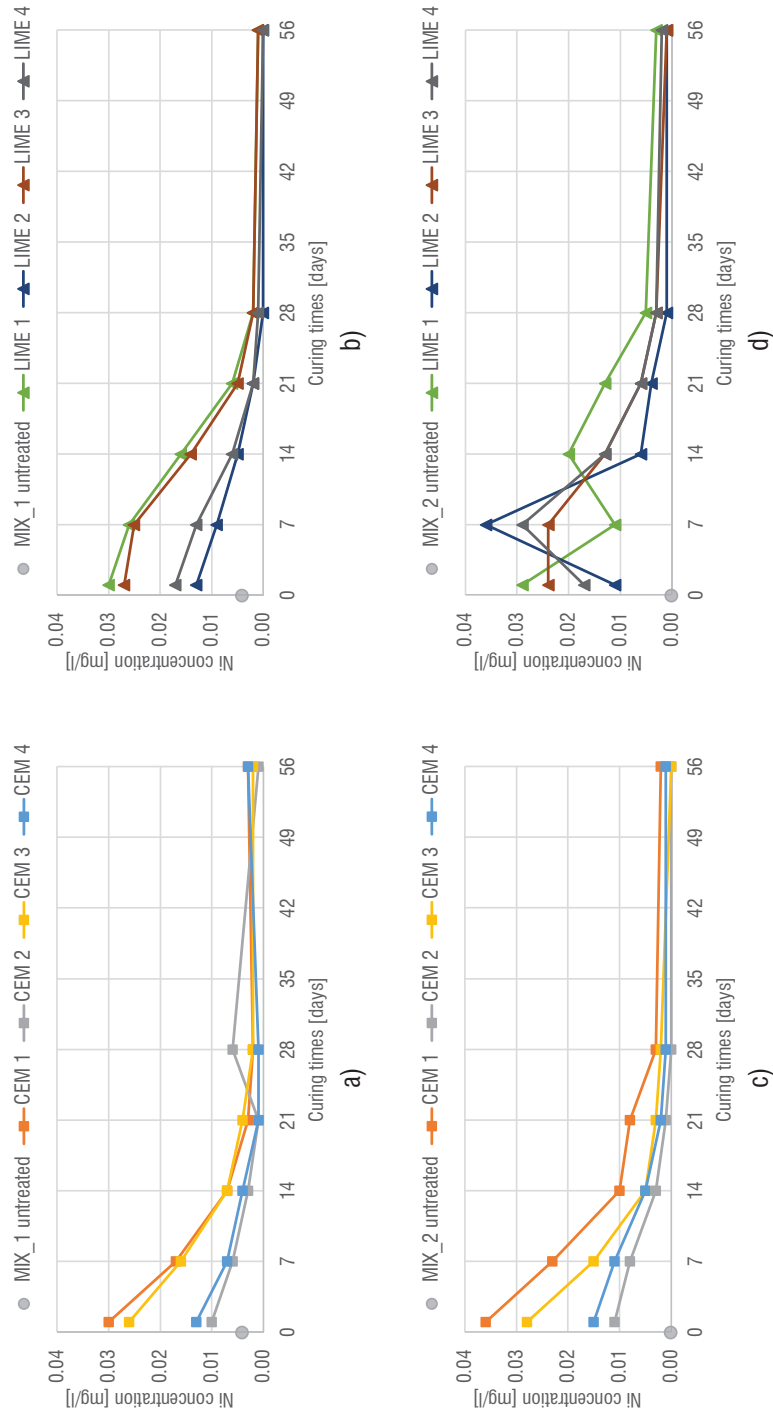


Fig. 7.38 - Variations of Ni concentrations after different curing time: a) MIX_1 treated with cement; b) MIX_1 treated with lime; c) MIX_2 treated with cement; d) MIX_2 treated with lime. (Regulatory standards 0.01 mg/l).

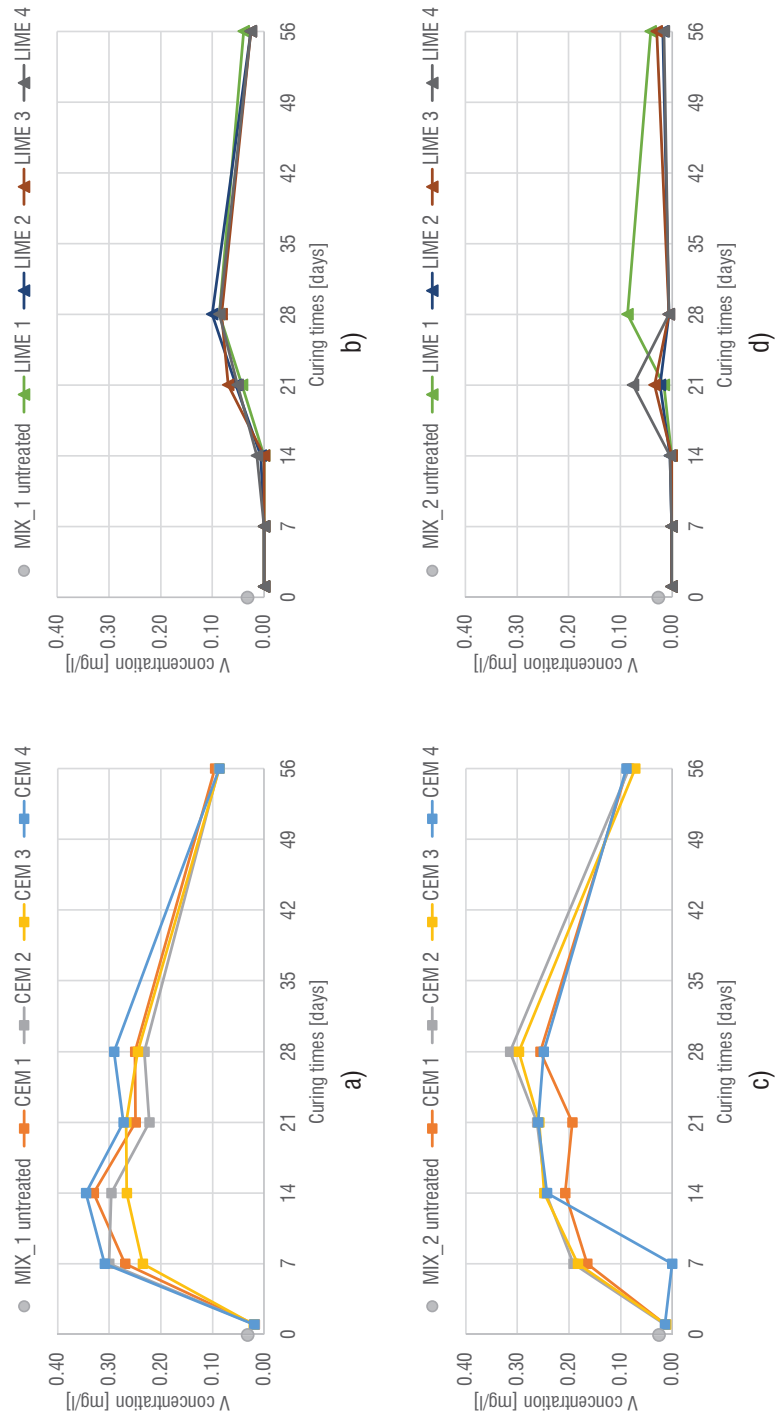


Fig. 7.39 - Variations of V concentrations after different curing time; a) MIX_1 treated with cement; b) MIX_1 treated with lime; c) MIX_2 treated with cement; d) MIX_2 treated with lime. (Regulatory standards 0.25 mg/l).

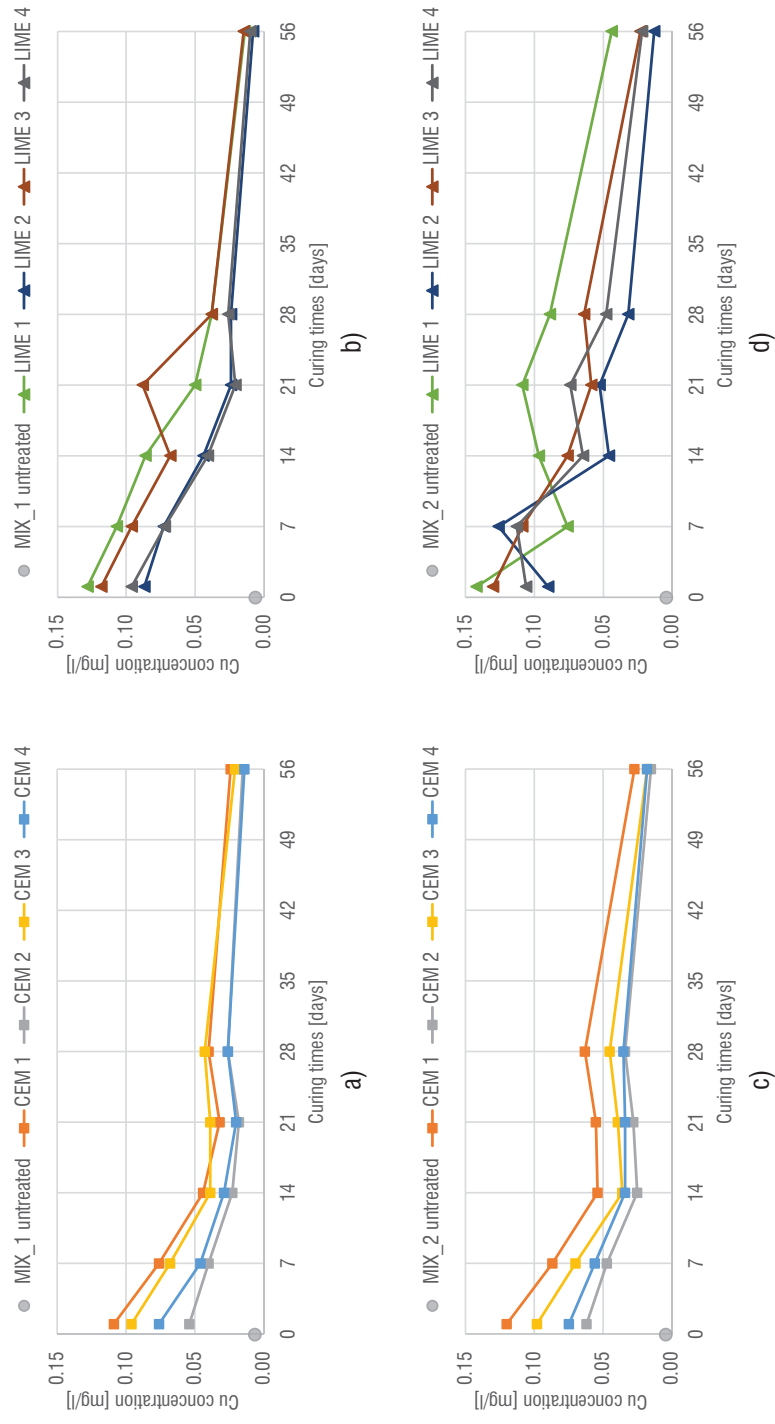


Fig. 7.40 - Variations of Cu concentrations after different curing time: a) MIX_1 treated with cement; b) MIX_1 treated with lime; c) MIX_2 treated with cement; d) MIX_2 treated with lime. (Regulatory standards 0.05 mg/l).

Sediment sample	Mix	Parameter	Unit	Metals							
				As	Co	Cr	Ni	Pb	V	Cu	Zn
MIX_1	CEM 1	Leachate concentration	mg/l	0.016	< LOD	0.006	< LOD	< LOD	0.250	0.040	< LOD
		Environmental goals	-	✓	✓	✓	✓	✓	✗	✓	✓
	CEM 2	Leachate concentration	mg/l	0.015	< LOD	0.006	0.006	< LOD	0.232	0.026	< LOD
		Environmental goals	-	✓	✓	✓	✓	✓	✓	✓	✓
	CEM 3	Leachate concentration	mg/l	0.016	< LOD	0.007	< LOD	< LOD	0.245	0.043	< LOD
		Environmental goals	-	✓	✓	✓	✓	✓	✓	✓	✓
	CEM 4	Leachate concentration	mg/l	0.017	< LOD	0.008	< LOD	0.001	0.291	0.026	< LOD
		Environmental goals	-	✓	✓	✓	✓	✓	✗	✓	✓
	LIME 1	Leachate concentration	mg/l	0.007	< LOD	0.007	0.002	< LOD	0.086	0.038	< LOD
		Environmental goals	-	✓	✓	✓	✓	✓	✓	✓	✓
	LIME 2	Leachate concentration	mg/l	0.006	< LOD	0.006	< LOD	< LOD	0.100	0.024	< LOD
		Environmental goals	-	✓	✓	✓	✓	✓	✓	✓	✓
	LIME 3	Leachate concentration	mg/l	< LOD	< LOD	0.006	0.002	< LOD	0.082	0.038	< LOD
		Environmental goals	-	✓	✓	✓	✓	✓	✓	✓	✓
	LIME 4	Leachate concentration	mg/l	< LOD	< LOD	0.006	0.001	< LOD	0.086	0.026	< LOD
		Environmental goals	-	✓	✓	✓	✓	✓	✓	✓	✓

Tab. 7.38 - Assessment of environmental performance of the mixtures in terms of metal stabilization. Environmental goals: positive (✓) and negative (✗) if the metal concentrations are, respectively, lower and higher than the law limits (according to the Ministerial Decree 1998).

Sediment sample	Mix	Parameter	Unit	Metals							
				As	Co	Cr	Ni	Pb	V	Cu	Zn
MIX_2	CEM 1	Leachate concentration	mg/l	0.009	< LOD	0.009	0.003	< LOD	0.255	0.087	< LOD
		Environmental goals	-	✓	✓	✓	✓	✓	✗	✗	✓
	CEM 2	Leachate concentration	mg/l	0.007	< LOD	0.011	< LOD	< LOD	0.314	0.034	< LOD
		Environmental goals	-	✓	✓	✓	✓	✓	✗	✓	✓
	CEM 3	Leachate concentration	mg/l	0.009	< LOD	0.010	< LOD	< LOD	0.297	0.045	< LOD
		Environmental goals	-	✓	✓	✓	✓	✓	✗	✓	✓
	CEM 4	Leachate concentration	mg/l	0.009	< LOD	0.008	< LOD	< LOD	0.250	0.035	< LOD
		Environmental goals	-	✓	✓	✓	✓	✓	✗	✓	✓
	LIME 1	Leachate concentration	mg/l	< LOD	< LOD	0.010	0.005	< LOD	0.086	0.089	< LOD
		Environmental goals	-	✓	✓	✓	✓	✓	✓	✗	✓
	LIME 2	Leachate concentration	mg/l	0.006	< LOD	0.007	< LOD	< LOD	0.006	0.032	< LOD
		Environmental goals	-	✓	✓	✓	✓	✓	✓	✓	✓
	LIME 3	Leachate concentration	mg/l	0.005	< LOD	0.010	< LOD	< LOD	0.006	0.064	< LOD
		Environmental goals	-	✓	✓	✓	✓	✓	✓	✗	✓
	LIME 4	Leachate concentration	mg/l	0.006	< LOD	0.007	< LOD	< LOD	0.006	0.048	< LOD
		Environmental goals	-	✓	✓	✓	✓	✓	✓	✓	✓

Tab. 7.39 - Assessment of environmental performance of the mixtures in terms of metal stabilization. Environmental goals: positive (✓) and negative (✗) if the metal concentrations are, respectively, lower and higher than the law limits (according to the Ministerial Decree 1998).

Geotechnical investigation

Fig. 7.41 and Fig. 7.42 show, respectively, the grain-size distributions of both untreated and cement and lime treated sediments after 28 days of curing. The data relative to the use of reagents are also reported in the Figures. In general, it can be observed that the untreated sediments have a significantly higher clay fraction than the treated ones, irrespective of the binder used. This is consistent with the creation of an open flocculated structure with clay–binder clusters interspersed by large voids (e.g. Chew et al., 2004). For both the cement and lime mixtures, the test results show a decrease in clay fraction, CF, and an increase in sand fraction, SF. This effect is more accentuated for the cement-treated sediments and, in particular, for those incorporating AC as reagent ($CF_{MIN}=13\%$ and $SF_{MAX}=31.2\%$). All the samples treated with lime have similar composition ($CF=22\%$; $MF=57\%$; $SF=21\%$; Fig. 7.41), i.e. the use of reagents does not seem to significantly influence lime-treated soil composition.

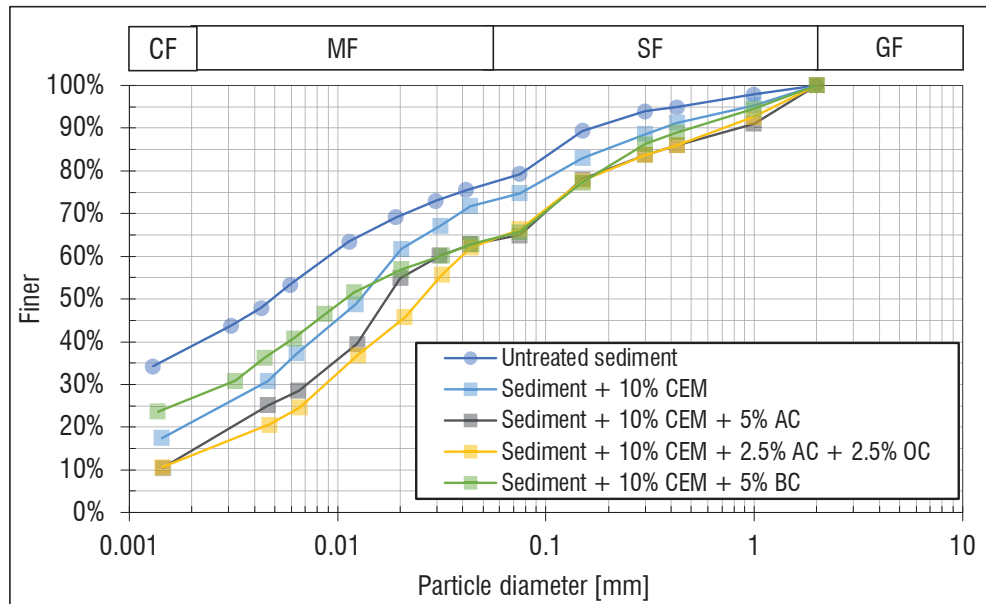


Fig. 7.41 - Treatments with cement and effect of reagents (i.e. active carbon, AC, and biochar, BC) on the grain size distributions (curing time: 28 days) of the submarine sediments.

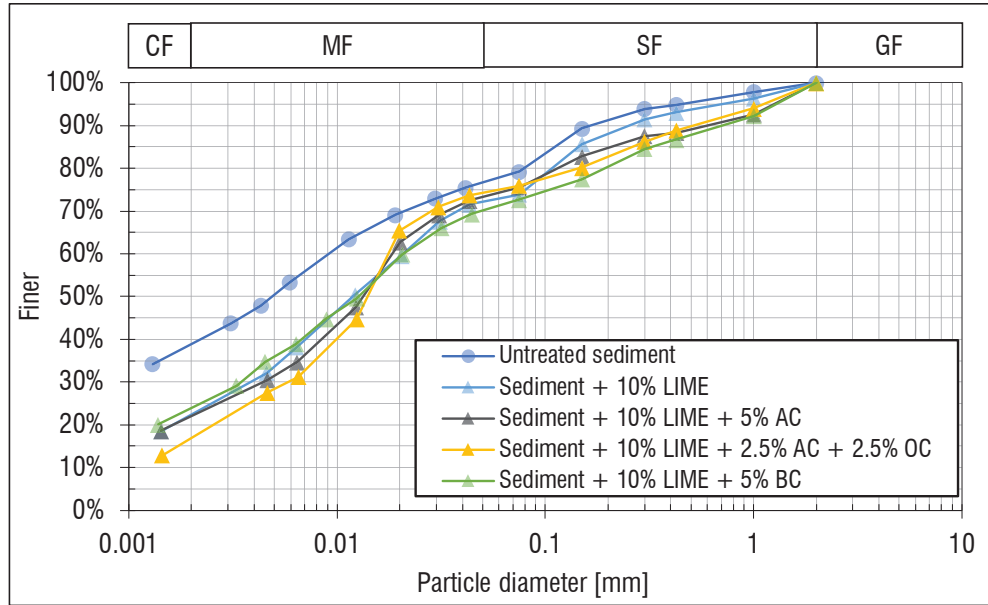


Fig. 7.42 - Treatments with lime and effect of reagents (i.e. active carbon, AC, and biochar, BC) on the grain size distributions (curing time: 28 days) of the submarine sediments.

The Casagrande's plasticity charts in Fig. 7.43a and Fig. 7.43b show the effects of the treatments on the Atterberg limits for the cement and lime-treated sediments, respectively. The data relative to the use of reagents are also reported in the Figures. For each mix design, the plasticity points have different colour and the symbol sizes are proportional to the curing times (i.e. 0, 14 and 28 days). The first consideration that can be made is that, although the untreated sediments are CH soils according to USCS classification (ASTM, 2011), the after-treatment material is classified as MH soil, irrespective of the additive or reagent used. These results appear to be consistent with those, reported by Federico et al. (2015) and relative to submarine sediments sampled down the Mar Grande area in Taranto and treated with similar percentages of traditional binders. For the cement-treated sediments (Fig. 7.43a), the increasing curing time makes the plasticity points move downwards and to the left in the chart (i.e. a reduction in both w_L and PI is recorded). Similar results have been found when also reagents are added. Specifically, after 28 days of curing, the sediments treated with cement and biochar (BC) show the maximum effect on the soil plasticity indices. When lime is used,

Fig. 7.42b depicts a milder reduction in the plasticity index if compared to the cement-treated sediments. Moreover, the data show that only the sediments treated with lime and AC appear to follow paths similar (i.e. both w_L and PI reduce) to those recurrent for cement-treated sediments in Fig. 7.43a.

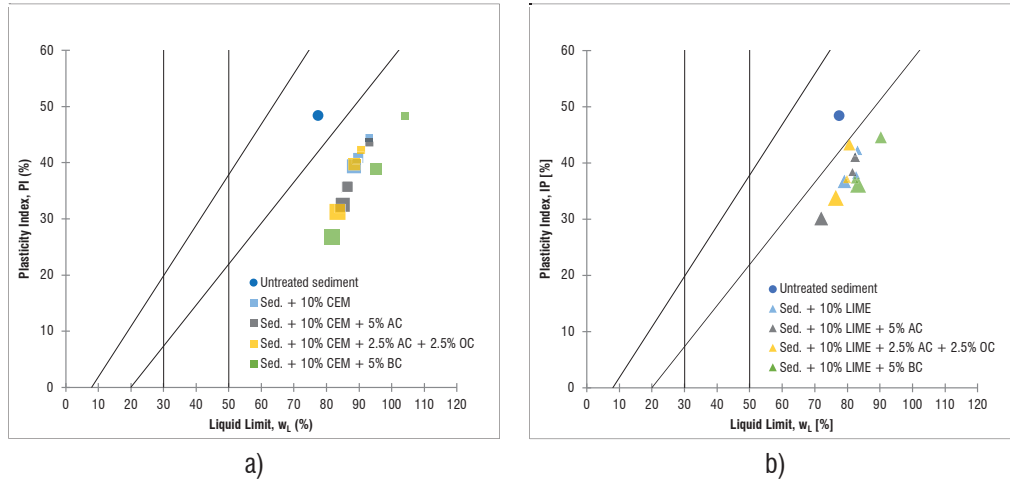


Fig. 7.43 - Plasticity paths of cement (a) and lime (b) treated sediments. The Figures also show the effect of the use of AC and BC on the soil plasticity. Symbol sizes are proportional to curing time (i.e. small symbols: 0 days, medium symbols: 14 days, large symbols: 28 days).

Figs. 7.44a and b show the results of the oedometer tests carried out on the untreated prototyped-sediment specimen and on the specimens treated with cement and lime after 28 days of curing, respectively. In the figures, the oedometer tests carried out on the specimens of sediments treated with traditional binders and reagents (i.e. active carbon, AC, and biochar, BC) are also shown. Irrespective of the typology of the additive used, the compression curves of the stabilised sediments always lie to the right of the compression line of the untreated sediment in the void ratio, e - vertical effective stress (σ'_v) plot. It is evident that, because of the cementation, treated sediments are more stable at higher void ratios than untreated ones, under the same consolidation vertical effective stress. Moreover, the data suggest that the use of reagents is not influencing the effect of stabilization on the one-dimensional compression behaviour: when either AC or BC are added, the compression curves are almost the same as those of specimens treated only with cement or lime. As expected, the cement-treated

sediments, exhibit the higher values of vertical effective stress at yield (derived by Using the Casagrande's construction, Casagrande, 1936): $\sigma'_y = 500\text{-}600$ kPa for cement-treated sediments and about 100-120 kPa for the lime-treated ones (see the arrows in the figures).

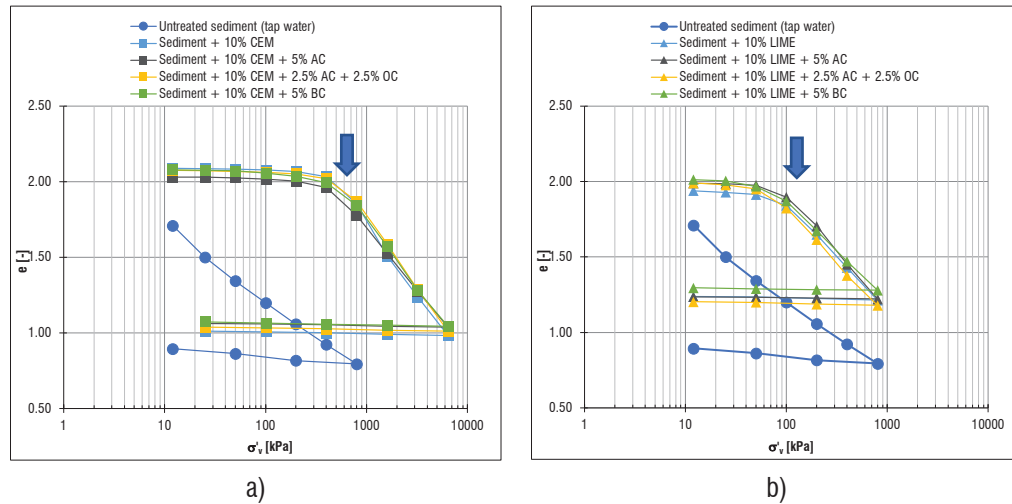


Fig. 7.44 - Treatments with a) cement and b) lime and effect of reagents on 1D compression behaviour (curing time: 28 days) of the submarine sediments. The arrows are for the yield stress.

The average recompression index, c_r , is about 0.01 for cement-treated sediments and 0.03 for lime-treated ones, respectively, the corresponding compression indices (c_c) are equal to, on average, 0.8 and 0.4, (Fig. 7.45a and b).

The swelling index, c_s , values are plotted against the average value of the vertical effective stress, σ'_v , at each loading step for both the cement and lime-treated specimens of sediments in Fig. 7.46a and b, respectively.

The values of the coefficient of permeability, k , are plotted in Fig. 7.47 against the vertical effective stress. They have been computed according to the consolidation theory by Terzaghi (1923), in both oedometer loading and unloading phases. For all the specimens, k in loading varies between $8.0 \cdot 10^{-12}$ and $8.7 \cdot 10^{-8}$ m/s and, in general, it decreases with void ratio (Fig. 7.48). In unloading, k is always lower than that in loading and it seems not to vary with the unloading phase. Based on these figures, the following observations can be made: i) the $e\text{-}\log(k)$ relationship after yielding is nearly linear,

which implies that Taylor's (1948) e - $\log(k)$ relationship can be applied to the treated sediments.; ii) in unloading the k values reduce considerably and seem not to depend on the vertical effective stress. The data in the Figures show that the pre-yield permeability values of the treated sediments depend on the binder and the reagent used. For the same values of vertical effective stress both cement and lime-treated sediments with AC and BC are more permeable than those with OC or just the binder. After yielding these differences appear to be cancelled out.

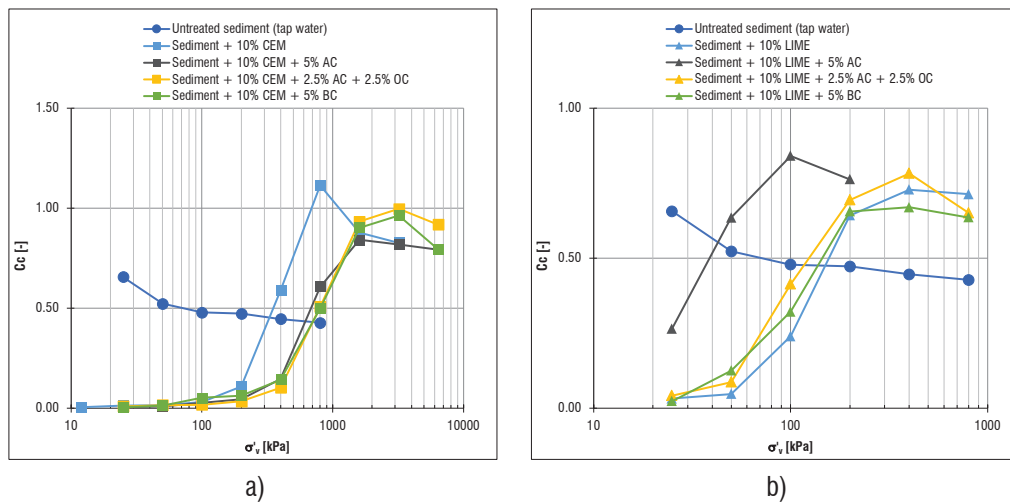


Fig. 7.45 - Compression index versus vertical effective stress for a) cement and b) lime treated specimens of sediments. Data in presence of are also reported (curing time: 28 days).

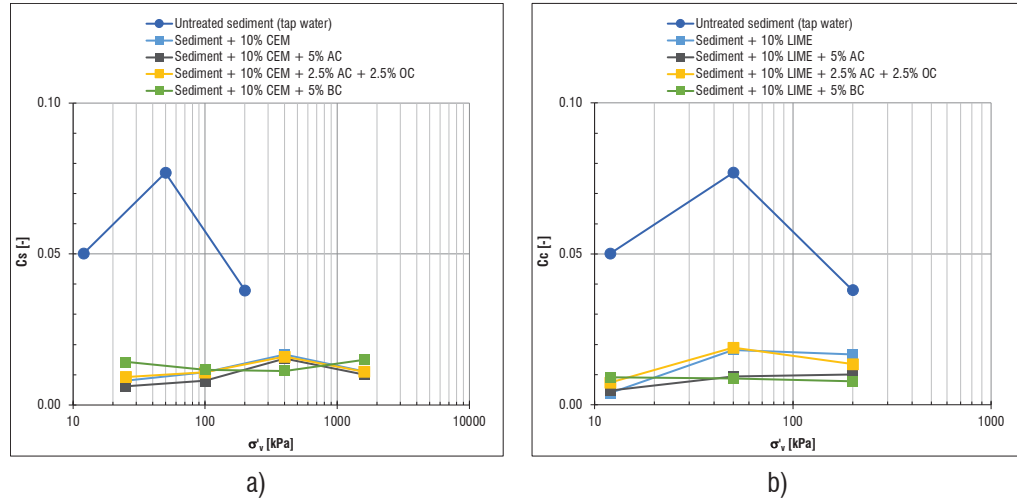


Fig. 7.46 - Swelling index versus vertical effective stress for a) cement or b) lime-treated specimens of sediments. Data in presence of reagents are also reported (curing time: 28 days).

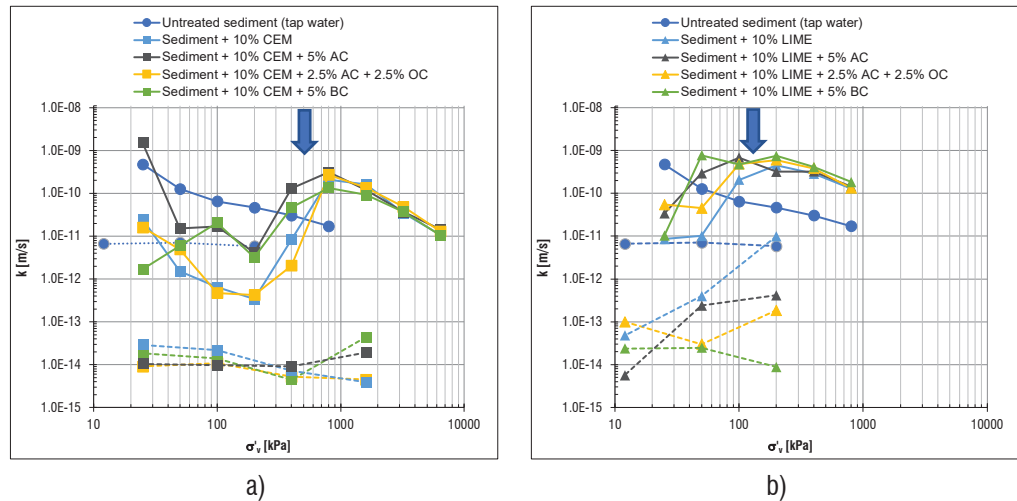


Fig. 7.47 - Coefficient of permeability versus vertical effective stress for a) cement or b) lime-treated specimens of sediments. Data in presence of reagents are also reported (curing time: 28 days). Continuous lines are used for loading paths and dashed lines for unloading paths. The arrows are for the yield stress.

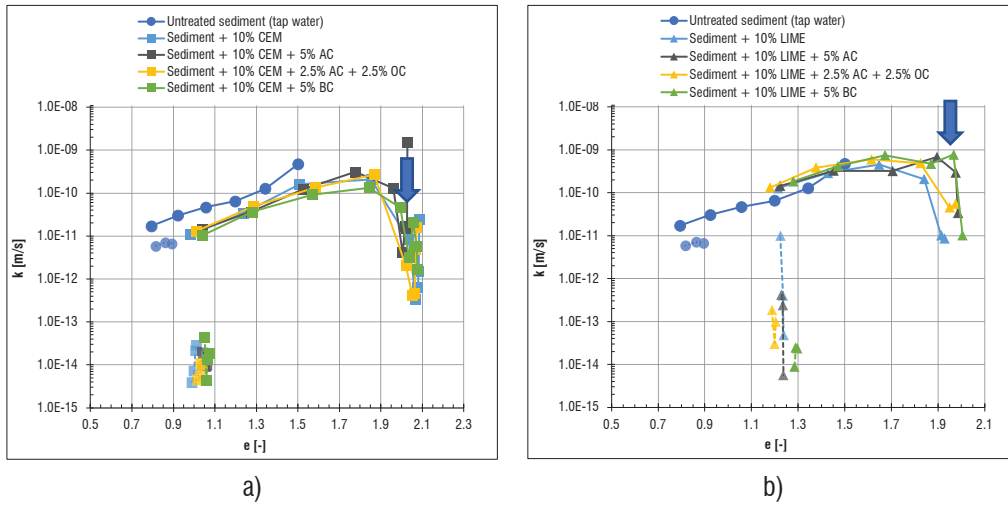


Fig. 7.48 - Coefficient of permeability versus void ratio for a) cement or b) lime-treated specimens of sediments. Data in presence of reagents are also reported (curing time: 28 days). Continuous lines are used for loading paths and dashed lines for unloading paths. The arrows are for the yield state.

In Tab. 7.40 the results obtained by the OED tests carried out on sediment treated with AC, OC and BC (5% compared to the weight of dry solid) are summarized.

Specimen	G_s [-]	w_i [%]	e_0 [-]	γ [kN/m ³]	w_f [%]	e_f [-]	c_c^{AV} [-]	c_s^{AV} [-]	M_L^{AV} [kPa]	M_U^{AV} [kPa]	k_L^{AV} [m/s]	k_U^{AV} [m/s]
Untreated sediment (tap water)	2.537	80.9	2.053	15.12	37.8	0.948	0.501	0.055	2485	31246	1.2E ⁻¹⁰	6.5E ⁻¹²
Sediment + 10% CEM	2.545	82.3	2.095	14.53	39.5	1.006	0.853	0.012	21393	678928	5.0E ⁻¹¹	1.6E ⁻¹⁴
Sed. + 10% CEM + 5% AC	2.551	79.7	2.035	13.94	43.0	2.086	0.766	0.010	19846	768740	2.4E ⁻¹⁰	1.2E ⁻¹⁴
Sed. +10% CEM + 2.5% AC + 2.5% OC	2.552	81.9	2.091	14.25	41.7	1.065	0.839	0.012	19504	704848	5.4E ⁻¹¹	7.4E ⁻¹⁴
Sed. + 10% CEM + 5% BC	2.505	83.0	2.080	14.18	43.4	1.086	0.790	0.013	16908	585684	3.5E ⁻¹⁰	2.0E ⁻¹⁴
Sed. + 10% LIME	2.549	76.5	1.950	14.87	50.3	1.283	0.581	0.013	3428	87408	1.8E ⁻¹⁰	3.5E ⁻¹²
Sed. + 10% LIME + 5% AC	2.552	78.2	1.996	14.61	50.3	1.284	0.624	0.008	5084	138043	3.0E ⁻¹⁰	2.2E ⁻¹³
Sed. + 10% LIME + 2.5% AC + 2.5% OC	2.563	78.6	2.018	14.76	49.1	1.260	0.636	0.013	2834	95143	1.7E ⁻⁹	3.2E ⁻¹³
Sed. + 10% LIME + 5% BC	2.507	80.8	2.026	14.37	53.7	1.346	0.573	0.009	3264	165332	4.3E ⁻¹⁰	1.9E ⁻¹⁴

Tab. 7.40 - Results of oedometer tests carried out on specimens of sediment treated with cement or lime and the AC, OC or BC reagents.

Key: G_s soil specific gravity, w_i initial water content, e_0 initial void ratio, γ bulk unit weight, w_f final water content, e_f final void ratio, c_c^{AV} average compression index, c_s^{AV} average swelling index, M_L^{AV} average oedometric stiffness in loading, M_U^{AV} average oedometric stiffness in unloading, k_L^{AV} average coefficient of hydraulic conductivity in loading, k_U^{AV} average coefficient of hydraulic conductivity in unloading, blue values: tests with tap water, red values: tests with seawater.

Figs. 7.49 and 7.50 illustrate the results of the unconfined compression strength (UCS) tests carried out on specimens of cement and lime-treated mixtures after different curing times, respectively. The Figure also shows the results of UCS tests carried out on specimens treated with both binders and reagents. The results confirm that, on average, the UCS values of lime-treated specimens is much lower than that of the cement-treated ones. After 28 days of curing, the treated specimens in the two Figures exhibit average UCS values of 174.4 kPa and 22.1 kPa, respectively. The maximum value of q_u (183.3 kPa) is obtained for cement and BC treated specimens. The best performance of the lime-treated specimens is achieved for the mixture based on lime and active carbon (AC) that, after 28 days of curing, exhibits an average UCS value of 28.1 kPa.

When AC is added to cement or lime, for Portland cement, the UCS values remained approximately the same with and without the addition of fly ash. For lime, slightly higher values of q_u have been found in presence of fly ash. The lime-AC combination may have prompted pozzolanic reactions.

It has to be noted that the results are relative to sediments that are characterised by high contents of organic matter, heavy metals (Cu, Zn, Pb, Cr, Ni and Cd), and pore water salinity (35 g/l). The aspects are coupling in interfering with cement hydration chemistry and influencing the mechanical properties (Gollmann et al., 2010; Pandey et al., 2012).

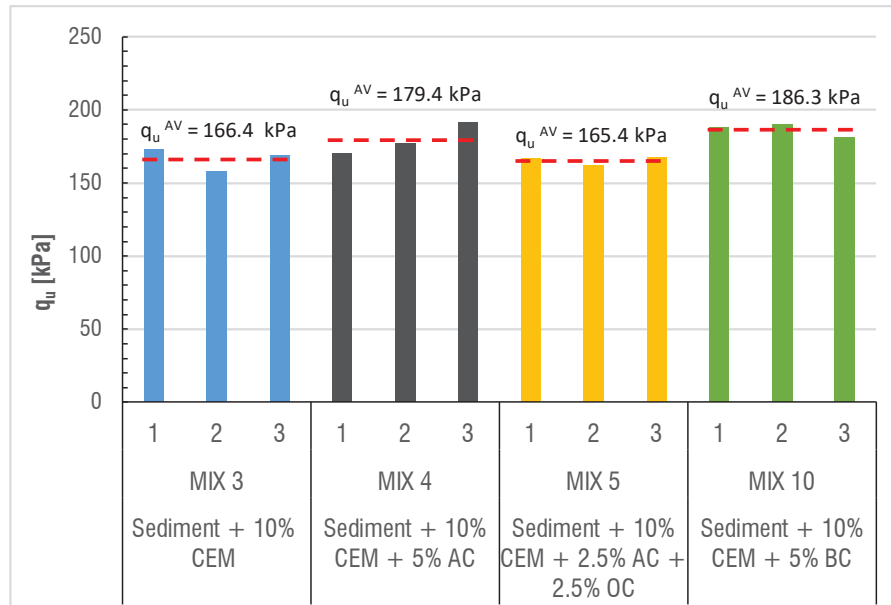


Fig. 7.49 - Unconfined compressive strength of specimens of sediments treated with cement (MIX 3), cement and AC (MIX 4), cement, AC and OC (MIX 5), cement and BC (MIX 10).

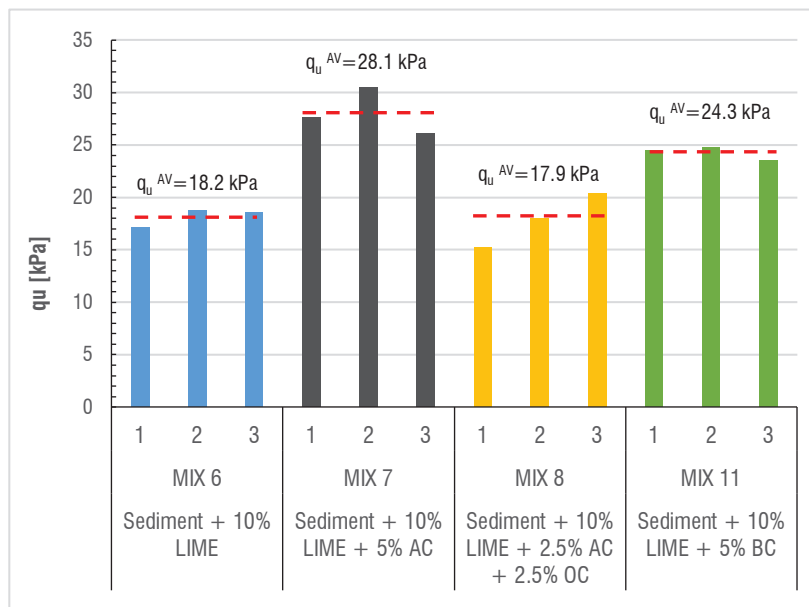


Fig. 7.50 - Unconfined compressive strength of specimens of sediments treated with lime (MIX 6), lime and AC (MIX 7), lime, AC and OC (MIX 8), lime and BC (MIX 11).

CONCLUSIONS

The present thesis was born in the context of the multidisciplinary investigation of a heavily polluted marine system. The study case is the Mar Piccolo basin (literally “Little Sea”) located in the city of Taranto (south of Italy), where the long-lasting industrial activities carried out near the coast have been responsible for the heavy environmental pollution of marine sediments. The research aimed at the identification of the most sustainable strategies for the remediation and management of the contaminated sediments. Among the different aspects involved in the design of the most appropriate remediation strategies, the research focused on the chemo-hydro-mechanical effects of two sustainable technologies: in situ reactive capping and ex situ stabilization/solidification.

The intense laboratory testing programme carried out on sediments contaminated by heavy metals, PHAs and PCBs required the design and the implementation of procedures and laboratory equipment. The tests performed in the laboratories of Chemistry and Environmental Technologies and Environmental Geotechnics of the Politecnico di Bari, resulted particularly complex due to the presence (sometimes) out-of-law contents of either heavy metals and organic pollutants, the salinity of the pore water, the soft consistency of the sediments themselves and the presence of heterogeneities in their clay matrix (i.e. algae, fragments and shells in the top layer).

With reference to in situ technologies, the experimental activity could verify the performance of both permeable reactive mats, with organoclay and / or activated carbon, and reactive granular materials based on active carbon, zero valent iron and an

inhibitor of methane production. Specifically, the monitoring of the reactors carried out in the preliminary phase of the experimental activity has highlighted the substantial absence (or low concentrations) of metals in solution both in porewater and in seawater. However, the analyses carried out on the cap materials after the treatment showed an adsorption of Be, Co, Cr, Ni, Pb, V, Cu and Zi by the organoclay and an adsorption of Cr, Ni, Pb, Cu and Zi for activated carbon. Without capping, a gradual increase in the concentrations of PAHs and PCBs in the water column was observed. The concentrations of PAHs in the water in the column are reduced by about 70% when using permeable reactive mat based on the organoclay and by 50% with permeable reactive mat based on activated carbon. It is clear that the tested technology allows, both in static and dynamic conditions, a reduction in the migration of the contaminants from the sediments towards the water column. Furthermore, in the dynamic phase, that has been designed in order to roughly simulate the typical boundary condition typical of shallow coastal marine basin, the cap prevented the resuspension of the contaminated sediments. The physical isolation obtained in the reactor would lead to an improvement of the in situ environmental conditions through a reduction of the contaminant bioavailability. In the advanced experimental phase of the experimentation (both for static scenario and dynamic scenarios) metals were detected in the seawater samples (all close to 1 $\mu\text{g/L}$), but these values were statistically equal to those measured for pre-cap conditions. However, the analysis of the post-treatment reactive materials showed the adsorption of different heavy metals. Furthermore, it is clear how the coupled use of materials increases the overall efficiency of the protection system. In fact, the maximum adsorption rate (expressed in mg of contaminant adsorbed on kg of adsorbent material) is obtained by the mat with organoclay (lower part in contact with the sediment) and activated carbon (upper part) and granular material with CH₄, ZVI and AC (in stratigraphic order). The monitoring of the water column without capping shows the tendency of the sediments to release PAHs with time. The release kinetics, after 20 days in static conditions, involves the achievement in the column water of a concentration equal to 0.17 $\mu\text{g/l}$. From the monitoring of reactors containing the reactive capping, the role of the protective layer emerges. The chemical barrier prevents the contaminant in

the sediments from migrating to the water column and, simultaneously, plays an active role in restoring the environmental quality standards (through the adsorption of the contaminant present in the water column). Differently to what was observed in the preliminary phase, PCBs - in all the investigated scenarios - did not migrate towards the water column, probably due to the physic-chemical properties of the sediments and the initial level of contamination. From the chemical analyses carried out on the sediments at the end of the treatments, the effectiveness of the cap in enhancing the (bio)decontamination of PAHs is observed. At the end of the tests, the sediments in contact with the reactive solutions had a concentration of PAHs lower than the site-specific limits proposed by ICRAM for the sediments of Taranto. Furthermore, reactive capping is also suitable for the (bio)degradation of sediments contaminated by PCBs. However, the concentrations of PCBs at the end of the treatment are higher than the ICRAM limits. Reactive capping cannot only remove target pollutants from the water phase quickly, but also provide an interface for biotic and abiotic processes. Hence, to enhance the risk management, biodegradation may be an important process for many pollutants.

The results obtained by the oedometer tests carried out on the untreated sediments and on the specimens mixed with adsorbent materials (i.e. 5% of AC, OC and BC) show that the sediment compressibility seem to be not significantly influenced by the use of the reagents. A reduction in the initial void ratio is recorded when BC and OC are used, irrespective of the water salinity. Moreover, specimens in seawater have generally lower compressibility with the exception of the sediment treated with OC. For all the specimens, coefficient of hydraulic conductivity, k , in loading varies between $8.0 \cdot 10^{-12}$ and $4.7 \cdot 10^{-10}$ m/s and, in general, it decreases with void ratio. Moreover, k decreases for those specimens in contact with seawater. The results of direct shear tests show that: i) the use of reagents can significantly influence the effective strength of the soil and ii) interestingly, lower effective friction angles are recorded for specimens put in contact with seawater. Despite the contract volumetric behaviour of all the treated specimens, those consolidated at vertical effective stress equal to 12 kPa exhibit maximum friction angles higher than those of specimens consolidated at $\sigma'_v = 50$ kPa.

The experimental activity carried out seems to demonstrate the high potential of reactive capping for the treatment of marine sediments contaminated by heavy metals, PAHs and PCBs. However, since the remediation of contaminated marine sediments is generally an environmental concern of particular complexity, due to the difficult characterisation of the geomaterial itself, the variability of the boundary conditions and the few data available in the literature on the remediation strategies used in this study (some of the reagents, i.e. biochar, were only recently discovered in this respect), further investigations would be necessary to increase the degree of knowledge and confirm the results were reported.

With respect to S/S treatments, during the preliminary stage, 3 mixtures were tested on three different types of sediments, with organic and inorganic contamination. The results show that, for each sediment sample, the variability of the transfer curves of the different mixtures is proportional to the different concentrations of lime and cement. A key to interpret the results could be the following: i) for sediments with just inorganic contamination (S14P), the mix with 15% (MIX A) of cement exhibited a better performance while maintaining the lowest concentration values of metals in the eluates, for 62.5% of the metals analysed; 2) for sediments with organic and inorganic contamination, it was observed that in 50% of cases MIX C (15% lime) is the most suitable. Finally, it has been possible to observe how the immobilization efficiency of the mixtures based on only lime or cement is always the highest when compared to MIX B (7.5% cement and 7.5% lime). Untreated sediments showed a low tendency to release in solution of the contaminants. However, following the addition of the binders, due to the consequent increase in pH values, a significant increase of release is observed. The advanced phase envisaged a phase of mix design based on the characteristics of the contaminated materials. In particular, the percentages of binders (i.e. cement and lime) and reagents (i.e. AC, OC and BC) have been determined to stabilize the pH of the mixtures on minimum solubility values for the various metal species. In all the mixtures, an initial leaching is observed. It is lower than the limit of D.M. 05/02/98 for some metals (Co, Cr, Pb and Zn) and exceeds the limit for Ni and Cu. Moreover, it has been found to decrease with curing time. In particular, after 28 days of curing time, the pH values

correspond to the minimum solubility of metals. Cement mixtures are characterised by Vanadium leaching; the V concentrations increase with the curing time and only after 56 days of curing they are lower than law limits. This metal is naturally present in the cement, so it is added to the specimens with the binder. From the analysis the results of mixtures based on adsorbent additives, a greater immobilization efficiency has been found to: 1) the mixture based on cement and activated carbon relative to the leaching of Cobalt, Lead and Copper for the MIX_1 sediment sample and Arsenic, Cobalt, Nickel and Lead sample for the MIX_2 sediment sample; 2) the mixture based on lime, activated carbon and organoclay for the leaching of Arsenic and Chromium for the MIX_1 and Arsenic, Chromium, Vanadium and Zinc for the MIX_2 sample.

The best mixtures were subjected to geotechnical characterisation aiming to explore the effects of treatments with traditional binders (i.e. cement or lime) and green additives (i.e. active carbon and biochar) on the geo-hydro-mechanical properties of the submarine sediments. The laboratory experiments suggest the following. The treated sediments (only when binders are used) have a significantly lower CF and higher SF than the untreated prototype-sediment. The use of reagents does not influence the treated soil composition if lime is used. Some changes are recorded, instead, for cement-treated materials. The use of traditional binders makes PI reduce and transform the soil from CH to MH, according to USCS classification. In particular, the effect of curing time on cement-treated sediments is a reduction of both w_L and PI. The highest reduction is recorded by adding both cement and biochar, after 28 days of curing. The 1D compression curves of the treated specimens are located to the right of the untreated material in the void ratio, e - vertical effective stress (σ'_v) plane. This is because the traditional binders are inducing a chemical bonding and the cement-treated specimens exhibit the highest vertical effective stress at yield. The results also show that the use of reagents does not change the pattern of compression behaviour in both loading and unloading but they are influencing the consolidation properties before yielding. Also the unconfined compression strength is larger for the cement-treated specimens and seems to be slightly affected by the use of green additives. Moreover, BC is a sustainable material (a recovered waste coming from the pyrolysis of biomass for energy

generation) and it is much less expensive than to AC. However, further studies should deepen the mechanical effects of their use on submarine sediments. Since the biochar quality and performance vary significantly depending on feedstock types and pyrolysis conditions, future improvements in biochar development are also expected to centre around 'tuning' the properties for tailored applications. For future experiments, one could think of using different additives, such as regenerated activated carbon or shells, also with a view to reducing treatment costs. Furthermore, the dynamics of release of organic contaminants could be explored through the use of sediments characterized by greater contamination of this type. Further analysis should be carried out regarding the presence of organic compounds that generally reduce the efficiency of stabilization and solidification processes.

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REFERENCES

- Acar YB, Olivieri I (1989). Pore Fluid Effects on the Fabric and Hydraulic Conductivity of Laboratory-Compacted Clay. *Transp. Res. Rec.*, vol. 1219, pp. 144–159.
- Ahnberg H (1996). Stress dependent parameters of cement and lime stabilised soils. *Grouting and deep mixing*, 387-392.
- Ahnberg H, Bengtsson PE, Holm G (2001). Effect of initial loading on the strength of stabilised peat. *Proceedings of the Institution of Civil Engineers-Ground Improvement*, 5(1): 35-40.
- Ahnberg H (2003). Measured Permeabilities in Stabilized Swedish Soils. In *Grouting and Ground Treatment*, 622-633.
- Åhnberg H (2004). Effects of back pressure and strain rate used in triaxial testing of stabilized organic soils and clays. *Geotechnical testing journal*, 27(3): 250-259.
- Ajmal M, Hussain Khan A, Ahmad S, Ahmad A (1998). Role of sawdust in the removal of copper (II) from industrial wastes. *Water Res* 32: 3085–3091.
- Anandarajah A, Zhao D (2000). Triaxial Behavior of Kaolinite in Different Pore Fluids,” *J. Geotech. Geoenviron. Eng.*, vol. 126, no. 2, pp. 148–156.
- Alshawabkeh AN, Rahbar N, Sheahan T (2005). A model for contaminant mass flux in capped sediment under consolidation. *J. Contam. Hydrol.* 78, 147–165.
- Allen HE (1994). Partitioning of toxic metals in natural water-sediment systems. In *Transport and Transformation of Contaminants Near the Sediment-Water Interface* DePinto, J. V., Lick, W., Paul, J.F., Ed. Lewis Publishers: Boca Raton, 1994.
- Alther G (2002a). Using organoclays to enhance carbon filtration. *Waste Manag* 22(5):507–513.

- Alther G (2002b). Organoclays remove organics and metals from water. In: Kostecki PT, Calabrese EJ, Dragun J (eds) Contaminated soils, vol 7. Amherst Scientific Publishers, Amherst, MA, pp. 223–231.
- Al-Tabbaa A, Perera ASR (2005a). UK stabilisation/solidification treatment and remediation, Part II: Binders & technologies – research. In: Tabbaa AA, Stegemann JA (eds) Stabilisation/ solidification treatment and remediation: advances in S/S for waste and contaminated land. Balkema, London, pp 387–398.
- Al-Tabbaa A, Perera ASR (2006). UK stabilization/solidification treatment and remediation – Part I: binders, technologies, testing and research. *Land Contam Reclam* 14:703
- Aouad G, Laboudigue A, Gineys N, Abriak NE (2012). Dredged sediments used as novel supply of raw material to produce Portland cement clinker. *Cem. Concr. Comp.* 34, 788-793.
- Arizzi Novelli A, Losso C, Libralato G, Tagliapietra D, Pantani C, Volpi Ghirardini A (2006). Is the 1:4 elutriation ratio reliable? Ecotoxicological comparison of four different sediment: water proportions. *Ecotoxicol Environ Saf* 65:306–313.
- Arnold WA, Roberts AL (1998). Pathways of chlorinated ethylene and chlorinated acetylene reaction with Zn(0). *Environmental Science & Technology*, 32, (19), 3017-3025.
- Arnold W, Roberts (2000). Pathways and kinetics of chlorinated ethylene and chlorinated acetylene reaction with Fe(0) particles *Environmental Science & Technology*, 34, (9), 1794-1805.
- Ashley GM, Sheridan RE (1994). Depositional model for valley fills on a passive continental margin. In: Dalrymple RW, Boyd RJ, Zaitlin BA (eds) Incised-valley systems: origin and sedimentary sequences. *SEPM Spec Publ* 51:285–301.
- ASTM D2487 (2011). Standard practice for classification of soils for engineering purposes (Unified Soil Classification System). ASTM standard D2487. American Society for Testing and Materials, West Conshohocken, Pa.

- Atlas RM, Unterman R (1999). Bioremediation. In *Industrial Microbiology and Biotechnology* 2 ed. Ed. American Society for Microbiology (ASM) Press: Washington, D.C., 1999.
- Azcue JM, Zeman AJ, Mudroch A, Rosa F, Patterson T (1998). Assessment of sediment and porewater after one year of subaqueous capping of contaminated sediments in Hamilton Harbour, Canada. *Water Science and Technology*, 37(6-7): 323-329.
- Barjoveanu G, De Gisi S, Casale R, Todaro F, Notarnicola M, Teodosiu C (2018). A life cycle assessment study on the stabilization/solidification treatment processes for contaminated marine sediments. *Journal of Cleaner Production*, 201: 391-402.
- Baker JR, Mihelcic JR, Luehrs DC, Hickey JP (1997). Evaluation of estimation methods for organic carbon normalized sorption coefficients. *Water Environ Res* 69:136–145.
- Beckingham B, Ghosh U (2011). Field-scale reduction of PCB bioavailability with activated carbon amendment to river sediments. *Environ Sci Technol*, 45(24):10567–10574.
- Bedard DL, Wagner RE, Brennan MJ, Haberl M, Brown JF (1987). Extensive degradation of aroclors and environmentally transformed polychlorinated biphenyls by *Alcaligenes eutrophus* H850. *Applied and Environmental Microbiology*. 1987, 53, (5), 1094-1102.
- Bedard DL, Quensen JF (1995). Microbial reductive dechlorination of polychlorinated biphenyls. In *Microbial Transformation and Degradation of Toxic Organic Chemicals* Young, L. Y., Cerniglia, C.E., Ed. Wiley-Liss: New York, 1995.
- Bedard DL, Ritalahti KM, Löffler FE (2007). The *Dehalococcoides* population in sediment-free mixed cultures metabolically dechlorinates the commercial polychlorinated biphenyl mixture Aroclor 1260. *Applied and Environmental Microbiology*, 73: 2513-2521.
- Belluomini G, Caldara M, Casini C, Cerasoli M, Manfra L, Mastronuzzi G, Palmentola G, Sanso' P, Tuccimei P, Vesica PL (2002). Age of Late Pleistocene shorelines, morphological evolution and tectonic history of Taranto area, Southern Italy. *Quaternary Science Reviews*, 21(4-6): 427-454.

- Benoit JM, Heyes A, Mason RP, Miller CL. (2003). Geochemical and biological controls over methylmercury production and degradation in aquatic ecosystems. In Biogeochemistry of Environmentally Important Trace Elements. Yong Cai, O. C. B., Ed. Boardman DL, Glendinning S, Rogers CDF (2001). Development of stabilisation and solidification in lime-clay mixes. *Géotechnique*, 50(6): 533-543.
- Boynton R (1980). Chemistry and technology of lime and limestone. John Wiley & Sons Inc., New York 1980.
- Botero W, de Oliveira L, Cunha B, de Oliveira L, Goveia D, Rocha J, Fraceto L, Rosa A, Braz J, (2011). Characterization of the interactions between endocrine disruptors and aquatic humic substances from tropical rivers. *Chem. Soc.*, 22, 1103. Oxford University Press: Washington, D.C., 2003.
- Bouazza A, Kwan PS, Chapman G (2004). Strength properties of cement treated Coode Island Silt by the soil mixing method. In *Geotechnical engineering for transportation projects*.
- Boudreau BP, Algar C, Johnson BD, Croudace I, Reed A, Furukawa Y, Dorgan KM, Jumars PA, Grader AS, Gardiner BS (2005). Bubble growth and rise in soft sediments. *Geol*, 33: 517–520.
- Boutin R (1999). Amélioration des connaissances sur le comportement des rejets en mer des produits de dragage type vase: phénomènes court terme champ proche. (Ph.D. thesis) Institut des sciences appliquées de Lyon, Lyon, France.
- Botero WG, Oliveira LCD, Cunha BB, Oliveira LKD, Goveia D, Rocha JC, Rosa A (2011). Characterization of the interactions between endocrine disruptors and aquatic humic substances from tropical rivers. *Journal of the Brazilian Chemical Society*, 22(6), 1103-1110.
- Braida WJ, Pignatello JJ, Lu YF, Ravikovitch P, Neimark A, Xing B (2003). Sorption hysteresis of benzene in charcoal particles. *Environmental Science & Technology*, 37(2): 409-417.
- Brandl H (1981). Alteration of soil parameters by stabilization with lime. *Proc., 10th Int. Conf. on Soil Mechanics and Foundation Engineering*, 3: 587–594.

- Brandl H (1999). Long-term behaviour of soils stabilised with lime and with cement. Proc. Geotechnics for Developing Africa, Durban 1999.
- Brusseau M, Jessup R, Rao P (1991). Nonequilibrium sorption of organic chemicals - elucidation of rate-limiting processes. *Environmental Science & Technology*, 25(1): 134-142.
- Brusseau M, Rao P (1989). The influence of sorbate-organic matter interactions on sorption nonequilibrium. *Chemosphere*, 18(9-10): 1691-1706.
- Burland JB (1990). On the compressibility and shear strength of natural clays. *Géotechnique*, 40(3): 329–378. doi:10.1680/geot.1990.40.3.329.
- Burland JB (1990). On the compressibility and shear strength of natural clays. *Géotechnique*, 40(3): 329-378.
- Burnett WC, Bokuniewicz H, Huettel M, Moore WS, Taniguchi M, (2003). Groundwater and pore water inputs to the coastal zone. *Biogeochemistry*, 66: 3–33.
- Cafaro F, Cotecchia F (2001). Structure degradation and changes in the mechanical behaviour of a stiff clay due to weathering. *Géotechnique*, 51(5): 441-443.
- Calmano W, Förstner U, Hong J (1994). Mobilization and scavenging of heavy metals following resuspension of anoxic sediments from the Elbe River.
- Cao X, Dermatas D, Xu X, Shen G (2008). Immobilization of lead in shooting range soils by means of cement, quicklime, and phosphate amendments. *Environmental Science and Pollution Research*, 15(2): 120-127.
- Cappuyns V, Deweirt V, Rousseau S (2015). Dredged sediments as a resource for brick production: Possibilities and barriers from a consumers' perspective, *Waste Management*, 8, 372-380.
- Cardellicchio N, Buccolieri A, Giandomenico S, Lopez L, Pizzulli F, Spada L (2007). Organic pollutants (PAHs. PCBs) in sediments from the Mar Piccolo in Taranto (Ionian Sea. Southern Italy). *Marine Pollution Bulletin*, 55: 451–458.
- Cardellicchio N, Buccolieri A, Di Leo A, Librando V, Minniti Z, Spada L (2009). Methodological approach for metal pollution evaluation in sediments collected from the Taranto Gulf. *Toxicol Environ Chem* 91(7): 1273–1290.

- Cardellicchio N, Annicchiarico C, Di Leo A, Giandomenico S, Spada L (2015). The Mar Piccolo of Taranto: an interesting marine ecosystem for the environmental problems studies. *Environ Sci Pollut Res*. doi: 10.1007/s11356-015-4924-6
- Caroppo C, Giordano L, Palmieri N, Bellio G, Paride Bisci A, Portacci G, Scafani P, Sawyer Hopkins T (2012). Progress towards sustainable mussel aquaculture in Mar Piccolo, Italy. *Ecol Soc.*, 17(3): 10.
- Carr CS, Hughes JB (1998). Enrichment of high rate PCE dechlorination and comparative study of lactate, methanol, and hydrogen as electron donors to sustain activity. *Environmental Science & Technology*, 32, (12), 1817-1824.
- Carlton R G, Klug MJ. Spatial and temporal variations in microbial processes in aquatic sediments: Implications for the nutrient status of lakes. In *Sediments: Chemistry and Toxicity of In-Place Pollutants* Baudo, R., Giesy, JP, Muntau, H., Ed. Lewis Publishers, Inc: Chelsea, MI, 1990.
- Casagrande A (1936). The determination of the pre-consolidation load and its practical significance. *Proc. Int. Conf. SMFE* 3: 60-64.
- CETCO (2015). Featured Case Studies: Sediment Remediation. <http://www.cetco.com/en-us/Case-Studies/Environmental-Products/> Sediment-Remediation. Accessed 9 May 2015
- Chakchouk A, Samet B, Bouaziz S. (2012). Difference in pozzolanic behavior of Tunisian clays with lime and cement, *Advances in Cement Research*, 24, 11-22.
- Chapra SC (1999). *Surface Water Quality Modeling*. McGraw-Hill, Boston, MA, USA.
- Chakraborty S, Bhattacharya T, Singh G, Maity JP (2014) Benthic macroalgae as biological indicators of heavy metal pollution in the marine environments: a biomonitoring approach for pollution assessment. *Ecotoxicol Environ Saf* 100: 61–68.
- Chatain V, Benzaazoua M, Cazalet ML, Bouzahzah H, Delolme C, Gautier M, De Brauer C (2013). Mineralogical study and leaching behavior of a stabilized harbor sediment with hydraulic binder. *Environmental Science and Pollution Research*, 20(1): 51-59.

- Chew SH, Kamruzzaman AH M, Lee F (2004). Physicochemical and Engineering Behavior of Cement Treated Clays, *Journal of Geotechnical and Geoenvironmental Engineering*, 130: 696-706.
- Cho YM, Ghosh U, Kennedy AJ, Grossman A, Ray G, Tomaszewski JE, Smithenry DW, Bridges TS, Luthy RG, (2009). Field application of activated carbon amendment for in-situ stabilization of polychlorinated biphenyls in marine sediment. *Environ Sci Technol* 43(10): 3815–3823.
- Choi Y, Cho YM, Gala WR, Luthy RG (2013). Measurement and modeling of activated carbon performance for the sequestration of parent- and alkylated-polycyclic aromatic hydrocarbons in petroleumimpacted sediments. *Environ. Sci. Technol*, 47 (2), 1024–1032.
- Choi Y, Cho YM, Luthy RG (2014). In situ sequestration of hydrophobic organic contaminants in sediments under stagnant contact with activated carbon. 1. Column studies. *Environ Sci Technol* 48(3): 1835-1842.
- Colangelo F, Messina F, Cioffi R (2015). Recycling of MSWI fly ash by means of cementitious double step cold bonding pelletization: technological assessment for the production of lightweight artificial aggregates. *J. Hazard Mater* 299: 181-191.
- Colangelo F, Cioffi R (2017). Mechanical properties and durability of mortar containing fine fraction of demolition wastes produced by selective demolition in South Italy. *Compos*, 115: 43-50.
- Colangelo F, Messina F, Di Palma L, Cioffi R (2017). Recycling of non-metallic automotive shredder residues and coal fly- ash in cold-bonded aggregates for sustainable concrete. *Compos. B Eng*. 116: 46-52.
- Colangelo F, Petrillo A, Cioffi R, Borrelli C, Forcina A (2018). Life cycle assessment of recycled concretes: a case study in southern Italy. *Sci. Total Environ*. 615, 1506-1517.
- Colin D, (2003). Valorisation de sédiments fins de dragage en technique routière. (Ph.D. thesis) Université de Caen, Caen, France 147.
- Compeau GC, Bartha R (1985). Sulfate-reducing bacteria: Principal methylators of mercury in anoxic estuarine sediment. *Appl Environ Microbiol* 50:498–502.

- Conner JR (1997). Guide to improving the effectiveness of cement-based stabilization/solidification. Portland Cement Association, Skokie.
- Consoli N, Lopes D, Foppa D, Heineck K (2009). Key parameters dictating strength of lime/cement-treated soils. *ICE Geotechnical Engineering*, 162(GE2): 111–18.
- Cornelissen G, Amstaetter K, Hauge A, Schaanning M, Beylich B, Gunnarsson JS, Breedveld GD, Oen AM, Eek E (2012). Largescale field study on thin-layer capping of marine PCDD/Fcontaminated sediments in Grenlandfjords, Norway: physico-chemical effects. *Environ Sci Technol* 46(21):12030-12037.
- Cornelissen G, Kruså ME, Breedveld GD, Eek E, Oen AM, Arp HP, Raymond C, Samuelsson G, Hedman JE, Stokland O, Gunnarsson JS (2011) Remediation of contaminated marine sediment using thinlayer capping with activated carbon—a field experiment in Trondheim harbor, Norway. *Environ Sci Technol* 45(14):6110-6116.
- Couvidat J, Benzaazoua M, Chatain V, Bouamrane A, Bouzahzah H (2016). Feasibility of the reuse of total and processed contaminated marine sediments as fine aggregates in cemented mortars. *Construct. Build. Mater.* 112, 892-902.
- Coutinho RQ, Lacerda WA (1987). Characterization and consolidation of Juturnaíba organic clays. In *Proceedings of the International Symposium on Geotechnical Engineering of Soft Soil, Mexico* (Vol. 1, pp. 17-24).
- Cotecchia V, Lollino G, Pagliarulo R, Stefanon A, Tadolini T, Trizzino R (1989). Studi e controlli in situ per la captazione della sorgente sottomarina Galeso, Mar Piccolo di Taranto. *International Congress on Geoengineering*, Torino, 27-30 settembre 1989, pp. 475-484.
- Cotecchia V (2005). Caratterizzazione geologica e geotecnica dei terreni pertinenti alla vasca di contenimento e alle opere a detto fine previste. *Relazione geologica e geotecnica*. Autorità portuale di Taranto.
- Cupples AM, Spormann AM, McCarty PL (2003). Growth of a Dehalococcoideslike microorganism on vinyl chloride and cis-dichloroethene as electron acceptors as determined by competitive PCR. *Applied and Environmental Microbiology*, 69(2): 953-959.

- Couvidat J, Benzaazoua M, Chatain V, Bouamrane A, Bouzahzah H (2016). Feasibility of the reuse of total and processed contaminated marine sediments as fine aggregates in cemented mortars, *Construction and Building Materials*, 112: 892-902.
- Dahal BK, Zheng JJ. Compression behaviour of reconstituted clay: a study on Kalamato.
- De Gisi S, Minetto M, Todaro F, Lanzolla A, Notarnicola M (2017a). Monitored Natural Recovery of contaminated marine sediments. Proposal of a monitoring plan for in situ continuous testing and sensing. In: I2MTC-2017. IEEE International Instrumentation and Measurement Technology Conference: proceedings papers. IEEE, Torino, Italy, May 22-25, 2017.
- De Gisi S, Todaro F, Notarnicola M (2017b). Effect of reactive mats on in-situ remediation of contaminated marine sediments. *Procedia Environmental Science, Engineering and Management*, 4(1): 17-22.
- DeLaune, RD, Smith CJ (1985). Release of Nutrients and Metals Following Oxidation of Freshwater and Saline Sediment 1. *Journal of Environmental Quality*, 14(2): 164-168.
- Desogus P, Manca P, Orrù G, Zucca A (2012). Stabilization–solidification treatment of fine tailings using Portland cement, potassium dihydrogen phosphate and ferric chloride hexahydrate. *Minerals Engineering* 45(2013): 47–54.
- Di Leo A, Annicchiarico C, Cardellicchio N, Giandomenico S, Conversano M, Castellano G, Spada L (2014). Monitoring of PCDD/Fs and dioxin-like PCBs and seasonal variations in mussels from the Mar Grande and the Mar Piccolo of Taranto (Ionian Sea, Southern Italy). *Environmental Science and Pollution Research*, 21(23): 13196-13207.
- Di Maio C, (1996). Exposure of bentonite to salt solution: osmotic and mechanical effects. *Geotechnique*, 46(4): 695-707
- Di Maio C, Santoli L, Schiavone P (2004). Volume change behaviour of clays: the influence of mineral composition, pore fluid composition and stress state. *Mechanics of Materials*, 36: 435-451.

- Dixon KL, Knox AS (2012). Sequestration of metals in active cap materials: A laboratory and numerical evaluation. *Remediation Journal*, 22(2): 81-91.
- Doglioni C, Mongelli F, Pieri P (1994). The Puglia uplift (SE-Italy): an anomaly in the foreland of the Apenninic subduction due to buckling of a thick continental lithosphere. *Tectonics*, 13(5): 1309-1321.
- Dyer K (1986). *Coastal and estuarine sediment dynamics*. John Wiley And Sons, Chichester, Sussex (UK), 358.
- Eggleton J, Thomas KVA (2004) review of factors affecting the release and bioavailability of contaminants during sediment disturbance events. *Environment International*, 30(7): 973-980.
- Eek E, Godøy O, Aagaard P, Breedveld P (2007). Experimental determination of efficiency of capping materials during consolidation of metal-contaminated dredged material. *Chemosphere*, 69: 719–728.
- Eek E, Cornelissen G, Kibsgaard A, Breedveld GD (2008). Diffusion of PAH and PCB from contaminated sediments with and without mineral capping; measurement and modelling. *Chemosphere*, 71(9): 1629-1638.
- Elsner M, Schwarzenbach RP, Haderlein SB (2004). Reactivity of Fe(II)-bearing minerals toward reductive transformation of organic contaminants. *Environmental Science & Technology*. 2004, 38, (3), 799-807.
- Erten MB, Gilbert R, El Mohtar CS, Reible DD (2011). Development of a laboratory procedure to evaluate the consolidation potential of soft contaminated sediments. *Geotech Test J* 34:10.1520/GTJ103689.
- Erten MB, Reible DD, Gilbert RB, El Mohtan C (2012). The performance of orographic clay on nonaqueous phase liquid contaminated sediments under anisotropic consolidation. In *Contaminated sediments: restoration of aquatic environmental*. STP 1554: 32-44.
- Federico A, Vitone C, Murianni A (2015). On the mechanical behaviour of dredged submarine clayey sediments stabilized with lime or cement, *Canadian Geotechnical Journal*, 52: 1–11.

- Fennell DE, Gossett JM, Zinder SH (1997). Comparison of butyric acid, ethanol, lactic acid, and propionic acid as hydrogen donors for the reductive dechlorination of tetrachloroethene. *Environmental Science & Technology*, 31(3): 918-926.
- Gadd G (2004). Microbial influence on metal mobility and application for bioremediation. *Geoderma* 122(2-4): 109-119.
- Ghosh U, Luthy R, Talley J, Tucker S, Furey J (2000). Kinetics and thermodynamics of PAH desorption processes from sediment particles. Abstracts of Papers of the American Chemical Society, 220: U325.
- Ghosh U, Luthy R, Cornelissen G, Werner D, Menzie CA (2011). In-situ sorbent amendments: a new direction in contaminated sediment management. *Environ Sci Technol* 45: 1163–1168.
- Ghosh U, Talley J, Luthy R (2001). Particle-scale investigation of PAH desorption kinetics and thermodynamics from sediment. *Environmental Science & Technology*, 35(17): 3468-3475.
- Gidley PT, Kwon S, Yakirevich A, Magar VS, Ghosh U (2012). Advection dominated transport of polycyclic aromatic hydrocarbons in amended sediment caps. *Environ Sci Technol* 46(9): 5032–5039.
- Gollmann MA, Da Silva MM, Masuero AB, Dos Santos JH (2010). Stabilization and solidification of Pb in cement matrices. *J. Hazard. Mater.*, 179: 507–14.
- Hale SE, Kwon S, Ghosh U, Werner D (2010). Polychlorinated biphenyl sorption to activated carbon and the attenuation caused by sediment. *G Nest J* 12(3): 318–326.
- Hale SE, Elmquist M, Brändli R, Hartnik T, Jakob L, Henriksen T, Werner D, Cornelissen G (2012). Activated carbon amendment to sequester PAHs in contaminated soil: a lysimeter field trial. *Chemosphere* 87(2): 177–184.
- Harris MR, Herbert SM, Smith MA (1995). Remedial treatment for contaminated land, vol VII, Ex-situ remedial methods for soils, sludges and sediments (SP 107). Construction Industry Research and Information Association (CIRIA), London.
- Hasegawa H, Rahman I, Rahman M (2016). *Environmental Remediation Technologies for Metal-Contaminated Soils*. Springer, Tokyo.

- Head KH (1986). Manual of soil laboratory testing, 3 Vols., London, Plympton, Pentek.
- Hjartland T, Jersak J, Collins J, Soldal O (2013). Using carbon-enriched materials for capping contaminated sediments at the Kirkebukten Site in Bergen, Norway. In: Proceedings Seventh International Conference on Remediation of Contaminated Sediments, 4–7 February, Dallas (TX) USA. Battelle. C-060.
- Ho EWL (1987). Geotechnical properties of deep-ocean sediments: a critical state approach. PhD thesis, City University, UK
- Hong YS, Kinney KA, Reible D (2011a). Acid volatile sulfides oxidation and metals (Mn, Zn) release upon sediment resuspension: Laboratory experiment and model development. *Environ Toxicol Chem*, 30: 564–575.
- Hong YS, Kinney AK, Reible DD (2011b). Effect of pH and salinity on sediment metals release and early diagenesis. *Environ Toxicol Chem*, 30: 1775–1784.
- Horpibulsuk S, Miura N, Nagaraj T (2003). Assessment of strength development in cement-admixed high-water content clays with Abrams' law as a basis. *Géotechnique*, 53(4): 439–44.
- Horpibulsuk S, Bergado D, Lorenzo G (2004). Compressibility of cement-admixed clays at high water content. *Géotechnique*, 54(2): 151–54.
- Horpibulsuk S, Phojan W, Suddeepong A, Chinkulkijniwat A, Liu M (2012). Strength development in blended cement admixed saline clay. *Applied Clay Science*, 55: 44–52.
- Imai G, Tsoruya K, Yano K (1978). A treatment of salinity in water content determination of very soft clays. Technical note. *Soils Found*, 19(3): 84–89.
- ICRAM. 2005. Certificati di prova. Laboratori Chimici "Stante".
- ISPRA. 2010. Elaborazione e valutazione dei risultati della caratterizzazione ai fini della individuazione degli opportuni interventi di messa in sicurezza e bonifica del Sito di Interesse Nazionale di Taranto - Mar Grande Il Lotto e Mar Piccolo. Report 2010.
- Italian Ministerial Decree 173/2016 (2016). Regulation containing technical procedures and criteria for the authorization of seabed excavation materials at sea, (in Italian), Italian Official Journal, No. 208/2016.

- ITRC (2011). Development of performance specifications for solidification/stabilization. Interstate Technology & Regulatory Council, Washington, DC.
- Janz M, Johansson SE (2001). The function of different binding agents in deep stabilization. Swedish Deep Stabilisation Research Centre. Report No. 9.
- Japanese Geotechnical Society, (2009). Practice for Making and Curing Stabilized Soil Specimens without Compaction, JGS T 0821-2009 (in Japanese).
- Johnston R, Kirtay V, Chadwick D, Rosen G, Guerrero J, Collins J, Ortega C, Webb R, May R, Germano J, Browning D, Beaver E, Wicklein M, Pittz J, Leisle D, Doyle L, Hsu L (2013). Installing an activated carbon sediment amendment at the Puget Sound Naval Shipyard and Intermediate Maintenance Facility, Bremerton, WA. In: Proceedings of the Seventh International Conference on Remediation of Contaminated Sediments, 4–7 February, Dallas (TX) USA. Battelle. B-024.
- Johnson BD, Boudreau BP, Gardiner BS, Maass R (2002). Mechanical response of sediments to bubble growth. *Mar Geol* 187:347–363.
- Josefsson S, Schaanning M, Samuelsson GS, Gunnarsson JS, Olofsson I, Eek E, Wiberg K (2012). Capping efficiency of various carbonaceous and mineral materials for in situ remediation of polychlorinated dibenzo-p-dioxin and dibenzofuran contaminated marine sediments: sediment-to-water fluxes and bioaccumulation in boxcosm tests. *Environ Sci Technol*, 46: 3343–3351.
- Kralj M, De Vittor C, Comici C, Relitti F, Auriemma R, Alabiso G, Del Negro P (2015). Recent evolution of the physicalchemical characteristics of a Site of National Interest - the Mar Piccolo of Taranto (Ionian Sea) - and changes over the last 20 years. *Environmental Science and Pollution Research*, 23: 12491–12494.
- Kershaw DS, Pamukcu S, (1997). Ground rubber: reactive permeable barrier sorption media. In: Conference on in situ remediation of the geoenvironment. Geotechnical special publication no. 71: 26-40.
- Kinuthia JM, Wild S, Jones GI (1999). Effects of monovalent and divalent metal sulphates on consistency and compaction of lime stabilized kaolinite. *Appl. Clay Sci.*, 14: 27–45.

- Kim YS, Nyberg LM, Jenkinson B, Jafvert CT (2013). PAH concentration gradients and fluxes through sand cap test cells installed in situ over river sediments containing coal tar. *Environ Sci Processes Impacts* 15: 1601–1612. doi:10.1039/C3EM00142C.
- Kile DE, Chiou CT, Zhou HD, Li H, Xu OY (1995). Partition of nonpolar organic pollutants from water to soil and sediment organic matters. *Environmental Science & Technology*, 29: 1401-1406.
- Kirtay V, Conder J, Rosen G, Magar V, Grover M, Arblaster J, Fettes K, Chadwick B, (2018). Performance of an In Situ Activated Carbon Treatment to Reduce PCB Availability in an Active Harbour, *Environmental Toxicology and Chemistry*, 37: 1767–1777.
- Kitazume M, Terashi M (2002). *The Deep Mixing Method – Principle, Design and Construction*. Ed. Coastal Development Institute of Technology (CDIT), Japan. A.A. Balkema Publishers Tokyo.
- Knight BP, Chaudri AM, McGrath SP, Giller KE (1998). Determination of chemical availability of cadmium and zinc in soils using inert soil moisture samplers. *Environ Pollut*, 99: 293–298. doi: 10.1016/S0269-7491(98)00021-9
- Knox AS, Paller MH, Roberts J (2012). Active capping technology. New approaches for in situ remediation of contaminated sediments. *Remediation Journal*, 22; 93-117.
- Knox AS, Dixon KL, Paller MH, Reible DD, Roberts JJ, Petrisor IG (2008). Innovative in situ remediation of contaminated sediments for simultaneous control of contamination and erosion. *Annual Report SRNL-RP-2008-012*.
- Kogbara RB (2014). A review of the mechanical and leaching performance of stabilized/solidified contaminated soils. *Environmental Reviews*, 22(1): 66-86.
- Krull M, Abessa DM, Hatje V, Barros F (2014). Integrated assessment of metal contamination in sediments from two tropical estuaries. *Ecotoxicol Environ Saf*. 106: 195–203.
- LaGrega MD, Buckingham PL, Evans JC, (2001). *Hazardous waste management*. McGraw-Hill, Boston.

- Landrum P F, Robinson SD, Gossiaux DC, Jing Y, Lydy MJ, Mitra S, Ten Hulscher T (2007). Predicting bioavailability of sediment-associated organic contaminants for *Diporeia* spp. and *oligochaetes*. *Environmental Science & Technology*, 41.
- Larsson S, Dahlström M, Nilsson B (2005). Uniformity of lime-cement columns for deep mixing: a field study. *Proceedings of the Institution of Civil Engineers-Ground Improvement*, 9(1): 1-15.
- Le MH (2008). *Caracterisation physique et mecanique des sols marins d'offshore profond*. PhD thesis, ENPC-CERMES.
- Lee C, Yun TS, Lee JS, Bahk JJ, Santamarina JC (2011). Geotechnical characterization of marine sediments in the Ulleung Basin, East Sea. *Engineering Geology*, 117: 151–158.
- Lee J, Fox P (2009). Investigation of Consolidation- Induced Solute Transport. II: Experimental and Numerical Results. *J. Geotech. Geoenviron. Eng.*, 135(9): 1239–1253.
- Lee J, Fox P, Lenhart JJ (2009). Investigation of Consolidation-Induced Solute Transport. I: Effect of Consolidation on Transport Parameters. *J. Geotech. Geoenviron. Eng.*, 135(9): 1228–1238.
- Lenhart J, Lee J, Hwang YS, Fox P (2009). Polychlorinated biphenyl transport from consolidation of contaminated sediments during in situ capping. *Journal of ASTM International*, 6: 68-85. DOI: 10.1520/JAI102160.
- Lerario VL, Giandomenico S, Lopez L, Cardellicchio N (2003). Sources and distribution of polycyclic aromatic hydrocarbons (PAHs) in sediments from the Mar Piccolo of Taranto, Ionian Sea, southern Italy. *Annali di chimica*, 93(4): 397-406.
- Levacher D, Sanchez M, (2011). Characterization of marine sediments for a reuse in land disposal and embankment. *Eur. J. Environ. Civ. Eng.*, 15(2): 167–178.
- Levacher D, Sanchez M, Duan Z, Liang Y, (2011). Valorization of Mediterranean sediments in a treatment plant: study of the geotechnical characterization and permeability. *Paralia*, 4: 1-20.
- Levesque C, Locat J, Leroueil S (2007). Characterization of postglacial sediments of the Saguenay Fjord, Quebec, Canada. In: *Characterization and engineering*

- properties of natural soils. Invited paper, Tan, Phoon, Hight et Leroueil (eds). Taylor & Francis, 3: 2645–2677.
- Libralato G, Losso C, Arizzi Novelli A, Citron M, Della Sala S, Zanutto E, Cepak F, Volpi Ghirardini A (2008). Ecotoxicological evaluation of industrial port of Venice (Italy) sediment samples after a decontamination treatment. *Environ Pollut*, 156: 644–650
- Lirer S, Liguori B, Capasso I, Flora A, Caputo D (2017). Mechanical and chemical properties of composite materials made of dredged sediments in a fly-ash based geopolymer, *Journal of Environmental Management*, 191: 1-7.
- Lin J., Zhan Y., Zhu Z., (2011). Evaluation of sediment capping with active barrier systems (ABS) using calcite/zeolite mixtures to simultaneously manage phosphorus and ammonium release, *Science of the Total Environment*, 409: 638-646.
- Lisco S, Corselli C, De Giosa F, Mastronuzzi G, Moretti M, Siniscalchi A, Marchese F, Bracchi V, Tessarolo C, Tursi A (2015). Geology of Mar Piccolo, Taranto (southern Italy): the physical basis for remediation of a polluted marine area. *Journal of Maps*, pp. 1-8.
- Liu C, Jay JA, Ika R, Shine JP, Ford TE (2001). Capping efficiency for metal-contaminated marine sediment under conditions of submarine groundwater discharge. *Environ. Sci. Technol.*, 35: 2334-2340.
- Lyman WJ, Reehl WF, Rosenblatt DH, eds. 1990. *Handbook of Chemical Property Estimation Methods*. American Chemical Society, Washington, DC, USA.
- Lofrano G., Libralato G., Minetto D., De Gisi S., Conte B., Todaro F., Calabrò D., Notaricola M., (2016), In situ remediation of contaminated marine sediment: an overview. *Environmental Science and Pollution Research*, 24: 5189-5206.
- Locat J, Tremblay H, Leroueil S (1996). Mechanical and hydraulic behaviour of a soft inorganic clay treated with lime. *Canadian Geotechnical Journal*, 33(4): 654-669.
- Lorenzo G, Bergado D (2004). Fundamental parameters of cement-admixed clay – New approach. *Journal of Geotechnical and Geoenvironmental Engineering*, 130(10): 1042–50.

- Lundh T, Hansen T, Nordvik H (2013). Demonstrating in situ remedies for contaminated sediment in Norway: applicability to Sandefjord Harbor and beyond. In: Proceedings of the Seventh International Conference on Remediation of Contaminated Sediments, 4–7 February, Dallas (TX) USA. Battelle. C–031.
- Luthy R, Aiken G, Brusseau M, Cunningham S, Gschwend P, Pignatello J, Reinhard M, Traina S, Weber W, Westall J (1997). Sequestration of hydrophobic organic contaminants by geosorbents. *Environmental Science & Technology*, 31(12): 3341–3347.
- Ma X, Reible D, Harris M (2010). Assessment feasibility of in-situ capping and contaminant mobility in NAPL-contaminated sediments. *International Journal of Geotechnical Engineering*, 4: 71–78. DOI 10.3328/IJGE.2010.04.01.71-78
- Maltseva O, Tsoi T, Quensen J, Fukuda M, Tiedje J (1999). Degradation of anaerobic reductive dechlorination products of Aroclor 1242 by four aerobic bacteria. *Biodegradation*, 10(5): 363–371.
- Mayer-Pinto M, Underwood AJ, Tolhurst T, Coleman RA (2010). Effects of metals on aquatic assemblages: what do we really know?. *J Exp Mar Biol Ecol* 391:1–9.
- Mastronuzzi G, Sansò P (2002). Pleistocene sea level changes, sapping processes and development of valleys network in Apulia region (southern Italy). *Geomorphology* 46: 19–34.
- Matthes W, Madsen FT, Kahr G, (1999). Sorption of heavy-metal cations by Al and Zr-hydroxyintercalated and pillared bentonite. *Clays Clay Miner* 47:617–629.
- Matturro B, Ubaldi C, Grenni P, Caracciolo AB, Rossetti S (2016). Polychlorinated biphenyl (PCB) anaerobic degradation in marine sediments: microcosm study and role of autochthonous microbial communities. *Environmental Science and Pollution Research*, 23(13): 12613–12623.
- McCoy CA, Corbett DR (2009). Review of submarine groundwater discharge (SGD) in coastal zones of the Southeast and Gulf regions of the United States with management implications. *J. Environ. Manage*, 90, 644–651.

- McDonough KM, Murphy P, Olsta J, Zhu Y, Reible D, Lowry GV (2007). Development and placement of a sorbent-amended thin layer sediment cap in the Anacostia River. *Soil Sediment Contam Int J* 16: 313–322.
- McGroddy SE, Gschwend P (1996). Comparison of the in situ and desorption sediment-water partitioning of polycyclic aromatic hydrocarbons and polychlorinated biphenyls *Environmental Science & Technology*, 30: 172-177.
- Ministerial Decree (1998). Individuazione dei rifiuti non pericolosi sottoposti alle procedure semplificate di recupero ai sensi degli articoli 31 e 33 del decreto legislativo 5 febbraio 1997, n. 22. *Gazzetta Ufficiale della Repubblica Italiana*, n. 88 del 16-04-1998.
- Meric D, Alshawabkeh AN, Shine JP, Sheahan T (2014). Bioavailability of hydrophobic organic compounds in thin-layered capped sediments. *Chemosphere*, 103: 281-289.
- Millington RJ, Quirk JP (1961). Permeability of porous solids. *Trans Faraday Soc*, 57:1200–1207.
- Miqueleiz L, Ramírez F, Seco A, Nidzam R, Kinuthia J, Tair A, Garcia R, (2012). The use of stabilised Spanish clay soil for sustainable construction materials. *Engineering Geology*, 133, 9-15.
- Miura N, Horpibulsuk S, Nagaraj TS (2001). Engineering behaviour of cement stabilized clay at high water content. *Soils and Foundations*, 41(5): 33–45. doi:10.3208/sandf.41.5_33.
- Moo-Young H, Myers T, Tardy B, Ledbetter R, Vanadit-Ellis W, Kim TH (2002). Modeling contaminant transport through capped dredged sediment using a centrifuge. *J. Soils Sediment*, 2: 117–128.
- Moon D, Park JW, Chang YY, Ok YS, Lee S, Ahmad M, Baek K (2013). Immobilization of lead in contaminated firing range soil using biochar. *Environmental Science and Pollution Research*, 20(12): 8464-8471.
- Moretti LK (2008). Evaluation of Capping NAPL-Contaminated Sediment, Univ. of Texas, Austin, TX.

- Murphy P, Marquette A, Reible D, Lowry GV (2006). Predicting the performance of activated carbon-, coke-, and soil-amended thin layer sediment caps. *Journal of Environmental Engineering*, 132: 787-794.
- Neville AM, Brooks JJ (2010). *Concrete technology*. Prentice Hall, Harlow.
- NRC (National Research Council) (2007). *Sediment dredging at superfund megasites: assessing the effectiveness*. National Academies Press, Washington, DC
- Oen AM, Beckingham B, Ghosh U, Kruså ME, Luthy RG, Hartnik T, Henriksen T, Cornelissen G (2012). Sorption of organic compounds to fresh and field-aged activated carbons in soils and sediments. *Environ Sci Technol*, 46(2): 810–817
- Oh SY, Cha SW, Kim IH, Lee H, Kang S, Choi S, (2011). Disposal of heavy metal-contaminated sediment from Ulsan Bay, South Korea: treatment processes and legal framework. *Water and Environment Journal*, 25(4): 445-4.
- Oliveira F, Patel A K, Jaisi D, Adhikari S, Lu H, Khanal S K. (2017). Environmental application of biochar: Current status and perspectives, *Bioresource Technology*.
- Olson RE, Mesri G (1970). Mechanisms Controlling Compressibility of Clays. *ASCE J. Soil Mech. Found. Div.*, 96(6): 1863–1878.
- Olst J, Hornaday C, Darlington J (2006). Reactive Material Options for In Situ Capping. *Journal of ASTM International*, 3: 1-6.
- Osovitz CJ, Julian D (2002). Burrow irrigation behavior of *Urechis caupo*, a filter-feeding marine invertebrate, in its natural habitat. *Mar Ecol Prog Ser*, 245:149–155.
- Paria S, Yuet PK (2006). Solidification–stabilization of organic and inorganic contaminants using portland cement: a literature review. *Environmental reviews*, 14(4): 217-255.
- Pandey B, Kinrade SD, Catalan LJ (2012). Effects of carbonation on the leachability and compressive strength of cement-solidified and geopolymer-solidified synthetic metal wastes. *Journal of environmental management*, 101: 59-67.
- Peakall D, Burger J (2003). Methodologies for assessing exposure to metals: speciation, bioavailability of metals, and ecological host factors. *Ecotoxicology and Environmental Safety*, 56(1): 110-121.

- Petersen JS, Henckel P, Maribo H, Oksbjerg N, Sørensen MT (1997). Muscle metabolic traits, post mortem-pH-decline and meat quality in pigs subjected to regular physical training and spontaneous activity. *Meat Science*, 46(3): 259-275.
- Petronio BM, Cardellicchio N, Calace N, Pietroletti M, Pietrantonio M, Caliandro L (2012). Spatial and temporal heavy metal concentration (Cu, Pb, Zn, Hg, Fe, Mn, Hg) in sediments of the mar piccolo in Taranto (Ionian Sea, Italy). *Water, Air, & Soil Pollution*, 223(2): 863-875.
- Piatt JJ, Brusseau ML (1998). Rate-limited sorption of hydrophobic organic compounds by soils with well-characterized organic matter. *Environmental Science & Technology*, 32: 1604-1608.
- Pignatello JJ, Xing B (1996). Mechanisms of slow sorption of organic chemicals to natural particles. *Environmental Science & Technology*, 30: 1-11.
- Pihl H, Kuusipuro K (2004). Temperature increase at hydration of binders. Internal work report. Nordkalk.
- Prusinski J, Bhattacharja S (1999). Effectiveness of Portland Cement and Lime in Stabilizing Clay Soils, *Transportation Research Record Journal of the Transportation Research Board*, 1: 215-227.
- Reible D (2014). Processes, Assessment and Remediation of Contaminated Sediments. SERDP and ESTCP Remediation Technology Monograph Series. Springer New York.
- Reible DD, Popov V, Valsaraj KT, Thibodeaux LJ, Lin F, Dikshit M, Todaro MA, Fleeger JW (1996). Contaminant fluxes from sediment due to tubificid oligochaete bioturbation. *Water Res*, 30: 704–714.
- Rodríguez FJ, Núñez LA (2011). Characterization of aquatic humic substances. *Water and Environment Journal*, 25(2): 163-170.
- Roscoe KH, Schofield A, Wroth CP (1958). On the yielding of soils. *Geotechnique*, 8(1): 22-53.
- Roy A, Eaton HC, Cartledge FK, Tittlebaum ME (1992). Solidification/stabilization of hazardous waste: evidence of physical encapsulation. *Environmental science & technology*, 26(7): 1349-1353.

- Rotta GV, Consoli NC, Prietto PDM, Coop MR, Graham J (2003). Isotropic yielding in an artificially cemented soil cured under stress. *Geotechnique*, 53(5): 493-501.
- Russo G, Croce G (2011). Experimental investigation on durability of a lime stabilised soil. In *Proceedings of the XV European Conference on Soil Mechanics and Geotechnical Engineering*, Athens, Greece.
- Russo G, Capotosto A, Croce P, Modoni G, Vitale E (2015). Lime treatment for the reuse of dredged marine Sediments, *Geotechnical Engineering for Infrastructure and Development*, 3: 1321-1326.
- Samanta SK, Singh OV, Jain R (2002). Polycyclic aromatic hydrocarbons: Environmental pollution and bioremediation. *Trends in Biotechnology*, 20(6): 243-248.
- Samuelsson GS, Hedman JE, Elmquist Kruså M, Gunnarsson JS, Cornelissen G (2015). Capping in situ with activated carbon in Trondheim harbor (Norway) reduces bioaccumulation of PCBs and PAHs in marine sediment fauna. *Mar Environ Res*, 109:103–112
- Santanu P, Yuet PK (2006). Solidification–stabilization of organic and inorganic contaminants using portland cement: a literature review. *Environ. Rev*, 14: 217–255.
- Schofield A, Wroth P (1968). *Critical state soil mechanics* (Vol. 310). London: McGraw-Hill.
- Schneider A, Porter ET, Baker JE (2007). Polychlorinated biphenyl release from resuspended Hudson River sediment. *Environmental Science & Technology*, 41, 1097-1103.
- Schwarzenbach R, Gschwend PM, Imboden DM (2003). *Environmental Organic Chemistry*, 2nd ed. Wiley-Interscience, Hoboken, NJ, USA.
- Scordia P, Lafhaj Z, Skoczylas F, Mongeois F (2008). Characterization and valorization in road technology of polluted and treated river sediments. *Eur. J. Environ. Civ. Eng.*, 12: 1087–1104.
- Seeberg-Elverfeldt J, Schlüter M, Feseker T, Kölling M (2005). Rhizon sampling of porewaters near the sediment-water interface of aquatic systems. *Limnology and oceanography: Methods*, 3(8): 361-371.
- Sherwood PT (1993). *Soil stabilization with cement and lime*. HMSO, London.

- Shor L, Kosson DS, Rockne KJ, Young LY, Taghon GL (2004). Combined effects of contaminant desorption and toxicity on risk from PAH contaminated sediments. *Risk Analysis*, 24(5): 1109-1120.
- Silitonga E, Levacher D, Mezazigh S, (2009). Effects of the use of fly ash as a binder on the mechanical behaviour of treated dredged sediments. *Environmental Technology*, 30(8): 799–807.
- Silitonga E, Levacher D, Mezazigh S (2010). Utilization of fly ash for stabilization of marine dredged sediments. *Eur. J. Environ. Civ. Eng.*, 14(2): 253–265.
- Silvani L, Di Palma PR, Riccardi C, Eek E, Hale SE, Viotti P, Papini MP (2017). Use of biochar as alternative sorbent for the active capping of oil contaminated sediments. *Journal of environmental chemical engineering*, 5(5): 5241-5249.
- Singh T, Pant K (2006). Solidification/Stabilization of arsenic containing solid waste using Portland cement, fly ash, and polymeric materials *J. Hazard. Mater.* 131(1-3): 29–36.
- Simpson SL, Apte SC, Batley GE (1998). Effect of short-term resuspension events on trace metal speciation in polluted anoxic sediments. *Environmental Science & Technology*, 32(5): 620-625.
- Sivapullaiah PV, Sridharan A, Bhaskar Raju KV (2000). Role of amount and type of clay in the lime stabilization of soils. *Ground Improvement*, 4: 37-45.
- Song X, Li J, Chen L, Cai Z, Liao C, Peng H, Xiong H, (2012). Determination of polychlorinated biphenyls in seawater using headspace solid-phase microextraction coupled with gas chromatography-mass spectrometry with the aid of experimental design. *Journal of the Brazilian Chemical Society*, 23(1): 132-141.
- Sridharan A, Nagaraj HB (2000). Compressibility behaviour of remoulded, fine-grained soils and correlation with index properties. *Canadian Geotechnical Journal*, 37(3): 712-722.
- Stephan D, Maleki H, Knöfel D, Eber B, Härdtl R (1999a). Influence of Cr, Ni, and Zn on the properties of pure clinker phases: Part I. C3S. *Cement and concrete research*, 29(4): 545-552.

- Stephan D, Maleki H, Knöfel D, Eber B, Härdtl R (1999b). Influence of Cr, Ni, and Zn on the properties of pure clinker phases: Part II. C3A and C4AF. *Cement and concrete research*, 29(5): 651-657.
- Stegemann JA, Zhou Q (2009). Screening tests for assessing treatability of inorganic industrial wastes by stabilisation/solidification with cement. *Journal of Hazardous Materials*, 161(1): 300-306.
- Steward KK (2007). Development of Apparatus and Method for Consolidating Very Soft, Contaminated Sediment, University of Texas, Austin, TX.
- Sun H, Xu X, Gao G, Zhang Z, Yin P (2010). A novel integrated active capping technique for the remediation of nitrobenzene-contaminated sediment. *J Hazard Mater* 182: 184–190.
- Tan TS, Goh TL, Yong KY (2002). Properties of Singapore marine clays improved by cement mixing. *Geotechnical Testing Journal*, 25(4): 422-433.
- Tang JX, Petersen EJ, Huang QG, Weber WJ (2007). Development of engineered natural organic sorbents for environmental applications: 3. Reducing pah mobility and bioavailability in contaminated soil and sediment systems. *Environmental Science & Technology*, 41(8): 2901-2907.
- Taylor DW (1948). *Fundamentals of soil mechanics*, John Wiley and Sons, New York.
- Taylor HFW, (1997). *Cement chemistry*. Academic Press, London.
- Tessier A, Carignan R, Belzile N (1994). Reactions of trace elements near the sedimentwater interface in lakes. In *Transport and Transformation of Contaminants Near the Sediment-Water Interface* DePinto, J. V., Lick, W., Paul, J.F., Ed. Lewis Publishers: Boca Raton.
- Terzaghi K (1923). Die Berechnung der Durchlässigkeit des Tones aus dem Verlauf der hydromechanischen Spannungserscheinungen. *Sitzungsber Akad Wiss Math* 32: 125-138.
- Terzaghi K, Frohlich OK (1936). *Theorie der Setzung von Tonschichten*, Deuticke, Leipzig, 1936.
- Terzaghi K (1944). Ends and means in Soil Mechanics. *Engineering Journal*, 27: 608.

- Terzaghi K, Peck RB (1967). *Soil Mechanics in Engineering Practice*, Second Edition: John Wiley & Sons, New York.
- Terzaghi K, Peck RB, Mesri G (1996). *Soil mechanics in engineering practice*. John Wiley & Sons.
- Todaro F, De Gisi S, Notarnicola M (2016). Contaminated marine sediments: waste or resource? An overview of treatment technologies, *Procedia Environmental Science, Engineering and Management*, 3, 157-164.
- Todaro F, De Gisi S, Notarnicola M (2018a). Sustainable remediation technologies for contaminated marine sediments: preliminary results of an experimental investigation. *Environmental Engineering and Management Journal*, 17(10): 2465-2471.
- Todaro F, Vitone C, Notarnicola M (2018b). Green remediation and recycling of contaminated marine sediments: first geotechnical results. *Incontro Annuale dei Ricercatori di Geotecnica 2018*. Genova, 4-6 Luglio 2018.
- Tomaszewski JE, Werner D, Luthy RG, (2007). Activated carbon amendment as a treatment for residual DDT in sediment from a superfund site in San Francisco Bay, Richmond, California, USA. *Environ Toxicol Chem*, 26:2143–2150.
- Tomasevic D, Dalmacija M, Prica M, Dalmacija B, Kerkez D, Becelic-Tomin M, Roncevic S (2013). Use of fly ash for remediation of metals polluted sediment – green remediation. *Chemosphere*, 92: 1490-1497.
- TRB (1987). *Lime stabilisation. Reactions, properties, design, and construction*. State-of-the-Art Report 5. Transportation Research Board, National Research Council, Washington.
- Tremblay H, Leroueil S, Locat J (2001). Mechanical improvement and vertical yield stress prediction of clayey soils from Eastern Canada treated with lime or cement. *Canadian Geotechnical Journal*, 38(3): 567–79. doi:10.1139/t00-119.
- Tremblay H, Duchesne J, Locat J, Leroueil S (2002). Influence of the nature of organic compounds on fine soil stabilization with cement. *Canadian Geotechnical Journal*, 39(3): 535-546.

- Tsang DC, Olds WE, Weber PA, Yip AC (2013). Soil stabilisation using AMD sludge, compost and lignite: TCLP leachability and continuous acid leaching. *Chemosphere*, 93(11): 2839-2847.
- Tsang DCW, Yip DCW (2014). Comparing chemical-enhanced washing and waste-based stabilization approach for soil remediation. *J. Soil Sediment*, 14: 936-947.
- US EPA, US Environmental Protection Agency, (1997). Clean up the nation's waste sites: markets and technology trends, EPA-542-R-96-005, April.1997.
- US EPA, US Environmental Protection Agency, (2004). Treatment technologies for site clean-up: annual status report (eleventh edition), EPA-542-R-03-009, February 2004.
- US EPA, US Environmental Protection Agency, (2005). Contaminated sediment remediation guidance for hazardous waste sites. EPA-540-R-05-012.
- US EPA, US Environmental Protection Agency, (2013a). Use of amendments for in situ remediation at superfund sediment sites. Office of Superfund Remediation and Technology Innovation.
- US EPA, US Environmental Protection Agency, (2013b). Superfund remedial program review action plan. Washington DC. November.
- UNI EN 12457-2. Leaching: compliance test for leaching of granular waste materials and sludges - Part 2: One stage batch test at a liquid to solid ratio of 10 L/kg for materials with particle size below 4 mm (without or with size reduction), October 2004.
- Yan F, Reible D (2015). Electro-bioremediation of contaminated sediment by electrode enhanced capping. *Journal of environmental management*, 155: 154-161.
- Yang YR, McCarty PL (1998). Competition for hydrogen within a chlorinated solvent dehalogenating anaerobic mixed culture. *Environmental Science & Technology*, 32(22): 3591-3597.
- You J, Landrum PF, Lydy MJ (2006). Comparison of chemical approaches for assessing bioavailability of sediment-associated contaminants. *Environmental Science & Technology*, 40: 6348-6353

- Yuan QZ, Valsaraj KT, Reible DD (2009). A model for contaminant and sediment transport via gas ebullition through a sediment cap. *Environ Eng Sci*, 26: 1381–1391.
- Van Cappellen P, Gaillard JF (1996). Biogeochemical dynamics in aquatic sediments. In *Reactive Transport in Porous Media* Lichtner, P. C. Steefel, C. I. Oelkers, E. H., Eds. Mineralogical Society of America: Washington, DC, 1996.
- Vitone C, Federico A, Puzrin A M, Ploetze M, Carrassi E, Todaro F. (2016). On the geotechnical characterization of the polluted submarine sediments from Taranto, *Environmental Science and Pollution Research*, 23: 535-553.
- Wang D, Abriak NE, Zentar R, Xu W, (2012). Solidification/stabilization of dredged marine sediments for road construction, *Environmental Technology*, 33: 95-101.
- Wang D, Abriak N E, Zentar R, Chen W, (2013). Effect of lime treatment on geotechnical properties of Dunkirk sediments in France, *Road Materials and Pavement Design*, 14: 485-503.
- Wang D, Abriak N (2015). Compressibility behavior of Dunkirk structured and reconstituted marine soils. *Marine Georesources & Geotechnology*, 33(5): 419–28.
- Wang D, Abriak NE, Zentar R (2015). One-dimensional consolidation of lime-treated dredged harbour sediments. *European Journal of Environmental and Civil Engineering*, 19(2): 199-218.
- Wang D, Zentar R, Abriak N, Di S, (2018). Long-term mechanical performance of marine sediments solidified with cement, lime, and fly ash. *Marine Georesources & Geotechnology*, 36(1): 123-130.
- Wang L, Chen L, Tsang D, Li JS, Yeung T, Ding S, Poon C, (2018). Green remediation of contaminated sediment by stabilization/solidification with industrial by-products and CO₂ utilization. *Sci. Total Environ*, 631-632, 1321-1327.
- Wang L, Kwok J S H, Tsang D C W, Poon C (2015). Mixture design and treatment methods for recycling contaminated sediment, *Journal of Hazardous Materials*, 283: 623-632.
- Wang Y, Li Y, Zhang J, Xu S, Yang S, Sun C (2009). A novel fluorinated polyaniline-based solid-phase microextraction coupled with gas chromatography for

- quantitative determination of polychlorinated biphenyls in water samples. *Analytica chimica acta*, 646(1-2), 78-84.
- Wang Z, Shen S, Yin Z, Xu Y (2014). Rapid field evaluation of the strength of cement-stabilized clayey soil. *Bulletin of Engineering Geology and the Environment*, 74: 1–9.
- Warner KA, Roden EE, Bonzongo J-C (2003). Microbial mercury transformation in anoxic freshwater sediments under iron reducing and other electron-accepting conditions. *Environ Sci Technol* 37:2159–2165.
- Weber W, Pennell K, Dekker T, Abriola L (1996). Sorption and retardation of organic contaminants in subsurface systems: Effects on transport and fate. In *Advances in Groundwater Pollution Control and Remediation* Aral, M. M., Ed. Kluwer Academic Publishers: Boston, MA, 1996.
- Werner D, Higgins CP, Luthy RG (2005). The sequestration of PCBs in Lake Hartwell sediment with activated carbon. *Water Res*, 39: 2105– 2113
- Wessels Perelo L (2010). Review: in situ and bioremediation of organic pollutants in aquatic sediments. *J Hazard Mater* 177(1): 81–89
- WDOE, Washington State Department of Ecology, (2012). Custom Plywood Interim Action: thin-layer capping pilot study, Anacortes, Washington. Work plan prepared by Hart Crowser, Inc. July.
- Wiles CC, (1987). A review of solidification/stabilization technology. *J. Hazard. Mater.* 14: 5–21.
- Zaitlin BA, Dalrymple RW, Boyd R (1994). The stratigraphic organisation of incised valley systems associated with relative sea-level change. In: Dalrymple RW, Boyd RJ and Zaitlin BA (eds) *Incised-valley systems: origin and sedimentary sequences*. *SEPM Spec Publ* 51:45–60.
- Zentar R, Wang D, Abriak N, Benzerzour M, Chen W (2012). Utilization of siliceous–aluminous fly ash and cement for solidification of marine sediments. *Construction and Building Materials*, 35: 856-863.

- Zhang C, Zhu M, Zeng G, Yu Z, Cui F, Yang Z, Shen L (2016). Active capping technology: a new environmental remediation of contaminated sediment *Environmental Science and Pollution Research*, 23: 4370-4386.
- Zimmerman JR, Werner D, Ghosh U, Millward RN, Bridges TS, Luthy RG (2005). Effects of dose and particle size on activated carbon treatment to sequester polychlorinated biphenyls and polycyclic aromatic hydrocarbons in marine sediments. *Environ Toxicol Chem* 24(7): 1594–1601
- Zimmerman JR, Ghosh U, Millward RN, Bridges TS, Luthy RG (2004). Addition of carbon sorbents to reduce PCB and PAH bioavailability in marine sediments: Physicochemical tests. *Environmental Science & Technology*, 38(20): 5458-5464.
- Zwank L, Elsner M, Aeberhard A, Schwarzenbach RP, Haderlein SB (2005). Carbon isotope fractionation in the reductive dehalogenation of carbon tetrachloride at iron (hydr)oxide and iron sulfide minerals. *Environmental Science & Technology*, 39(15): 5634-5641.

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Born in Taranto (Italy) in 1988, graduated in Environmental Engineering at Polytechnic University of Bari, in 2014, discussing the thesis in Environmental Geotechnics: “Characterization of contaminated sediments of the Mar Piccolo basin of Taranto and geotechnical design for remediation by capping” advisors Proff. Antonio Federico and Claudia Vitone, vote 110/110 cum laude. In 2005, second-level Postgraduate Master in “Characterization and Technologies for Remediation of Contaminated Sites” at the Sapienza University of Roma. From October 2015 to October 2018, PhD student in Environmental and Building Risk and Development at the Polytechnic University of Bari. His research program aimed at developing new remediation technologies for contaminated marine sediments. In particular, he explored the sustainability of two remediation technologies: i) in situ reactive capping and ii) ex situ stabilization/ solidification. Author of 17 papers in refereed journals with major interests in the fields of remediation technologies, characterization of contaminated marine sediments, solid waste management and life cycle assessment (LCA).

Publications

1. Vitone C, Federico A, Puzrin AM, Ploetze M, Carrassi E, **Todaro F** (2016). On the geotechnical characterization of the polluted submarine sediments from Taranto. *Environ. Sci. Pollut. Res.*, 23: 12535–12553.
2. Lofrano G, Libralato G, Minetto D, De Gisi S, Conte B, **Todaro F**, Calabrò D, Quararo L, Notarnicola M (2016). In situ remediation of contaminated marine sediment: an overview. *Environ. Sci. Pollut. Res.*, 24: 5189-5206.
3. **Todaro F**, De Gisi S, Notarnicola M (2016). Contaminated marine sediments: waste or resource? An overview of treatment technologies. *Procedia Environmental Science, Engineering Management*, 3: 157-164.
4. Notarnicola M, **Todaro F**, Campanaro V, De Gisi S (2016). Setting appropriate technologies in the remediation of brownfield contaminated with hydrocarbons: The case study of the ex-Gasometer in Bari, Italy. *Procedia Environmental Science, Engineering and Management*, 3: 49-57.
5. De Gisi S, **Todaro F**, Carella C, Fedele G, Notarnicola M (2016). Pure oxygen-based MSW bio-stabilization: Energy, engineering, environmental and process safety aspects. *Procedia Environmental Science, Engineering and Management*, 3: 41-47.
6. De Gisi S, Minetto M, **Todaro F**, Lanzolla A, Notarnicola M (2017). Monitored Natural Recovery of contaminated marine sediments. Proposal of a monitoring plan for in situ continuous testing and sensing. In: *I2MTC-2017. IEEE International Instrumentation and Measurement Technology Conference: proceedings papers*. IEEE, Torino, Italy, May 22-25, 2017.
7. Adamo F, Andria G, Di Nisio A, Lanzolla A, Spadavecchia M, Cotecchia F, Miccoli D, Sollecito F, **Todaro F**, Vitone C (2017). Development of an Automatic System for Geotechnical Testing. In: *IEEE International Instrumentation and Measurement Technology Conference (I2MTC)*. p. 523-528, IEEE, Torino, Italy, May 22-25, 2017.
8. De Gisi S, Minetto D, Lofrano G, Libralato G, Conte B, **Todaro F**, Notarnicola M (2017). Nano-scale Zero Valent Iron (nZVI) treatment of marine sediments slightly polluted by heavy metals. *Chemical Engineering Transactions*, 60: 139-144.

9. De Gisi S, **Todaro F**, Notarnicola M (2017). Effect of reactive mats on in-situ remediation of contaminated marine sediments. *Procedia Environmental Science, Engineering and Management*, 4: 17-22.
10. **Todaro F**, De Gisi S, Notarnicola M (2017). Pure oxygen-based MSW bio-stabilization: Preliminary results of a full-scale investigation. *Procedia Environmental Science, Engineering and Management*, 4: 23-28.
11. De Gisi S, Pastore F, **Todaro F**, Chiarelli A, Tagliente L, Notarnicola M (2017). Theoretical and experimental investigation on agglomeration phenomena in a SRF-fired fluidized bed waste-to-energy plant. *Journal of Applied Biomaterials and Functional Biomaterials*, 15: 9.
12. De Gisi S, **Todaro F**, Fedele G, Carella C, Notarnicola M (2018). Alternating pure oxygen and air cycles for the biostabilization of unsorted fraction of municipal solid waste. *Waste Management*, 79: 404-414.
13. Adamo F, Andria G, Bottiglieri O, Cotecchia F, Di Nisio A, Miccoli D, Sollecito F, Spadavecchia M, **Todaro F**, Trotta M, Vitone V (2018). GeoLab, a measurement system for the geotechnical characterization of polluted submarine sediments. *Measurement*, 127: 335-347.
14. Coppola L, Bellezze T, Belli A, ..., **Todaro F**, Vilardi G, Yang F (2018). Binders alternative to Portland cement and waste management for sustainable construction – Part 1. *Journal of Applied Biomaterials and Functional Biomaterials*, 16: 186-202.
15. Coppola L, Bellezze T, Belli A, ..., **Todaro F**, Vilardi G, Yang F (2018). Binders alternative to Portland cement and waste management for sustainable construction – Part 2. *Journal of Applied Biomaterials and Functional Biomaterials*, 16: 207-221.
16. Barjoveanu G, De Gisi S, Casale R, **Todaro F**, Notarnicola M, Teodosiu C (2018). A life cycle assessment study on the stabilization/solidification treatment processes for contaminated marine sediments. *Journal of Cleaner Production*, 201: 391-402.
17. **Todaro F**, De Gisi S, Notarnicola M (2018). Sustainable remediation technologies for contaminated marine sediments: preliminary results of an experimental investigation. *Environmental Engineering and Management Journal*, 10: 2465-2471.