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ABSTRACT

Contaminated marine sediment management strategies involves *in situ* and *ex situ* options for preventing pollutants from re-entering the water column, thus becoming available to benthic organisms and subsequently entering aquatic food chains. These pollution abatement strategies can cause significant secondary environmental impacts which in some cases have been considered to be even higher than the primary ones. This study aims at identifying and quantifying through life cycle assessment (LCA) the environmental impacts of the application of Stabilization/Solidification (S/S) options for the remediation of contaminated marine sediments from the Mar Piccolo in Taranto (Southern Italy). The analysis considers all the stages involved in marine sediments processing (dredging, transport, storage, treatment, safe disposal of the treated sediments) but focuses on several S/S options (4 S/S mixes with cement and 4 mixes with lime). These S/S options were tested at lab scale with different results in immobilizing heavy metals and organic

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pollutants. The LCA suggests that the ex-situ treatment could contribute to improving the current situation and that the marine sediments S/S operation generates a complex environmental profile which is dominated by the treatment phase, which in turn shows that optimization of this stage could lower these impacts.

Keywords: Ex-situ treatment; LCA; Leaching test; Marine sediments contamination; Organic clay; Portland cement

1. INTRODUCTION

Sediment-bound pollutants pose major concerns for human health and the environment, because these contaminants can re-enter the overlying water column and become available to benthic organisms and subsequently enter aquatic food chains. Sediment acts as both carriers and long-term secondary sources of contaminants to aquatic ecosystems.

Sediment management strategies may involve *in situ* and *ex situ* options. In situ remedial alternatives generally involve Monitored Natural Recovery (MNR) (De Gisi *et al.*, 2017a) and in situ containment and treatment (Lofrano *et al.*, 2016). While the MNR is based on the assumption that natural processes can reduce risk over time in a reasonably safe manner, in containment and in situ treatments, contaminated sediments are physically and chemically isolated from aquatic ecosystems or contaminants in sediments and further sequestered and degraded. An example of in situ containment and treatment is In Situ Capping (ISC) (De Gisi *et al.*, 2017b; Lin *et al.*, 2011). Ex situ remedial alternatives typically require several component technologies to dredging or excavation, transport, pre-treatment, treatment, and/or disposal of sediments and treatment residues. Among the most widely applied are Stabilization/Solidification (S/S) (Tang *et al.*, 2015; Wang *et al.*, 2015),

Nano-scale Zero Valent Iron (nZVI) treatment (De Gisi *et al.*, 2017c), landfarming (NSW EPA, 2014), composting (Mattei *et al.*, 2017), sediment washing (Stern *et al.*, 2007), thermal desorption (Bortone and Palumbo, 2007), vitrification (Colombo *et al.*, 2009), biological treatment (Matturro *et al.*, 2016) and/or their combination (Careghini *et al.*, 2010).

Long-applied, S/S is based on adding chemical compounds to dredged material in order to chemically immobilize contaminants and thus reduce leachability and bioavailability. Therefore, S/S does not remove the contaminants from the dredged material, but they are transformed into a less mobile, and less harmful species (Akcil *et al.,* 2015; Bonomo *et al.*, 2009). The simplest form of treatment involves Portland cement although further materials can be added such as calcium aluminates, fly ashes, bentonite or other clays, phosphates, lime, oil residue and silicate fume (Marques *et al.*, 2011). However, the additive used depends on the type of contaminants, water content and characteristics of the dredged material. In the last years, innovative binders and mixtures, alone or in combination with cement, have been tested (Roviello *et al.*, 2017).

Today, S/S is experiencing renewed importance; 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, 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. The 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. They 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 CO_2 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.

Life Cycle Assessment (LCA) is one of the most important methods for evaluating the environmental performance of alternative treatment systems considering their entire life cycle (De Feo and Ferrara, 2017; Colangelo *et al*., 2018). LCA allows to compare different systems considering the consumption of resources as well as the emission of pollutants that may occur during their life cycle (secondary impacts), which may include the extraction of raw materials, the production and processing of materials, the transport, the phase of use and, finally, the end of life (ISO 14040, 2006; ISO 14044, 2006).

Table 1. Life cycle assessments of contaminated marine sediments treatment options.

Although LCA has been used previously to evaluate various treatment options for contaminated sites (Morais and Delerue-Matos, 2010), in the case of marine sediments, there are few studies that mention LCA as an environmental performance assessment tool, except the ones presented in Table 1. Most of these studies focus mainly on comparing

different options for marine sediments manipulation: in-situ vs. natural remediation (Sparrevik *et al.*, 2011; Choi *et al.* (2016), in-situ vs. ex-situ placement (Bates *et al.*, 2015), primary vs. secondary vs. tertiary impacts (Hou *et al.*, 2014). The study of Falciglia *et al.* (2018) compares actual treatment technologies for the removal (destruction) of hydrocarbons from MS by heat. To our current knowledge, information on the assessment by life cycle assessment of impacts associated to the use of ex-situ S/S for the remediation of contaminated sediments is currently limited.

In this context, the article presents the implementation of a complex LCA study aimed at identifying, quantifying and analysing the primary, secondary and tertiary environmental impacts of the remediation options for marine sediments coming from Mar Piccolo in Taranto (Southern Italy). This area is known for its economic and tourism activities as well as for sea–food production, but also for being one of the most polluted in Europe. This assessment is intended to evaluate various MS stabilization/solidification options in a wider context that considers the current local situation (primary impacts); the manipulation of sediments (including dredging, transport and on-shore operations); the specific performance of solidification/stabilization mixes (secondary impacts) and finally the tertiary impacts due to final MS disposal. The sensitivity analysis (SA) considered the measured variability of key flows (i.e. pollutant releases and material consumption, measured as standard deviations) and default variability of background processes in the inventory. Alongside the LCA study, the paper discusses the technical performance of 8 S/S mixes that use various proportions of Portland cement, lime, activated carbon and organic clays.

2. MATERIALS AND METHODS

2.1 Background information

Taranto is a coastal city in Southern Italy, an important commercial port as well as the main Italian naval base. Taranto faces the Ionian Sea and is known as the "city of two seas" because it is extended around the Big Sea and the vast reservoir of the Little Sea, composed of the two internal basins (Fig. 1).

Figure 1. The "Mar Piccolo of Taranto" study area (Southern Italy): sampling area, main phases of the intervention (dredging, intermediate storage and treatment) and the S/S pilot treatment plant located at the Taranto Bellavista municipal wastewater treatment plant.

The relatively shallow waters in the Gulf of Taranto yield large numbers of mussels *Mytilus Galloprovincialis* so, 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.*, 2007a).

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. Although there were conducted some studies to evaluate the local impacts of intensive mussel's production even through LCA (Iribarren *et al.*, 2010), the objective of this paper is driven on investigating how the causes of declining mussel's quality may be addressed through marine sediments stabilization and solidification.

The city is one of the areas declared as "at high risk of environmental crisis" by the national government (Italian Law n. 349. 1986) because it represents one of the most complex industrial sites in Europe, located near urban areas of high population density. All the industrial activities are responsible for the high environmental contamination, mainly due to heavy metals and organic pollutants. This explains why Taranto has been recently included into the list of polluted Sites of National Interest (SIN) by the Italian Government (Italian Law n. 426, 1998), for which the environmental remediation has been identified as a national priority (Ministerial Decree n. 468, 2002) (Vitone *et al.*, 2016).

In the last ten years, the seabed of the basins has been investigated through a widespread survey. The submarine sediments in the Mar Piccolo contain high concentrations of heavy metals (i.e., Hg, Pb, Cd, Cu and Zn) and organic pollutants (PCBs, PAHs and dioxins) (Bellucci *et al.*, 2016; Kralj *et al.*, 2016; Matturro *et al.*, 2016, Cardellicchio *et al.*, 2007b).

2.2 Experimentation plan

The investigation presented in this study has involved two main phases, namely S/S testing and LCA evaluation as presented in Figure 2, which shows the schematization of the main lab-scale studies, LCA phases, the MS treatment life cycle steps (processes that were

considered in the life cycle inventory) and the specific impact categories of Recipe 2008 mid-point method which was used for the life cycle impact assessment.

Figure 2. Experimental framework for marine sediments treatment and LCA approach.

2.2.1 S/S testing

Sediments, coming from one of most contaminated areas of Mar Piccolo, were taken up to depths of about 1.5 m from the seafloor, that is about the depth of interest in view of any mitigation solution. These were passed through a 2 cm sieve, homogenized by mixing and stored at 4 °C until use. The standard protocols of ISPRA (the Italian Institute for the Environmental Protection and Research) was used for determining grain-size, moisture content and organic matter of sediments (ICRAM-APAT, 2007). The concentrations of metals were obtained by ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometry) in accordance to EPA method 200.8 (EPA, 1994). For the determination of the total PAHs and PCBs concentrations as well as each compound or homologue group, a Gas Chromatograph - Mass Spectrometer (GC-MS) and EPA method 8275A was used. In the present case, the sediment samples were only contaminated by inorganic pollutants, shown in Table 2.

Table 2. Physical-chemical properties of the sediments samples used for the tests.

The mixtures were prepared by using different contents (by dry soil weight) of several additives, namely CEM I 42.5 R Portland cement (C), lime (L), activated carbon (AC) and organoclay (OC) (Table 3).

Table 3. Mixture design for S/S testing.

All the materials were initially mixed for 5 min with a standard mixer and, then, a steel trowel to ensure a homogeneous paste was used. In the casting phase, the prepared mixture was introduced into different silicone molds with hemispherical shape. The samples, in the curing phase, were kept at 20 ± 5 °C and 80% moisture.

The leaching tests were carried out according to the EN standard 12457-2 (EN 12457-2, 2002). For several samples, a 40g portion was sampled and transferred to a polyethylene bottle. Distiller 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 hours using Rotax 6.8 (Velp Scientifica). To end of the 24 hours, 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. The soluble concentrations of heavy metals of interest (As, Co, Cr, Ni, V and Zn) were analysed by using ICP-OES.

2.2.2 LCA evaluation

The objective of the LCA study was to investigate the environmental impacts associated to the current situation in Mar Piccolo (primary impacts), the impacts associated to the S/S options (secondary impacts), and the potential impacts that appear during the post-treatment phases (tertiary impacts)

The functional unit of the LCA study was chosen to be one square meter of sea bed in Mar Piccolo from which the top layer of 50 cm was considered in the next phases of the LCA analysis. The characteristics of this sediment are presented in Table 2. This surface-based functional unit definition is motivated by the need to improve the local sea-bed quality.

The system under study was organized as pre-treatment operations which included the dredging process, dockyard operations (unloading and transfer to a storage site); marine sediment treatment (8 options of S/S with various mixes stabilizers, according to Table 3) and post-treatment operations which included final placement in a specially designed storage facility.

Dredging was modelled considering a hydraulic dredger, which is very efficient when working with fine materials, because they can easily be held in suspension (Blažauskas *et al.*, 2006), so it suits to this case study as the characterization of the seabed shows a high percentage of silt and clay. This category of dredge has been chosen as it is suitable for navigational dredging and environmental dredging, even if they present a quite high water content of the removed material (Blažauskas *et al.*, 2006).

The dredge characteristics that were included in the life cycle inventory have considered the dredge transport power (1950 kW), the dredge jet pump power (800 kW) and a maximum production rate of 581.53 m^3/h. Also, modelling of this process has considered that the dredger aspires a mix of water and sediment in a 5:1 proportion. The Jet pump collects the top layer of sediments (50 cm) and then the two phases are separated on a barge while the excess of water is expelled back to the sea.

The volume of sediments to be dredged has been estimated to about 900,000 m^3, covering a surface of about 180 ha.

Then, the life cycle inventory included a transfer process in which the dredged marine sediments are moved from the Port of Taranto by lorry to a Pilot Technology Platform for treatment and temporary storage. This platform is located at the municipal wastewater treatment plant (WWTP) of Taranto Bellavista, less than 4 km away from the port (Fig. 1).

For the LCA modelling, the S/S treatment was imagined as a mixing process that it would take place in the Pilot Technology Platform. Because of the high moisture content, the

sediment needs to lose some of the excess water. This process was modelled by using the sludge drying beds in the WWTP of Taranto Bellavista. Once the moisture rate reaches a suitable value, the sediment is moved to the hopper and the treating begins. After mixing, a granulation step is provided, then the granular material needs a maturation phase of 28 days, then it can be reused or deposited in landfill.

The post-treatment phase was modelled in LCA as a landfill of residual materials. Detailed information of the life cycle inventory organization is presented in the supplementary material (Table S1 – inventory data).

3. RESULTS AND DISCUSSION

3.1 S/S testing

This study proposed a remediation approach to treat and recycle the contaminated sediment by means of stabilization/solidification enhanced by the addition of absorbent materials. Stabilization/solidification of contaminated sediments has proved to be an appealing technology for metal immobilization, such that the treated sediments can be recycled (Couvidat *et al*., 2016; Pinto *et al.*, 2011).

For the beneficial reuse of contaminated marine sediments, the leaching of each metal has to be lower than limits imposed by legislation. 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 Table 4.

Table 4. Lab-scale S/S performance in terms of metals removal and leaching test.

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 Vanadium (V) from mixtures with cement (Mix 1, Mix 2, Mix 3 and Mix 4) and the Copper (Cu) from Mix 5 and Mix 7 are released with concentrations higher than the legal limits. However, with greater curing times (i.e., 56 days) the leaching of metals was well controlled, especially it was less than 0.02 mg/L.

Usage of 10% lime in combination with 5% AC (Mix 2) or with 2.5% AC and 2.5% OC (Mix 8) is effective such that all metal concentrations meet the regulatory standards.

The main results shown in this study indicate that, despite the total concentrations of heavy metals in the studied marine sediment, 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 (Chatain *et al.*, 2013). In particular, mobility of the metals appears to be governed by pH. However, the adding of cement appears to increase the leaching of vanadium; whereas the adding of lime appears to increase the leaching of copper. A possible effect of the contaminants (i.e., organic matter and heavy metals) that interfered with the chemistry of binder's hydration, compromising the effectiveness of metal stabilization and development of hardening (Wang *et al.,* 2015).

3.2 Life cycle impact assessment

The life cycle impact assessment was performed using the Recipe 2008 mid-point method with the impact categories and the normalization values presented in Table 5. This method was selected based on a preliminary LCIA method screening considering aspects like impacts relevance and data representability. The ReCiPe 2008 method covers a multitude of environmental aspects and it has a good inventory data coverage as it provides characterization factors (which are particularized for the sea compartment) for more pollutant species than the other considered methods.

Table 5. Impacts categories defined in the Recipe 2008 midpoint method.

3.2.1 Reference case and environmental benefices

Since the goal of the LCA study was to evaluate the performance of the eight options for marine sediment stabilization, it was important to determine the impacts of a "no-action" scenario and to use it as a reference case against which all other actions would be compared. This scenario characterizes the "primary impacts" of the contaminated marine sediments in Mar Piccolo, as it was important to have this reference case impact done with the same evaluation tool.

In a similar way to the previous studies, (Sparrevik *et al.*, 2011, Hou *et al.*, 2014) which have used multi-compartment fate models, in the "no-action" scenario considered in this study, pollutants from the marine sediments cause impacts to the local marine eco-system via a resuspension process in which pollutants are released from the solid phase of the sediments to the liquid phase of the sea water. This resuspension process was modelled in LCA as a discharge into the seawater of a virtual wastewater containing pollutant concentrations corresponding to the complex transport and transformation phenomena of the resuspension process. Although there were some laboratory data available for the marine sediment leaching behaviour, these were not used, as they were performed in standard lab conditions (with deionized water at neutral pH), which are completely different from the real sea-bed situation. In this case, the released pollutant concentrations were determined with the help of a model (Martín-Torre *et al.*, 2015) which considers the complex processes (redox reactions of the metal species found in the marine sediments, pollutant release and sorption processes), as well as the local conditions (pH, ionic strength).

In Fig. 3a a comparison between the "no-action" scenario and the marine sediments removal is presented and it shows that the modelled resuspension of the marine sediments would cause an impact in the marine toxicity category, as expected.

Fig. 3. (a) Environmental comparison of three marine sediments management options; (b) Comparison of potential environmental toxicity-related impacts of the 8 S/S options. Symbols in the figure: HT = Human toxicity; TTOX = Terrestrial ecotoxicity; FTOX = Freshwater ecotoxicity; MTOX = Marine ecotoxicity.

By removing the contaminated sediments from the sea-bed, the impact in this environmental compartment was greatly diminished (from 0.235 to 0.0007 impact points) which shows that the ex-situ treatment of sediments is a viable option for solving the Mar Piccolo pollution problem. At the same time, landfilling the marine sediments without treatment represents a pollution transfer from the sea to the land, as impacts in the human toxicity, terrestrial toxicity and freshwater toxicity increase. This showed that the stabilization of the pollutants is required for a safe landfilling, as demonstrated by the great decrease of the impact values in these categories after a S/S with Portland cement.

In figure 3b a performance comparison of the eight S/S options based on the stabilization potentials determined by laboratory testing (Fig. 4a) highlights how the highest impacts were caused in the terrestrial toxicity (TTOX) category, with much smaller impacts in the other toxicity compartments. In general, the quick lime S/S mixes generated considerable smaller impacts than the cement options in the toxicity-related categories, but it has to be noted that these impacts consider only to the leaching potential of the treated marine sediments.

3.2.2 Evaluation of S/S options

Fig. 4a presents the full environmental impact profile of the marine sediments S/S options considering the specific materials inputs, as well as the S/S potential. The results showed that the impacts are higher with increasing quantity of additives in the S/S mix. Thus, the smallest impacts were caused by Mix 5 in most impact categories (quicklime 10%, 0% AC, 0% OC), followed by Mix 1 (cement 10%, 0% AC, 0% OC), while the highest were caused by Mixes 2 and 6 (due to the addition of AC).

Fig. 4. Potential additional impacts due to sediment treatment options (a) (characterization) and (b) (normalization); Symbols in the figure are those designated in Table 5.

An impact analysis which considers the specific impact categories was possible after the normalization step (Fig. 4b). The highest impacts appeared in the natural land transformation (NLT), followed by impacts in the toxicity related categories (Mtox, Ftox, Htox) and freshwater eutrophication. The main contributors in these categories were related to the use of AC and OC.

Figure 5. Comparison of secondary environmental impacts (treatment costs)/tertiary environmental impacts (benefices).

As presented before, the treatment of marine sediments with various mixes was successful in stabilizing/immobilizing various metal pollutants, but it also introduced some secondary environmental impacts due to the use of stabilizers (cement, quicklime, activated carbon and organic clay). From this point of view, it was important to identify and understand the

trade-offs that need to be made to find an optimal solution. In Fig. 5, a comparison between the environmental benefices (orange bars, expressed as % of the maximal impact per treatment mix) and the secondary environmental impacts due to treatment (blue bars, expressed as % of the maximal impacts) is presented. This comparison quantified the environmental benefices as the potential impacts due to pollutant leaching in accordance with the treatment options (Table 3), so the best treatment options referred to the ones with the smallest value (quicklime mixes). The secondary environmental impacts due to marine sediment treatment (blue bars) were quantified considering the consumption of treatment agents and, again, the most environmentally advantageous were the ones with the smallest values. In consequence, from Fig. 4b one may notice that the quicklime treatment options have considerably smaller potential direct impacts (via pollutant leaching), compared to the cement treatment mixes. At the same time, the options involving the addition of activated carbon induced the greatest additional impacts, followed by the mixes with both activated carbon, then organoclay and finally, the lowest environmental impacts appeared when using only cement or quicklime, respectively.

3.2.3 Complete environmental profiles

The environmental analysis of the treatment options was refined to include data regarding all the steps; these environmental profiles were included in Figs. 6a and 6b, respectively.

Figure 6. Environmental profile of marine sediment treatment with (a) Mix 2 (cement 10%, GAC 5%) and (b) Mix 5 (quicklime 10%); Symbols in the figure are those presented in Table 5.

These results presented the fact that the determining treatment step in the total

environmental impact balance was the ex-situ treatment step, because it shows a great variability of impact values with changing treatment options. For example, in Fig. 5a the environmental profile of marine sediment treatment option 2, which is the least favourable option from an environmental point of view (mix with 10% cement, and 5% activated carbon), generated much higher impacts compared to the other treatment steps, as well as compared to the most favourable option (approximately one order of magnitude), which is presented in Fig. 5b. These higher impacts were associated in all the impact categories with the use of the activated carbon. This showed that the stabilization material has a high importance in this environmental balance (in most of the impact categories, as it can be seen in the snippet of Fig. 5a) and its choice and dosage can be a good option for the environmental optimization of marine sediments treatment options. This is supported by the fact that in the life cycle inventory, the activated carbon was modelled as being produced from a carbon-based source, thus giving the high impacts, whereas if it had been modelled from bio-based source the impacts would have been lower, as suggested in other studies (Sparrevik *et al.*, 2011).

The environmental impact profile of the most environmentally friendly treatment option (Mix 5), presented in Fig. 5a showed a more balanced distribution of impact contributors. Higher impacts appeared in the land use categories (NLT and ULO) due to landfilling and in the environmental pollution categories (FE, HT, Ftox, Mtox) mainly due to the use of solidification agents.

It was important to note that the pre-treatment operations which include the marine sediments dredging, transfers and storage account for small portions in the overall impact budgets.

3.2.4 Sensitivity analysis

The many uncertainty sources that arise in LCA studies are usually grouped into three categories (European Commission 2010): stochastic uncertainty, choice uncertainty. Stochastic uncertainty refers to inventory and assessment data uncertainty and is usually estimated with the help of probability distributions that statistically describe how a variable varies around a value (i.e. mean and standard deviation). Choice uncertainty refers to discrete values which usually are modelled in LCA as independent scenarios, while the lack of knowledge uncertainty reflects omission of data or incorrect assumptions (Sabia *et al.*, 2016).

Because in this study we consider only some stochastic uncertainties which refer to inventory data variability, the uncertainty analysis is restrained to a sensitivity analysis which considers the measured variability of key flows (i.e. pollutant releases and material consumption, measured as standard deviations) and default variability of background processes in the inventory (default standard deviations and probability distributions of flows in the Eco-Invent data base). While other sensitivity issues may be important, like impact assessment factors uncertainty, these were not included in our sensitivity analysis as all the scenarios were compared against the same reference (characterization factors).

The SA was performed to investigate how different contributor's variation affect the impact results by means of Monte Carlo simulations (in 10,000 points).

With respect to the input data, a preliminary sensitivity analysis was carried out in order to evaluate how different data quality aspects would impact the LCIA results. In particular, the impacts in the marine toxicity category (MTOX) were investigated for the reference case as a function of pollutant release data variability. This was investigated by developing 3 scenarios: 2 data scattering sets, (measured as 2 sets of standard deviation of the mean) and 1 scenario for the type of distribution (normal vs. uniform distributions). The configuration of the SA analysis and results are presented in Table 6.

Table 6. Sensitivity analysis for Marine ecotoxicity, reference case (sediment resuspension).

The first two input data sets refer to two independent sampling locations for which time series of determinations were performed (so they would fit a normal distribution), while the last one was obtained from samples collected all over the Mar Piccolo, and which were better described with a uniform distribution, due to their more random character. The output of Monte Carlo analysis show that the first two cases fit very well a normal distribution (indicated by the low chi squared values), and that the variability of results is very low (coefficient of variation of 1.31 %). For the third case, and the best fit was a beta probability distribution which describes better the much greater variability of the results (coefficient of variation of 27.78%). In terms of contributions, data in Table 6 shows that in all 3 cases the major source of variance is V, followed by Cu and Ni, while the other species have negligible impact on the variability of the total impact.

Individual SA were performed to investigate how different sources of variability influence the complex profiles that consider multiple environmental categories. In figure 7 a comparison of uncertainties between the option with the highest (mix 2) and smallest (mix 5) overall impacts is represented as percentage of variation (with a 95% confidence interval around the most probable value). Data shows in general low variability, the highest deviation is 23% for natural land transformation for mix 2, and 20% for freshwater eutrophication for mix 5, which indicates a high confidence in the LCA model and its results. The deviation profiles in Figure 7 are backed up by data regarding the contribution sources, for each impact category, which are presented in the Supplementary material (file S2) and may be explained by the relative low number of variables that generate a high

sensitivity in the majority of impact categories.

Figure 7. Uncertainty comparison between mix 2 and mix 5 (expressed as a variation coefficient calculated for a 95% confidence interval around the most probable value).

This SA was then used to compare the impact values obtained for the MS treatment options, especially in the categories where these impacts were closer. Data in Table 7 presents the results of Monte Carlo analysis, the goodness of fit parameters, and the probability for each impact category, showing that impacts of mix 2 are higher than those of mix 5 (for highest overall impacts and lowest ones, respectively). While for most categories, mix 2 has 100% chances to have higher impacts than mix 5, for ozone depletion this probability is only 63% and for natural land transformation is 86%, which indicates that interpretation of greater this data should be done attentively.

Table 7. Monte Carlo analysis comparison across multiple impact categories for the total impacts of mix 2 and mix 5.

4. CONCLUSIONS

This study approaches the environmental analysis of ex-situ marine sediment treatment options by stabilization-solidification with the use of the life cycle assessment methodology. The study is applied on sea region in the Mar Piccolo of Taranto in Italy, where the historic pollution with heavy metals and persistent organic pollutants cause significant impacts to the local sea-farming economies, as these pollutants that originate in the top-layer of the marine sediments tend to bio-accumulate in the tissues of some

molluscs that are commercially farmed in the area.

This research analyses from an environmental standpoint the potential impacts caused by all the marine sediment treatment steps (dredging, transport, transfer, storage, actual treatment and final disposal) and discusses the types and values environmental impacts that are associated to these processes.

By means of LCA it was possible to demonstrate that the ex-situ treatment of these marine sediments can lead to an improvement of the local situation. With respect to the evaluation of the treatment options it has to be noted that, based on their performances, these can diminish greatly the potential risks associated to metals leaching, but they induce additional impacts in various other categories that are associated to the use of stabilizers and solidification agents.

ACKNOWLEDGEMENTS

The study was carried out under the ERASMUS+ Agreement between the Polytechnic University of Bari and the "Gheorghe Asachi" Technical University of Iasi.

DECLARATION OF INTEREST

None

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Figures

Figure 1. The "Mar Piccolo of Taranto" study area (Southern Italy): sampling area, main phases of the intervention (dredging, intermediate storage and treatment) and the S/S pilot treatment plant located at the Taranto Bellavista municipal wastewater treatment plant.

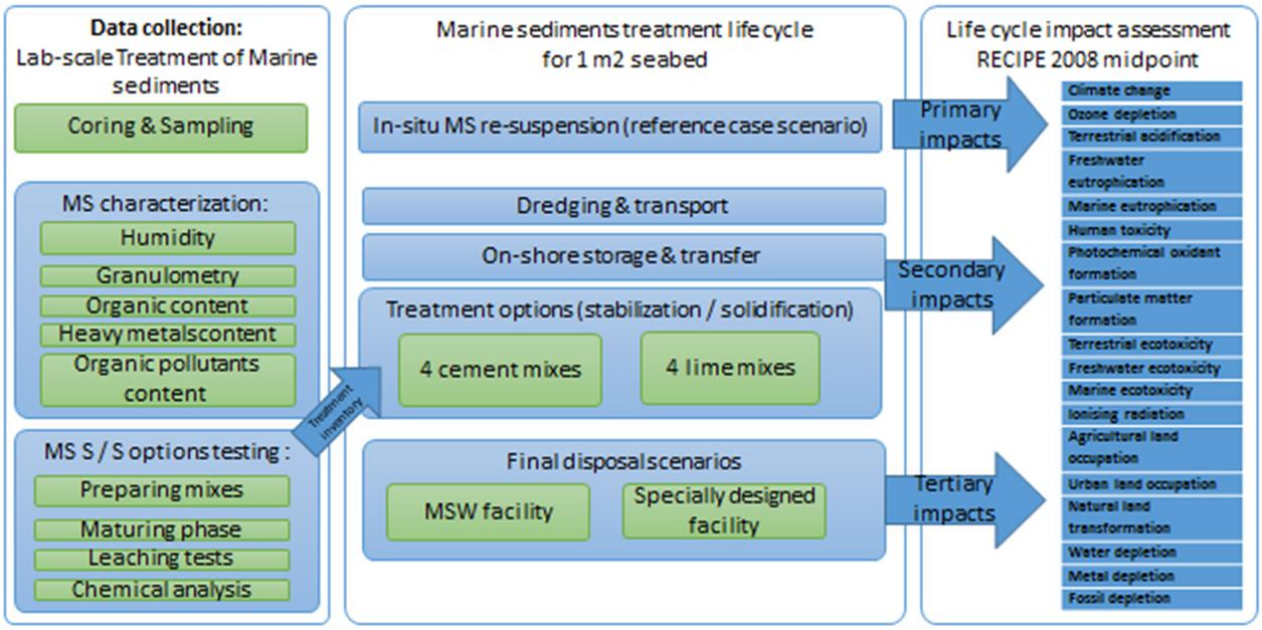


Figure 2. LCA framework for MS treatment and LCA approach.

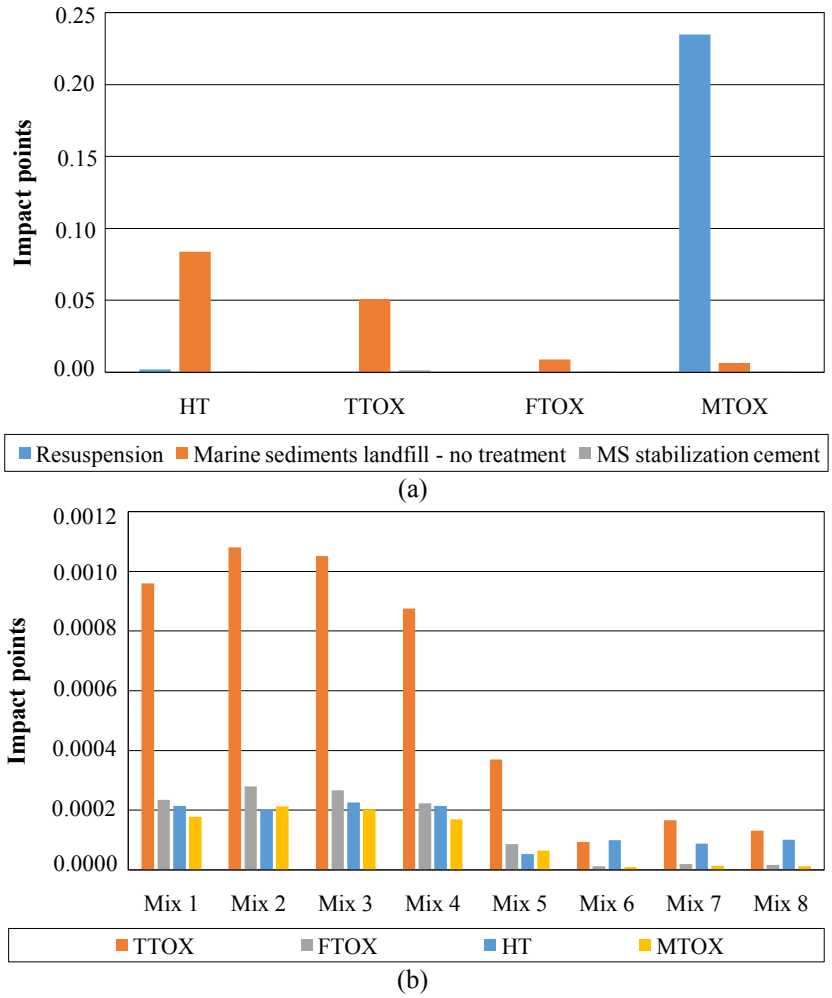
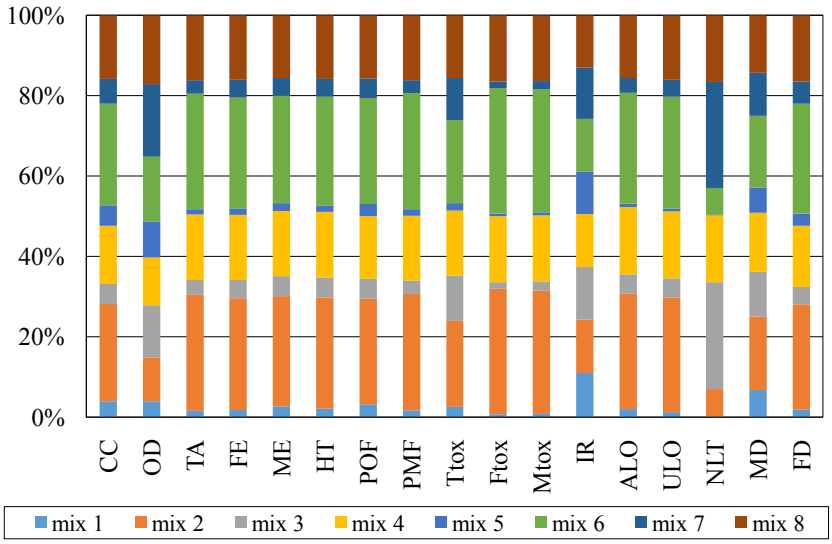
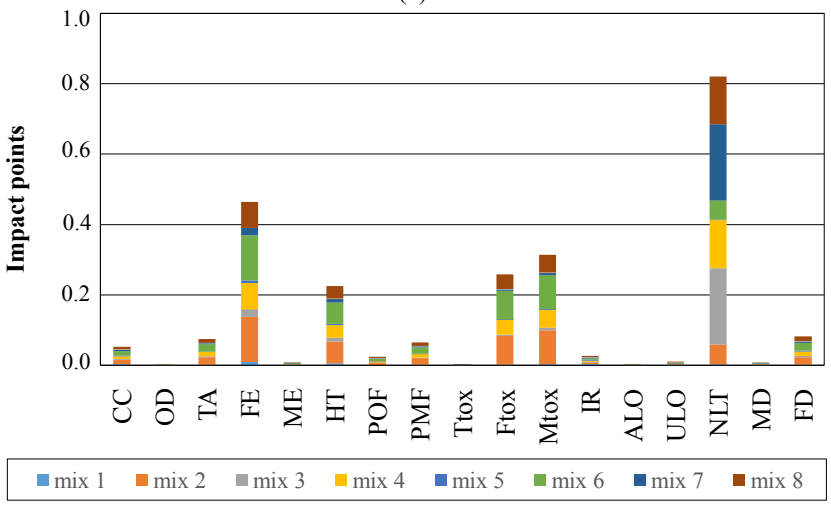


Figure 3. (a) Environmental comparison of three marine sediments management options; (b) Comparison of potential environmental impacts of various S/S options. Symbols in the figure: HT = Human toxicity; TTOX = Terrestrial ecotoxicity; FTOX = Freshwater ecotoxicity; MTOX = Marine ecotoxicity.



(a)



(b)

Figure 4. Potential additional impacts due to sediment treatment options (a) (characterization) and (b) (normalization); Symbols in the figure, as presented in Table 4.

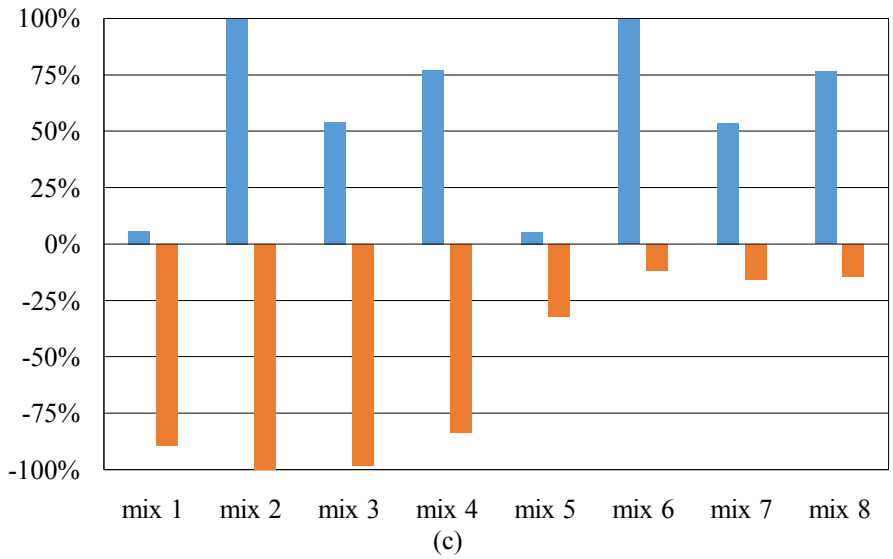


Figure 5. Comparison of secondary environmental impacts (treatment costs)/tertiary environmental impacts (benefices).

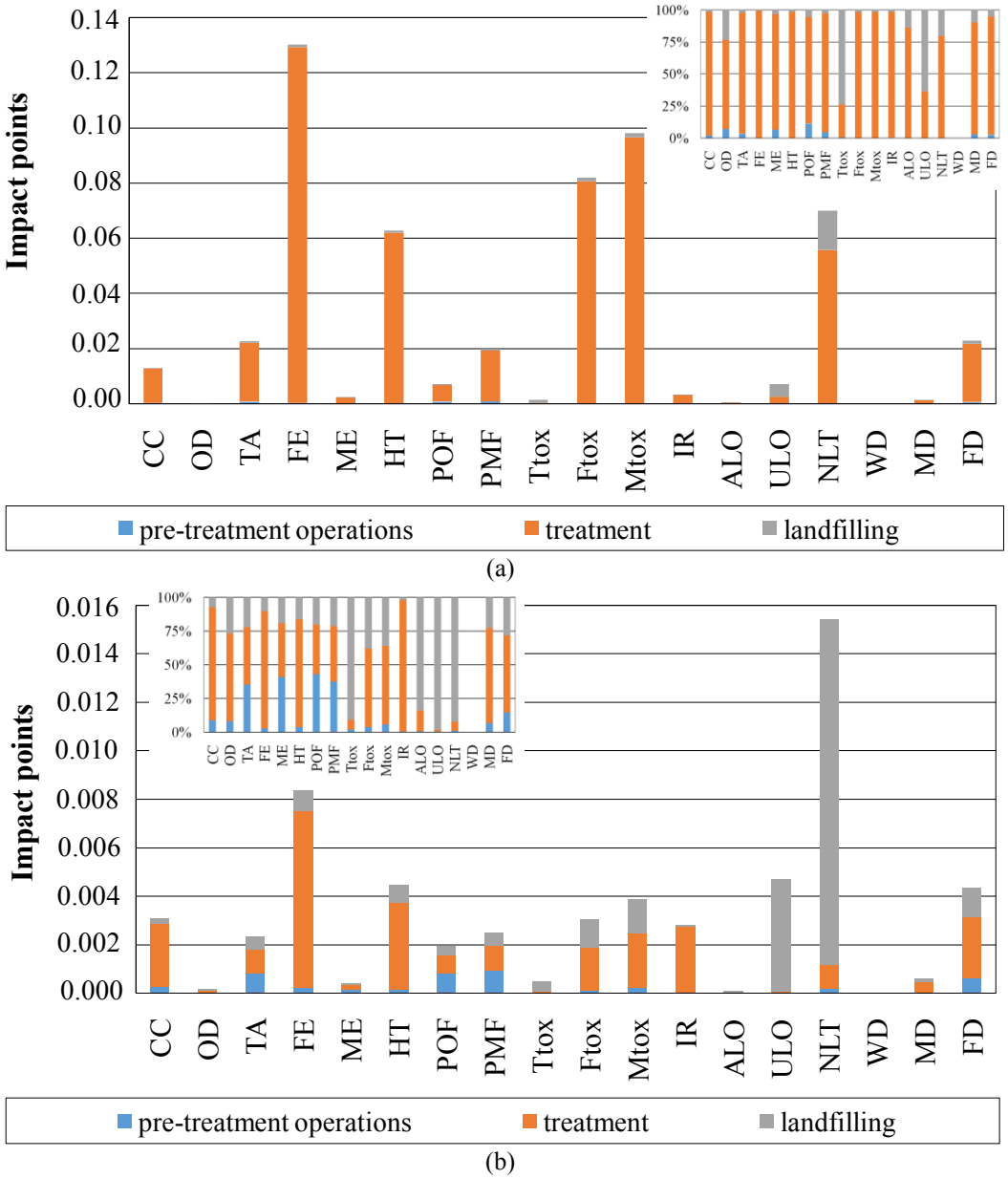


Figure 6. Environmental profile of marine sediment treatment with (a) Mix 2 (cement 10%, GAC 5%) and (b) Mix 5 (quicklime 10%). Symbols in the figure as those presented in Table 4.

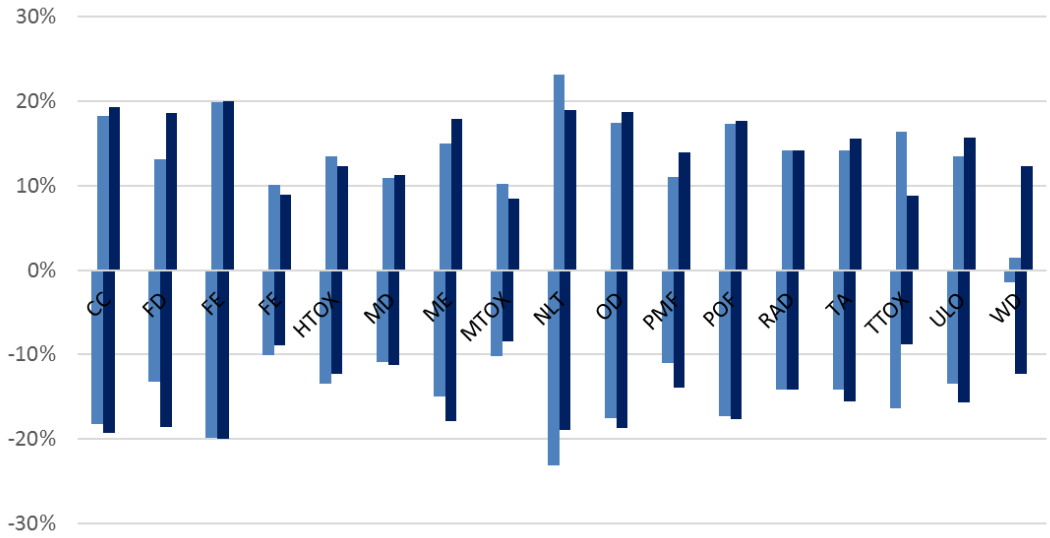


Figure 7. Uncertainty comparison between mix 2 and mix 5 (expressed as a variation coefficient calculated for a 95% confidence interval around the most probable value).

Tables

Table 1. LCA studies of marine sediments decontamination operations.

No.	Location/main contaminants	Goal and scope, functional unit (FU)	LCIA method	Results/impacts	Reference
1	Grenland fjord, Norway polluted with polychlorinated dibenzo-p-dioxins and -furans	Comparison of natural remediation and capping, and in-situ treatment with various materials FU: whole inner fjord area (23.4 km^2)	Modified Recipe to account for local toxicity conditions	Secondary impacts due to capping are higher than primary impacts (natural remediation)	Sparrevik *et al.* (2011)
2	London Olympic Park, London, UK. Sediments contaminated with lubricating range organics (LRO) and polycyclic aromatic hydrocarbons (PAHs)	Comparison of "primary impacts" associated with the state of the site (e.g. site contamination), "secondary impacts" associated with remediation operations, and "tertiary impacts" associated with the effects of the post-rehabilitation fate of the site FU: 2500 m of waterways for 100 years; 30,000 m^3 of sediment when evaluating the different treatment methods	IO-based hybrid LCA coupled with social and economic data. default ReCiPe endpoint method, hierarchist version for environmental assessment	adverse secondary environmental impacts can exceed environmental benefit resulting from contamination removal, but the consequential benefit (i.e. tertiary impact) resulting from site use change can far exceed the secondary environmental impact	Hou *et al.* (2014)
3.	Long Island Sound, NewYork, USA Dredged material is considered uncontaminated	Comparison of three types of placement alternatives (open water, containment island, and upland) for dredged material at three different transport distances. FU: 100,000 cubic yards (cy) of uncontaminated sediment	IMPACT 2002+ Recipe	Transport-related impacts (climate change, fossil fuel depletion, etc.)	Bates *et al.* (2015)
4	Hunters Point Shipyard, San Francisco (USA) polluted with polychlorinated biphenyls (PCBs)	Comparison of dredge-and-fill; capping, and in-situ activated carbon. FU: for 1000 m^2 of remediated area.	Eco-Indicator 95	Comparable impacts for dredge-and-fill and in-situ AC amendment using C-VAC, and smaller for capping.	Choi *et al.* (2016)
5	Augusta Bay (Sicily, Southern Italy), marine sediment contaminated with hydrocarbons	Evaluation decontamination by citric acid enhanced-microwave heating and electrokinetic processes. Dredging and transport not included FU: 1 ton of sediments	Impact 2002+	MW technology is 75.74% lower the electrokinetic decontamination Electricity consumption related impacts	Falciglia *et al.* (2018)

Table 2. Physical-chemical properties of the sediments samples used for the tests.

Parameter	Unit	Sample			Assessment			
		1	2	3	Min	Max	Average value	St. Dev.
pH	u. pH	8.50	8.62	8.98	8.50	8.98	8.70	±0.25
Eh	mV	-95.3	-103.0	-105.0	-105.0	-95.3	-101.1	±5.12
Conductivity	mS/cm	3.2	3.6	3.4	3.2	3.6	3.4	±0.20
Moisture content	%	45.1	42.7	46.9	42.7	46.9	44.9	±2.10
Ashes at 600°C	%	83.7	88.3	84.5	83.7	88.3	85.5	±2.50
Organic matter content	%	12.0	16.9	14.6	12.0	16.9	14.5	±2.50
Particle size distribution								
Sand fraction	%	19.4	15.3	23.1	15.3	23.1	19.3	±3.9
Silt fraction	%	43.2	42.0	44.4	42.0	44.4	43.2	±1.2
Clay fraction	%	37.4	42.7	32.5	32.5	42.7	37.5	±5.1
Metals								
As	mg/kgSS	11.85	11.90	11.92	11.85	11.92	11.89	±0.036
Co	mg/kgSS	7.07	7.10	7.10	7.07	7.10	7.09	±0.017
Cr	mg/kgSS	57.20	57.49	57.60	57.20	57.60	57.43	±0.207
Ni	mg/kgSS	38.80	38.90	38.55	38.55	38.90	38.75	±0.180
Pb	mg/kgSS	83.29	83.57	83.07	83.07	83.57	83.31	±0.251
V	mg/kgSS	57.35	57.38	57.02	57.02	57.38	57.25	±0.200
Cu	mg/kgSS	79.97	79.94	80.40	79.90	80.40	80.08	±0.278
Zn	mg/kgSS	205.08	205.93	206.24	205.08	206.24	205.75	±0.601

Table 3. Mixture design for S/S testing.

Mixture element	**Mixture design (% of dry sediment)**							
	Mix 1	**Mix 2**	**Mix 3**	**Mix 4**	**Mix 5**	**Mix 6**	**Mix 7**	**Mix 8**
Additive								
Portland cement	10.0	10.0	10.0	10.0	-	-	-	-
Lime	-	-	-	-	10.0	10.0	10.0	10.0
Reagent								
Activated Carbon	-	5.0	-	2.50	-	5.0	-	2.50
Organic Clay	-	-	5.0	2.50	-	-	5.0	2.50
A+R content[(a)]	10.0	15.0	15.0	15.0	10.0	15.0	15.0	15.0
Water content	70.0	70.0	70.0	70.0	70.0	70.0	70.0	70.0

[(a)]: Sum of the Additive (A) and Reagent (R) contents.

Table 4. Lab-Scale stabilization performance in terms of metals removal and leaching test.

Mixes	Parameter	Unit	Metals							
			As	**Co**	**Cr**	**Ni**	**Pb**	**V**	**Cu**	**Zn**
Mix 1	leachate concentration	mg/l	0.009	0.001	0.009	0.003	0.012	0.255	0.063	< LOD
	Stabilization potential[(a)]	%	99.924	99.986	99.984	99.992	99.985	99.555	99.921	100
	Stabilization goals[(b)]	-	✓	✓	✓	✓	✓	✗	✓	✓
Mix 2	leachate concentration	mg/l	0.007	< LOD[(d)]	0.011	< LOD	0.013	0.314	0.034	< LOD
	Stabilization potential	%	99.941	100	99.981	100	99.984	99.452	99.958	100
	Stabilization goals[(b)]	-	✓	✓	✓	✓	✓	✗	✓	✓
Mix 3	leachate concentration	mg/l	0.009	< LOD	0.010	0.002	0.013	0.297	0.045	< LOD
	Stabilization potential	%	99.924	100	99.983	99.995	99.984	99.481	99.944	100
	Stabilization goals[(b)]	-	✓	✓	✓	✓	✓	✗	✓	✓
Mix 4	leachate concentration	mg/l	0.009	< LOD	0.008	0.001	0.013	0.250	0.035	< LOD
	Stabilization potential	%	99.924	100	99.986	99.997	99.984	99.565	99.956	100
	Stabilization goals[(b)]	-	✓	✓	✓	✓	✓	✗	✓	✓
Mix 5	leachate concentration	mg/l	< LOD	0.001	0.010	0.005	0.008	0.086	0.089	< LOD
	Stabilization potential	%	100	99.986	99.983	99.987	99.990	99.850	99.889	100
	Stabilization goals[(b)]	-	✓	✓	✓	✓	✓	✓	✗	✓
Mix 6	leachate concentration	mg/l	0.006	< LOD	0.007	0.001	0.006	0.006	0.032	< LOD
	Stabilization potential	%	99.949	100	99.988	99.997	99.993	99.989	99.960	100
	Stabilization goals[(b)]	-	✓	✓	✓	✓	✓	✓	✓	✓
Mix 7	leachate concentration	mg/l	0.005	0.001	0.010	0.003	0.006	0.006	0.064	< LOD
	Stabilization potential	%	99.958	99.986	99.983	99.992	99.993	99.989	99.920	100
	Stabilization goals[(b)]	-	✓	✓	✓	✓	✓	✓	✗	✓
Mix 8	leachate concentration	mg/l	0.006	0.001	0.007	0.003	0.006	0.006	0.048	< LOD
	Stabilization potential	%	99.949	99.986	99.988	99.992	99.993	99.989	99.940	100
	Stabilization goals[(b)]	-	✓	✓	✓	✓	✓	✓	✓	✓
Legal limit value leaching test[(c)]		mg/l	0.05	0.25	0.05	0.01	0.05	0.25	0.05	3.00

Symbols in Table 4: [(a)]: Stabilization potential is evaluated as: % = $[(C_{TOT}-C_{LEACHATE})/C_{TOT}] \times 100$; [(b)]: Stabilization goals is evaluated: positively (✓) if the metal concentrations are lower than the limit of law; negatively (✗) if the metal concentrations are higher than the limit of law; [(c)]: According to the Ministerial Decree 5/02/1998; [(d)]: Limit of Detection (LOD) < 0.001 mg/l.

Table 5. Impacts categories defined in the Recipe 1.13. midpoint method.

N.	Impact Category	Symbol	Unit	Normalization values (European set)
1	Climate change	CC	kg CO_2 eq	0.0000892
2	Ozone depletion	OD	kg CFC-11 eq	45.4
3	Terrestrial acidification	TA	kg SO_2 eq	0.0291
4	Freshwater eutrophication	FE	kg P eq	2.41
5	Marine eutrophication	ME	kg N eq	0.0988
6	Human toxicity	HT	kg 1,4-DB eq	0.00159
7	Photochemical oxidant formation	POF	kg NMVOC	0.0176
8	Particulate matter formation	PMF	kg PM_{10} eq	0.0671
9	Terrestrial ecotoxicity	Ttox	kg 1,4-DB eq	0.121
10	Freshwater ecotoxicity	Ftox	kg 1,4-DB eq	0.091
11	Marine ecotoxicity	Mtox	kg 1,4-DB eq	0.115
12	Ionising radiation	IR	kBq U235 eq	0.00016
13	Agricultural land occupation	ALO	m^2a	0.000221
14	Urban land occupation	ULO	m^2a	0.00246
15	Natural land transformation	NLT	m^2	6.19
16	Water depletion	WD	m^3	0
17	Metal depletion	MD	kg Fe eq	0.0014
18	Fossil depletion	FD	kg oil eq	0.000643

Table 6. Sensitivity analysis for Marine ecotoxicity, reference case (sediment resuspension).

No	Substance	Input							Output							
		Scenario 1 normal			Scenario 2 normal		Scenario 3 uniform		Contribution to variance (%)			Parameter	Scenario 1	Scenario 2	Scenario 3	
		Mean	St. Dev. 1	CV (%)	St. Dev. 2	CV (%)	Min	Max	Scenario 1	Scenario 2	Scenario 3	Distribution	Normal	Normal	Beta	Normal
-	Total	5.57E-02	-	-	-	-	-	-				Most likely value	0.00901	0.00901	0.07849	0.08
1	Arsenic	1.75E-04	5.29E-07	0.303	5.29E-07	0.303	3.49E-05	8.93E-04	0.0	0.0	0.0	St. Dev.	0.000118	0.000122	0.021809	0.020000
2	Chromium	2.29E-05	8.00E-08	0.350	8.24E-08	0.360	5.84E-06	5.24E-05	0.0%	0.0	1.0	Skewness	-0.00318	-0.01914	0.01885	0.01880
3	Cobalt	8.70E-03	1.72E-05	0.197	2.09E-05	0.240	8.66E-03	8.73E-03	0.0%	1.8	0.0	Kurtosis	2.99	2.96523	2.24876	2.25000
4	Copper	7.54E-03	2.64E-05	0.350	2.62E-05	0.347	8.26E-04	3.64E-02	4.4%	4.3	20.8	CV	1.31%	1.36%	27.78%	27.78%
5	Lead	1.02E-05	3.07E-08	0.300	3.08E-08	0.301	9.43E-07	3.18E-05	0.0%	0.0	0.0	IL, 95%	0.0088	0.0088	0.0349	0.0400
6	Nickel	5.03E-03	1.51E-05	0.299	2.34E-05	0.465	1.58E-03	1.09E-02	1.4%	3.0	0.0	SL, 95%	0.0092	0.0093	0.1221	0.1200
7	Vanadium	3.28E-02	1.15E-04	0.349	1.15E-04	0.349	9.83E-03	7.51E-02	92.1%	90.8	77.8	MSE	1.2E-06	1.2E-06	0.000218	
8	Zinc	1.38E-03	3.46E-06	0.252	4.02E-06	0.292	1.31E-04	4.44E-03	0.1%	0.0	0.3	Chi sq.	74.434	56.8812	90.8176	488.76

Table 7. Monte Carlo analysis comparison across multiple impact categories for the total impacts of mix 2 and mix 5.

Impact category	Most probable value	St. Dev.	CV (%)	Most probable value	St. Dev.	CV (%)	P Mix 2 > mix 5 (%)
CC	199.47	18.250	9.1	86.88	8.366	9.6	100.0
FD	51.81	3.413	6.6	22.68	2.114	9.3	100.0
FE	0.06	0.006	10.0	0.01	0.001	10.0	100.0
FTOX	1.10	0.055	4.5	0.23	0.011	4.5	100.0
HTOX	45.95	3.102	6.8	9.19	0.567	6.2	100.0
MD	3.99	0.218	5.5	3.41	0.191	5.6	97.8
ME	0.05	0.004	7.5	0.03	0.002	8.9	100.0
MTOX	1.05	0.053	5.1	0.23	0.010	4.2	100.0
NLT	0.06	0.007	11.6	0.05	0.005	9.4	86.4
OD	0.00	0.000	8.7	0.00	0.000	9.4	63.0
PMF	0.47	0.026	5.5	0.21	0.015	6.9	100.0
POF	1.03	0.089	8.6	0.72	0.063	8.8	99.7
RAD	25.71	1.817	7.1	21.53	1.521	7.1	96.1
TA	1.18	0.084	7.1	0.48	0.037	7.8	100.0
TTOX	0.01	0.001	8.2	0.01	0.000	4.4	94.2
ULO	5.85	0.395	6.7	4.82	0.379	7.9	97.1
WD	3.31	0.024	0.7	1.54	0.095	6.2	100.0