

Heavy metal distribution in a sediment phytoremediation system at pilot scale

S. Doni^{a,*}

serena.doni@ise.cnr.it

C. Macci^a

E. Peruzzi^a

R. Iannelli^b

G. Masciandaro^a

^aNational Research Council, Institute of Ecosystem Study, [Via Moruzzi 1](#), 56124 Pisa, Italy

^bUniversity of Pisa, Department of Engineering for Energy, Systems, Territory and Constructions, [Via Gabba 22](#), 56122 Pisa, Italy

*Corresponding [tel: +39 0503152476](tel:+39-0503152476); [fax: +39 050312473](tel:+39-050312473) author. Tel.: +39 0 503152476; fax: +39 0 503152473.

Abstract

The continuous stream of polluted sediments, dredged from harbors and water bodies in order to maintain the navigation, is a common practice, but the fate of these sediments is an issue recognized worldwide. This pilot case study evaluated the application of phytoremediation as sustainable management strategy for the decontamination of polluted dredged marine sediments.

The treatments were based on the use of different plant species (*Paspalum vaginatum* Sw.; *P. vaginatum* Sw. + *Spartium junceum* L. and *P. vaginatum* Sw. + *Tamarix gallica* L.) and organic matter (compost). The synergic action of plants and compost in removing both heavy metals (Cd, Ni, Zn, Pb and Cu) and total petroleum hydrocarbons, and in recovering the nutritive and biological sediment properties were evaluated. In addition to the detection of total metal removal efficiency, the chemical distribution of metals in the sediment phases (exchangeable, manganese and iron oxides, organic matter and residual minerals) was also measured in order to make a more realistic estimation of the phytoremediation efficiency for the sediment decontamination. Finally, a complete picture of the metal flux was obtained by investigating the metal mass-balance in the treated sediments. The results of metal content in the sediment phases showed that metal distribution was not uniform and each metal predominated in different fractions; the bioavailability of metals in the initial and treated sediments at 0–20 cm in the decreasing order was: Cd > Zn > Cu > Pb > Zn > Cu > Pb > Ni. The higher proportion of Ni and Pb in the residual phase can be the reason of the lower translocation of these metals in the plant tissues. On the other hand, Cd, Zn and Cu were the metals most easily translocated in plant tissues, both aboveground and roots, confirming their higher bioavailability for the plants.

The results of mass balance indicated that, at the end of the experimentation, a high content of metals were still found in the sediment. The greatest contribution in metal containment was attributed to a phytostabilization process at rhizosphere level followed by gravel and sand absorption. The capacity of rhizosphere to precipitate heavy metals, could be considered as an alternative option for reducing the metal availability and, consequently, the toxicity in contaminated sediments.

Keywords: Sediment decontamination; Organic and inorganic contaminants; Translocation factor; Bioaccumulation factor; Metal fractionation; Mass balance

1 Introduction

A large amount of sediments is dredged every year from ports and waterways in order to maintain adequate depths for ship navigation, but the fate of these sediments is an issue worldwide recognized. Usually, dredged sediments are disposed in specific facilities and may cause environmental problems due to their contamination by metals and organic compounds. Marine sediments, especially in coastal and estuarine regions in the vicinity of urban and harbor areas, are, in fact, becoming increasingly polluted with heavy metals (Loring and Rantala, 1992; Szefer et al., 1995).

Phytoremediation, which involves plants and their associated microorganisms to stabilize or reduce contamination, is a low-cost and environmental friendly technology of soil restoration, targeting phytoextraction, phytodegradation or phytostabilization of contaminants (Schwitzer et al., 2009). The three different plant-based technologies of phytoremediation, each having a different mechanism of action for remediating polluted matrices generally include: (1)

phytoextraction, in which plants absorb metals from soil and sediment and translocate them to harvestable shoots where they accumulate (2) phytodegradation, utilizing plants to degrade organic contaminants from soil and sediment; and (3) phytostabilization, where plants stabilize, rather than remove contaminants by plant root metal retention.

Compared to physico-chemical and engineering techniques, phytoremediation represents an attractive alternative for low or medium polluted matrices decontamination which, in addition, results in increased ecosystem fertility by promoting restoration and biodiversity (Mench et al., 2010; Vangronsveld et al., 2009). However, phytoremediation is still regarded as an emerging technology that has to prove its sustainability for dredged sediment treatment (Bert et al., 2009; Doni et al., 2013).

The proper selection of plants is crucial for phytoremediation success on contaminated sediments due to specific traits and conditions of sediments (e.g., moisture, flooding, elevated organic matter, clay, and salinity); in view of this, the selection of potential plants to be used in sediments reclamation should not be based solely on plant metal uptake capacity, but also on the basis of their ecological adaptability (Antoniadis and Alloway, 2001; Moreno et al., 2002).

King et al. (2006) reported cases of failed phytoremediation application to canal sediments due to low metal uptake and high mortality of various tree species, such as poplars, willows, and alders. However, Vervaeke et al. (2003) showed that hydraulically raised dredged sediment can be successfully planted with willow species.

In some previous experiments, organic residues and liming materials were added to sediment in order to attenuate the phytotoxic effect (Adriano et al., 2004; Brown et al., 2005). Similarly, several authors reported that the application of inorganic fertilizer in combination with compost was effective in providing nutrients and organic matter for plant growth in degraded sites or metal-rich substrates (De Coninck and Karam, 2008).

The plants *Tamarix gallica* L. and *Spartium junceum* L. have shown an extensive capability of adaptation to adverse environmental conditions. These plants have been able to colonize marginal areas and contaminated soil (Moreno-Jimenez et al., 2011; Muzzi and Fabbri, 2007). In addition, in two mesoscale phytoremediation studies on marine and brackish dredged sediments, *Tamarix gallica* L. and *Spartium gallica* L. and *S. junceum* L. in combination with *Paspalum vaginatum* Sw. were effective in decontaminating polluted sediments from both organic and inorganic pollutants (Bianchi et al., 2010; Doni et al., 2013). Nevertheless, in both these studies, the preliminary bio-physical conditioning of sediments by mixing the sediment with a sandy soil and by applying green compost have been necessary in order to obtain the proper establishment of plants.

The purpose of this paper is to approach the phytoremediation for the decontamination of dredged marine sediments. The efficiency of different plant species in association with compost for phytoremediating contaminated sediments was investigated at pilot scale experiment. The plants *Tamarix gallica* L. and *Spartium gallica* L. and *S. junceum* L. in combination with the grass *Paspalum vaginatum* Sw. were selected on the basis of the previous results at mesoscale level. In order to obtain a better insight of the expected period of time for sediment decontamination, the heavy metal content in the different compartments of the system (sediment, leachate, draining layer, rhizosphere, and plant tissues) and the mass balance were calculated.

2 Materials and Methods

2.1 Experimental layout

Polluted marine sediments were dredged from the port of Livorno (Centre of Italy, 43°33'25"N, 10°17'39"E). These sediments were mixed with a sandy soil (calculated as 30% in volume) to improve the particle size composition. The construction of the facility (19 m length, 5 m width and 1.3 m depth, 1.3 m depth, and volume 110 m³) was performed on December 2009 in the Livorno's harbour area (Figure's harbour area (Fig. 1)). The treatment basin was lined with a low and high density polyethylene composite (LDPE-HDPE) waterproof membrane to prevent the leachate from draining into the ground and ensure the correct inflow-outflow water balance. A 30 cm draining layer made of gravel (32.7 tons, 0.8 d_{50} ≤ 20 mm) and sand (20.3 tons, 1 d_{50} ≤ 3 mm) was hand laid on the bottom of the facility before filling it with the soil-sediments mixture. The facility was designed to treat about 80 m³ of sediments, previously mixed with 24 m³ of soil (146 tons). Finally, the top of the soil-sediment mixture was mixed with 4 kg m⁻² of compost in order to favor the initial plant adaptation and growth. The main characteristics of sediment, soil, compost, and soil-sediment mixture used for the experimentation are shown in Table 1. The heavy metals (Zn, Pb, Ni, Cu, and Cd) in the initial sediment were higher (more than two fold) with respect to the reference sediments collected outside from the port of Livorno (average values of ten sampling points: 108 mg Zn kg⁻¹; 38 mg Pb kg⁻¹; 26 mg Ni kg⁻¹; 27 mg Cu kg⁻¹ and 0.5 mg Cd kg⁻¹), thus, revealing the contamination of sediments from anthropogenic sources. On the basis of the contamination factor (2.2–3.2), geoaccumulation index (1–1.45), and pollution load index (2.7), the initial sediment can be considered "moderate polluted" (Chakraborty et al., 2014).

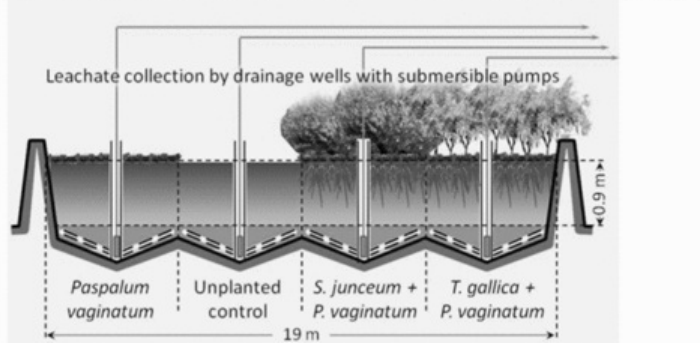


Figure 1 Plan view of the facility.

Table 1 Main characteristics of sediment, soil, compost, and soil-sediment mixture used for the experimentation.

	Sediment	Soil	Compost	Mix soil-sediment
Clay (%) 38.0 ± 0.7	38.0 ± 0.7	4.6 ± 0.4	—	18.8 ± 2.0
Silt (%) 46.5 ± 1.1	46.5 ± 1.1	26.2 ± 1.6	—	25.0 ± 0.7
Sand (%) 15.4 ± 0.3	15.4 ± 0.3	69.2 ± 1.1	—	56.2 ± 2.7
pH 7.78 ± 0.05	7.78 ± 0.05	7.99 ± 0.05	6.92 ± 0.1	7.1 ± 0.1
E.C. (dS m ⁻¹) 201 ± 10	201 ± 103.69 ± 0.421.9 ± 0.2 (%)1.20 ± 0.040.075 ± 0.00945.1 ± 0.40.860 ± 0.07 (%)0.119 ± 0.00801.49 ± 0.060.078 ± 0.002	201 ± 10	3.69 ± 0.42	1.9 ± 0.2
TOC (%) 1.20 ± 0.04	1.20 ± 0.04	0.075 ± 0.009	45.1 ± 0.4	0.860 ± 0.07
TN (%) 0.119 ± 0.008	0.119 ± 0.008	0	1.49 ± 0.06	0.078 ± 0.002
TEC (%)	—	—	5.9	—
FA (%)	—	—	3.4	—
HA (%)	—	—	2.5	—
TP (mg P kg ⁻¹) 640 ± 21	640 ± 21	197 ± 10	2015 ± 27	536 ± 17
Cd (mg Cd kg ⁻¹) 1.55 ± 0.18	1.55 ± 0.18	—	1.44 ± 0.12	1.43 ± 0.08

Cu (mg Cu kg ⁻¹)	65 ± 4	=	80.7 ± 9.6	52.0 ± 3.4
Zn (mg Zn kg ⁻¹)	278 ± 24	=	258 ± 16	256 ± 17
Ni (mg Ni kg ⁻¹)	84 ± 5	=	21.7 ± 2.3	63.0 ± 9.5
Pb (mg Pb kg ⁻¹)	83 ± 6	=	35.5 ± 7.7	64.0 ± 8.6
TPH (mg TPH kg ⁻¹)	1566 ± 67	=	=	1430 ± 96

E.C., electrical conductivity; TOC, total organic carbon; TN, total nitrogen; TP, total phosphorus; and TPH, total petroleum hydrocarbon. Standard reference material: SRM (92–108% recovery), Continuing check standard, CSTD (93–109%), Lablab, spike blank, LSB (94–105%), Lablab, spike matrix, LSM (89–112%). Limits of quantification (LOQ) (mg l⁻¹): Cd 0.008, Cu 0.006, Zn 0.013, Ni 0.02, and Pb 0.06.

In May 2010, four areas of about 5 m × 5 m × 5 m each were marked out in the facility and planted as follows: (1) *Paspalum vaginatum* P. *vaginatum* Sw. (P treatment); (2) Control (unplanted); (3) *Paspalum vaginatum* Sw. + *Spartium junceum* L. (P+S treatment); (4) *Paspalum vaginatum* Sw. + *Tamarix gallica* L. (P+T treatment) (Figure 1). *P. vaginatum* Sw. + *S. junceum* L. (P + S treatment); (4) *P. vaginatum* Sw. + *T. gallica* L. (P + T treatment) (Fig. 1).

The pilot system was monitored for two years after planting by performing sediment samplings twice a year: two weeks (June 2010), six weeks (June 2010), 6 months (December 2010), one year (June 2011), eighteen months (June 2011), 18 months (December 2011) and two and two years (June 2012) after the experiment set up. In the present paper, the results of the initial sampling time (June 2010, T_i) and after two years from the beginning of the experimentation (June 2012, T_f) are reported.

Each sediment sample was a composite of three sub-samples collected at 25 cm from shrub plant trunk mixed, homogenized, sieved (2 mm), dried and stored at room temperature until chemical analysis, and stored at 4 °C until biological analysis. Three composite sediment samples for each treatment were collected at surface (0–20 cm) and subsurfaces (20–40 cm and 40–60 cm) layers and analyzed separately.

2.2 Analytical methods

Electrical conductivity (E.C.) and pH were measured in a 1/10 (w/v) aqueous solution. Particle size distribution (<700 μm) was measured using a laser light diffraction device X100 (Microtrac Inc., U.S.A.). Total organic C and total N contents were determined by dry combustion with a RC-412 multiphase carbon and a FP-528 protein/nitrogen analyzer, respectively (LECO corporation). Total Fe was measured using the method reported by Murphy and Riley (1962). Heavy metal concentration analysis was performed by atomic absorption spectrometry using a ContrAA300 (Analytical Jena) spectrometer with air/acetylene flame. Total petroleum hydrocarbons (TPH) were determined by the gravimetric method 1664 (US Environmental Protection Agency, EPA 1983; APHA-American Public Health Association 1992) using *n*-pentane instead of *n*-hexane, as modified by Ceccanti et al. (2006).

Dehydrogenase activity was determined by the method of Masciandaro et al. (2000). To test dehydrogenase activity, 0.4% of INT (2-*p*-iodophenyl-3-*p*-iodophenyl-5-*p*-nitrophenyl-4-*p*-nitrophenyl-5-phenyltetrazolium chloride) was used as substrate. The INTF (iodonitrotetrazolium formazan) released as product of dehydrogenase activity was extracted and determined spectrophotometrically at 490 nm. Colony forming units (CFU) were determined in aqueous solutions (1:10 w/v sediment:water solution) based on the surface-plate counting procedure (Jayasekara et al., 1998). The extraction was carried out in tubes with sterile water by vortexing for 2 min at room temperature. Serial dilutions were made for the extracts using distilled water. A volume of 0.2 ml was spread onto plates prepared with plate count agar (Sigma-Aldrich) as adequate growing medium. Plates were incubated at 29 °C for 48 hours and the number of CFU per gram of sediment were calculated.

At the end of the experimentation, roots and aboveground parts of the selected plant species were harvested and carefully washed with distilled water. The whole plant of *Paspalum vaginatum* Sw. and the aboveground and root of *Spartium junceum* L. and *Tamarix gallica* L. separately were analyzed. Fresh and oven dry (55 °C, 72 h) biomass were determined. Oven-dried plant material was finely milled prior to hot digestion. Samples were digested with hydrogen peroxide–nitric acid (H₂O₂/HNO₃ 1:3) in microwave.

A three-step sequential extraction technique was used to determine the chemical association of heavy metals (Cd, Cu, Ni, Pb, and Zn) with major sediment phases (exchangeable, manganese and iron oxides, organic matter and residual minerals) at the beginning and at the end of the experimentation at surface layer (0–20 cm). The total metal content was also determined.

The procedure for fractionation differentiated the sediment heavy metals into the following fractions:

1. Exchangeable fraction associated with carbonated phase (Fraction 1). Metals are adsorbed on the sediment components and Fe and Mn hydroxides. This is the most mobile fraction potentially toxic for plants.
2. Reducible fraction associated with Fe and Mn oxides (Fraction 2). Heavy metals are strongly bound to these oxides but are thermodynamically unstable in anoxic and acidic conditions.
3. Oxidizable fraction bound to organic matter (Fraction 3). It is well known that metals may be complexed by natural organic substances. These forms become soluble when organic matter is degraded in oxidizing conditions. This fraction is not considered to be bioavailable and mobile because the metals are incorporated into stable high molecular weight humic substances, which release small amounts of metals very slowly.

0-20 cm	P	7.93aA	8.09aB	1.24aA	1.32aA	2.26aB	1.72bB	647aB	458b	0.133aC	0.134aA
	C	7.84aA	8.16AaB	1.42aA	1.02bB	3.03aA	1.28bC	813aA	444b	0.240aA	0.106bB
	P+ \pm S	7.95bA	8.35aA	1.20aA	1.00bB	2.44aB	1.99bA	655aB	364b	0.152aB	0.139aA
	P+ \pm T	7.95bA	8.51aA	1.28aA	0.66bC	2.69bAB	2.11bA	658aB	439b	0.143aBC	0.129aA
20-40 cm	P	7.70bA	8.22aA	2.15aA	1.49bA	1.25aB	0.99bA	380aB	309bC	0.057bA	0.078aB
	C	7.77bA	8.20aA	1.73aB	1.36bA	1.31aAB	1.09bA	316bB	358aB	0.045bA	0.069aB
	P+ \pm S	7.73bA	8.45aA	2.19aA	1.12bB	1.68aA	0.93bA	301bB	353aB	0.053bA	0.111aA
	P+ \pm T	7.72bA	8.48aA	1.66aB	1.07bB	1.40aA	0.89bA	506aA	384bA	0.052aA	0.068aB
40-60 cm	P	7.78aA	8.07aB	2.08aA	1.73bA	1.28aA	0.86bA	527aA	422bB	0.046aA	0.055aB
	C	7.91aA	8.15aB	1.95aA	1.36bB	1.25aA	0.92bA	470aA	426bB	0.036aA	0.045aB
	P+ \pm S	7.89bA	8.43aA	1.86aA	1.47bB	1.22aA	0.90bA	420bB	502aA	0.042bA	0.089aA
	P+ \pm T	7.98bA	8.50aA	1.12aB	1.28aB	1.21aA	0.89bA	385bB	510aA	0.043aA	0.049aB

E.C., ~~Electrical Conductivity~~; ~~TOC, Total Organic Carbon~~; ~~TP, Total Phosphorus~~; ~~TN, Total Nelectrical conductivity~~; ~~TOC, total organic carbon~~; ~~TP, totalphosphorus~~; and ~~TN, total nitrogen~~. Values are the average of three replicates; coefficient of variation of the three replicates ranging from 3 to 10%. The lower case letters indicate significant differences ($P < P \leq 0.05$) between the sampling times of each treatment. The capital letters indicate significant differences ($P < P \leq 0.05$) between the treatments at the same sampling time (P, C, P+S and P+ \pm S and P+ \pm T) in each depth (0-20, 20-40, and 40-60 cm).

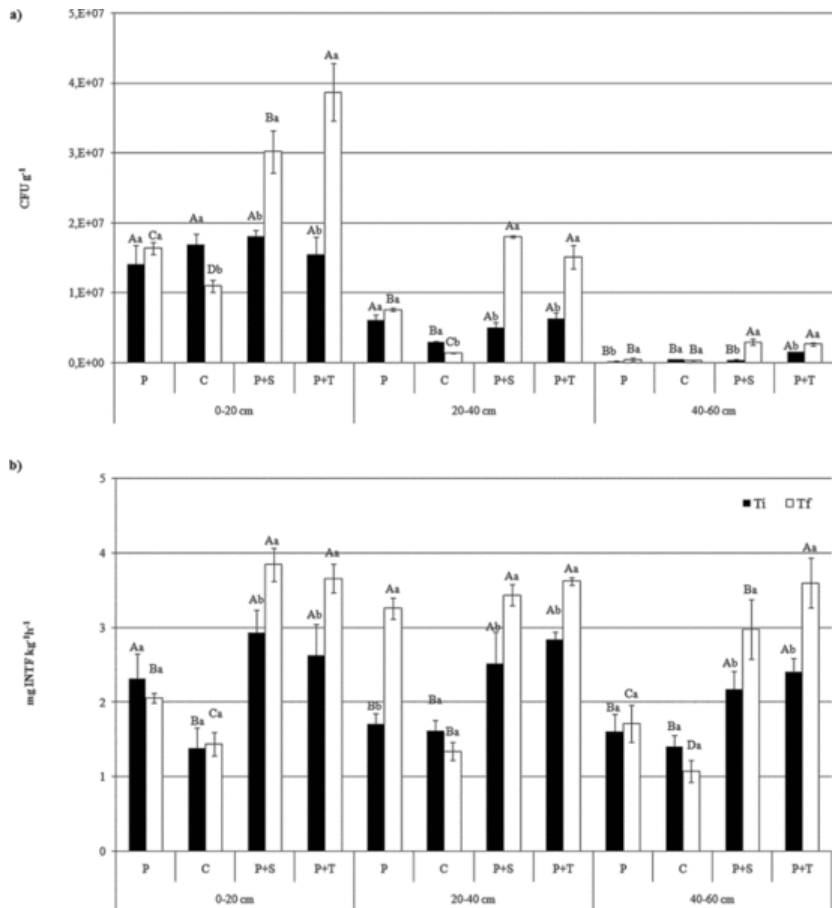


Figure 2 (a) Total cultivable microbial population (CFU: Colony Forming Unit) and (b) dehydrogenase activity at the initial (Ti) and final (Tf) sampling times in the different plant treatments at the three depths (0-20, 20-40 and 40-60 cm).

Values are the average of three replicates \pm standard deviation. The lower case letters indicate significant differences ($P < 0.05$) between the sampling times of each treatment. The capital letters indicate significant differences ($P < 0.05$) between the treatments (P, C, P+S and P+T) at the same sampling time in each depth (0-20, 20-40 and 40-60 cm). Ti, June 2010; Tf, June 2012, P *Paspalum vaginatum* Sw., C control, P+S *Paspalum vaginatum* Sw. + *Spartium junceum* L., P+T *Paspalum vaginatum* Sw. + *Tamarix gallica* L.

The count of total cultivable microbial population, although too general, has been usually used to give an idea of the total microbial number, especially when different treatments are compared (Delorme et al., 2001). In the present study, the reactivation of microbial populations, in terms of microorganism abundance (CFU, Colony Forming Unit), depended on the selected plant species for revegetation, with *S. junceum* L. and *T. gallica* L. treatments (P+T and P+S) being more efficient in improving the microbiological properties of the sediment (Figure 2a). In addition, being the organic contaminant degradation carried out by microorganisms as a part of their metabolic processes, an higher decontamination capability of these treatments is expected.

Nevertheless, it is nowadays well known that most of the diverse bacterial colonies and biomasses, especially in soils and sediments, are represented by uncultivable bacteria (Kennedy et al., 2008). In view of this, the number of cultivable microorganisms should not reflect the overall microbiological status of sediments.

In line with microbial population trend, dehydrogenase activity, which is considered a direct measure of the microbial population growth and activity (Garcia et al., 1997a), was significantly higher in the planted sediments, in particular in P+S and P+T treatments (Figure 2b). This enzyme activity has been considered as a sensitive indicator of soil quality in degraded soils and it has been proposed as a valid biomarker to indicate the changes in total microbial activity due to changes in management of soil (Ceccanti et al., 1994), sediment (Bianchi et al., 2010), and other matrices (Peruzzi et al., 2013).

3.2 Organic contaminants in sediments

After two years (Tf), at sediment surface (0–20 cm), TPH degradation was most pronounced in the shrub (P+T and P+S) treatments (reduction of about 60%) with respect to P and control treatments (reduction of about 50%) (Figure 3). The fact that the control treatment showed a similar TPH-degradation efficiency to that of P treatment, suggested the positive effect of organic matter application in supporting the growth and metabolic activities of microorganisms capable of degrading organic contaminants. The effectiveness of organic fertilizers in enhancing total petroleum hydrocarbon degradation in environmental matrices, such soil and sediments, has been extensively reported in previous studies (Ceccanti et al., 2006; Choi et al., 2002; Doni et al., 2012; Kim et al., 2005; Okolo et al., 2005).

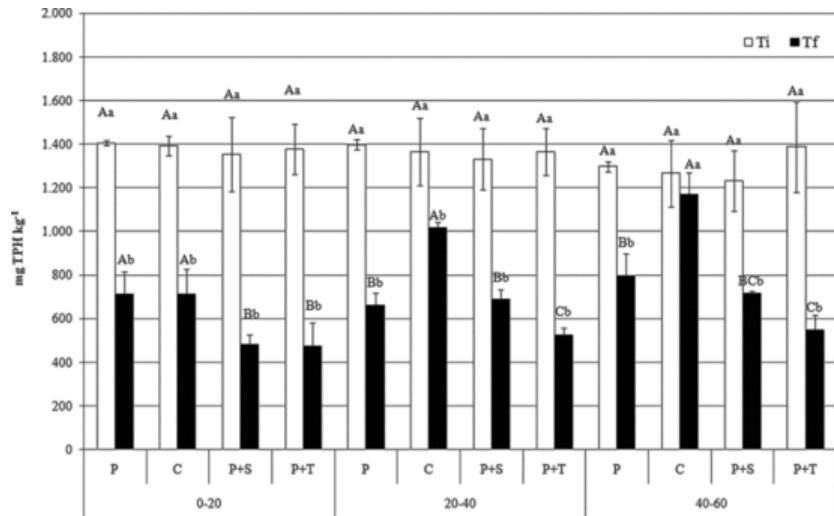


Figure 3 Total petroleum hydrocarbons (TPHs) at the initial (Ti) and final (Tf) sampling times in the different plant treatments at the three depths (0–20, 20–40 and 40–60 cm).

Values are the average of three replicates ± standard deviation. The lower case letters indicate significant differences ($P < 0.05$) between the sampling times of each treatment. The capital letters indicate significant differences ($P < 0.05$) between the treatments (P, C, P+S and P+T) at the same sampling time in each depth (0–20, 20–40 and 40–60 cm). Ti, June 2010; Tf, June 2012, P *Paspalum vaginatum* Sw., C control, P+S *Paspalum vaginatum* Sw. + *Spartium junceum* L., P+T *Paspalum vaginatum* Sw. + *Tamarix gallica* L.

In addition, the higher microbial activity and TPH degradation in planted sediments with respect to control at 20–40 cm depth, indicated the positive influence of plant rhizosphere. Probably, plants release root exudates which may serve as a carbon and nitrogen sources to support the growth and activities of microorganisms, and/or accumulate organic pollutants in plant tissues (Anderson et al., 1993). The ability of vegetation cover in accelerating the disappearance of organic contaminants at root zone is confirmed by the general decrease in TPH degradation with increasing depth (from 0–20 cm to 20–40 cm to 40–60 cm), especially in the sediment without plants (control treatment). In fact, at 40–60 cm depth, TPH concentration significantly decreased more than 40% in the planted sediments, in particular in P+T and P+S treatments, while a degradation of only 13% was observed in the control sediment (Figure 3).

3.3 Heavy metals in sediments

Geochemical fractionation of heavy metals in sediments at the initial and final sampling times was performed in order to assess the degree of their association and to what extent they may be remobilized into the environment. This is of particular relevance for both in-situ immobilization, aiming at reducing the plant-available heavy metal fraction and, thus, their uptake by plants, and phytoextraction, where information on the plant-available fraction is a prerequisite to predict the efficiency of the remediation.

Figure 4 shows, in percent bar graphs, the distribution of the heavy metals in the four fractions obtained by the sequential extraction procedure in the control sediment at the start (C-Ti) and in the plant treatments at the end (Tf) of the experimentation at surface layer (0–20 cm). The results showed that metal distribution pattern was not uniform and that each metal predominates in different forms in the sediment. Ni was strongly associated with the residual fraction (>60%). At the beginning of the experimentation (C-Ti), Ni bound to organic matter, Mn and Fe oxides and exchangeable fractions were 14%, 8% and 7%, respectively. The distribution of this metal is consistent with the findings of an earlier study carried out on contaminated soils (Olajire et al., 2003). Similarly, Pb was mainly found in the residual fraction (>50%); in the control sediment at the initial sampling time the amount of Pb in the other fractions was in the following order: Mn and Fe oxides (31%) > organic fraction (12%) > exchangeable (7%). On the other hand, Cd was mainly found in the exchangeable (>40%) and Mn and Fe oxides (>35%) and thus, can be considered available for uptake by the total biota. Other authors have found a higher content of Cd in the exchangeable fraction of sediments (Turki 2007; Zhang et al., 2012; Li et al., 2007). In the initial control sediment (C-Ti), the chemical partitioning of Zn was similar to Cd behaviour. The percentage of Zn associated with different fraction distribution, such as for Cd, was in the order: exchangeable > Mn and Fe oxides > organic > residual. Generally Zn in acidic soil had a high percentage of exchangeable fraction (Hseu, 2006). The extent to which the metals are present in the exchangeable fraction is, in fact, influenced by soil properties, such as pH, cation exchange capacity, etc. Cu is well known to be predominantly associated with the organic matter fraction due to the high affinity and stability of organic-Cu complexes (Amir et al., 2005; Fuentes et al., 2004). In this study, the control sediment at the

initial sampling time showed 35% of total Cu in this fraction. Several studies reported high concentration of Cu associated with organic matter in sediments (Fytianos and Lorantou, 2004; Ramirez et al., 2005; Arias et al., 2007; Wong et al., 2007). In this sediment sample, a similar content of Cu (39%) was observed in the residual fraction, indicating that Cu was also probably occluded in the minerals, as suggested for sludge matrix by Fuentes et al. (2004). The residual fraction consists, in fact, in metals incorporated into the crystalline structures of primary and secondary minerals.

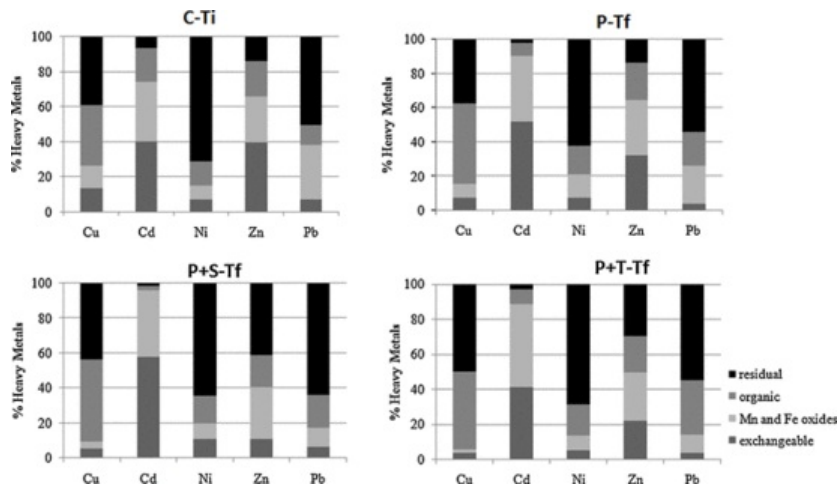


Figure 4 Heavy metal fractionation at the initial and final sampling times at surface layer (0–20 cm).

Ti, June 2010; Tf, June 2012, P *Paspalum vaginatum* Sw., C control, P+S *Paspalum vaginatum* Sw. + *Spartium junceum* L., P+T *Paspalum vaginatum* Sw. + *Tamarix gallica* L.

The different plant treatments showed, over time, a similar evolution of the heavy metal distribution in the four fractions. In particular, an increase of Pb and Cu in the organic fraction of all plant treatments and of Zn in the residual fraction of P+S and P+T treatments was observed at surface layer (0–20 cm). Conflicting results were found on the influence of plants and their associated microorganisms on metal leaching from contaminated soils. Plants were found to exhibit both mobilizing and immobilizing effects on metals in the root zone. These effects depended on the plant species, the metal type, the soil properties, and the experimental setup (Nowack et al., 2010).

Summarizing, the bioavailability of metals in the sediments in the decreasing order was: Cd > Zn > Cu > Pb > Ni. The higher presence of Cd and Zn in labile fraction and of Ni in residual fraction in sediments have been previously reported (Velimirović et al., 2011).

Total Ni and Pb reduction percentages in planted sediments were, at surface layer (8–19% and 6–19% and 6–12%, respectively), lower than those of Cu (31–36%) and Zn (13–32%) and Cd (6–36%) and Zn (13–32%) and Cd (6–25%) (Table 3); this may be caused by the higher proportion of Ni and Pb in the residual phase (Figure 4). These results are in line with the view that Zn and Cd can easily be solubilized at a larger pH range with respect to that necessary for the solubilization of Pb (Schmidt, 2003).

Table 3 Heavy metal concentration in mg kg⁻¹ in the sediments at the initial (Ti) and final (Tf) sampling time and their reduction percentage.

		Tf			Cd			CuNiZnPbCu			Ni			Zn			Pb		
		Kg of sediment			Ti	Tf	%	Ti	Tf	%	Ti	Tf	%	Ti	Tf	%	Ti	Tf	%
0–20 cm	P	8060	1.43aA	1.34aA	6	82aA	55bB	33	70aA	64aA	8	298aA	258bB	13	62aA	56aA	10		
	C	12167	1.46aA	1.40aA	4	82aA	74aA	11	73aA	70aA	3	295aA	294aA	0	59aA	58aA	1		
	P+S	7087	1.43aA	1.17bB	18	77aA	53bB	31	69aA	56bB	19	300aA	252bB	16	57aA	54aA	6		
	P+T	6920	1.48aA	1.11bB	25	85aA	54bB	36	69aA	56bB	19	303aA	206bC	32	64aA	57aA	12		
20–40 cm	P	12167	1.23aA	1.21aA	2	84aA	56bB	33	65aA	62aA	5	300aB	265bAB	5	58aA	52aA	11		
	C	12167	1.42aA	1.39aA	2	81aA	81aA	0	68aA	68aA	0	320aB	295aA	8	60aA	59aA	3		

	P+ \pm S	7087	1.32aA	1.15bB	13	73aA	52bB	29	64aA	62A	3	309aB	234bB	24	55aA	54aA	3
	P+ \pm T	6920	1.30aA	1.12bB	14	78aA	51bB	35	67aA	67aA	0	340aA	287bA	16	60aA	52aA	13
40-60 cm	P	12167	1.28aA	1.25aA	2	87aA	85aA	2	66aA	64aA	3	304aA	296aA	3	56aA	50aA	10
	C	12167	1.43aA	1.40aA	2	84aA	81aA	3	69aA	69aA	0	329aA	319aA	3	62aA	60aA	3
	P+ \pm S	12167	1.30aA	1.18bB	9	71aA	69aA	2	66aA	64aA	4	294aA	240bB	18	60aA	44bB	27
	P+ \pm T	12167	1.30aA	1.24aA	5	75aA	68aA	9	66aA	64aA	4	317aA	305aA	4	63aA	57aA	9

Values are the average of three replicates; coefficient of variation of the three replicates ranging from 3 to 10%. The lower case letters indicate significant differences ($P < 0.05$) between the sampling times of each treatment. The capital letters indicate significant differences ($P < 0.05$) between the treatments at the same sampling time (P, C, P+S and P+ \pm S and P+ \pm T) in each depth (0–20, 20–40 and 40–60 cm).

At the end of the experimentation, the concentration of these inorganic contaminants was generally lower at the 0–20 cm layer compared with 40–60 cm.

In addition, the removal efficiency depended on the selected plant species for revegetation, with *S. junceum* treatment generally more efficient in promoting heavy metal decontamination. In particular, comparing the two shrub species with the control sediment at 40–60 cm, a significant reduction in Cd, Zn and Pb was only showed in *S. junceum* treatment (P+ \pm S).

3.4 Metals in plant tissues

At the end of the experimentation (Tf), roots and aboveground parts of the selected plant species were harvested and analyzed for metal content. The ability of shrub plants (*Spartium-junceum L. and Tamarix. junceum L. and T. gallica L.*) to translocate metals from roots to aboveground was estimated using the translocation factor (TF), which is the ratio of aboveground to root metals (Rezvani and Zaefarian, 2011). The data indicated that metals accumulated by the selected plant species were largely retained in roots, as shown by general TF values <1 (Figure 5-5a), with the exception of Zn.

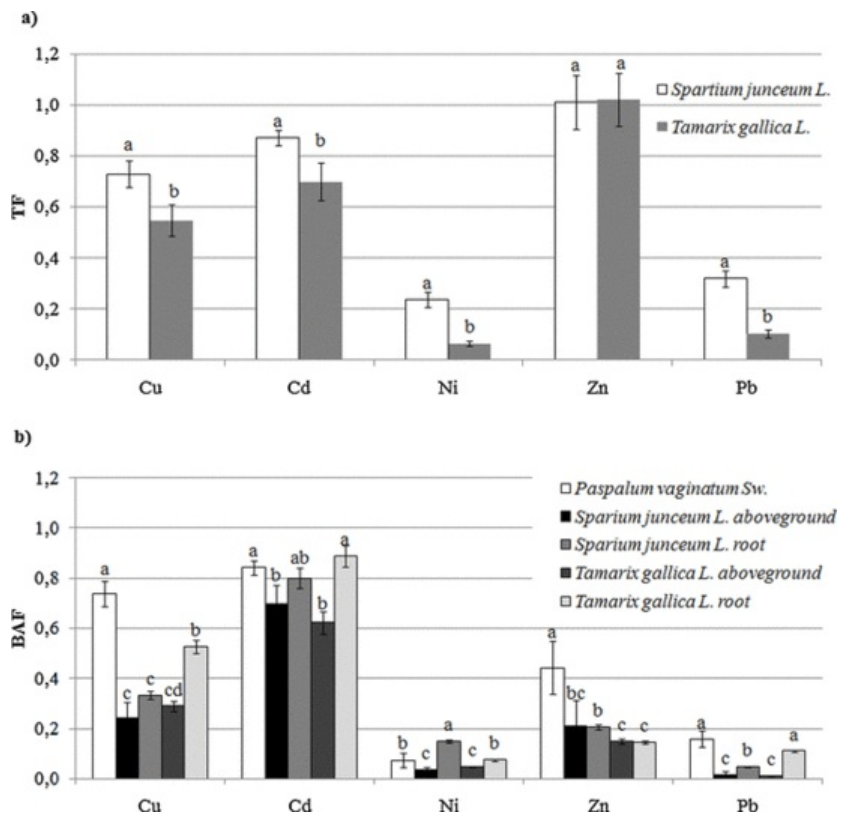


Figure 5 (a) Translocation Factor (TF) and (b) Bioaccumulation Factor (BAF).

The lower case letters indicate significant differences ($P < 0.05$) between the plant treatment indicated in the (one way ANOVA).

The higher ability of plants to translocate Zn is probably associated to the fact that this metal, at low concentration, is an essential micronutrient for plant growth. At the end of experimentation, Zn concentration in aboveground tissues of *Spartium junceum L.* and *Tamarix junceum L.* and *T. gallica L.* were 54 mg kg^{-1} and 38 mg kg^{-1} , respectively.

Similarly, Cu, being an essential element for plant growth, showed a higher TF value with respect to Ni and Pb in both plant species (Figure 5-5a). The concentration of Cu in *Spartium junceum L.* and *Tamarix junceum L.* and *T. gallica L.* aboveground parts were 13 mg kg^{-1} and 15 mg kg^{-1} , respectively.

Pb and Ni, especially in *Tamarix gallica L.*, showed a low translocation; the higher concentration of these heavy metals in the root tissues compared to the aboveground parts is consistent with previous observations on macrophytes (Fitzgerald et al., 2003) and monocotyledonous species (Outridge and Noller, 1991) from polluted areas.

Comparing the two shrub species, *S. junceum* showed generally higher TF values with respect to *T. gallica*, thus indicating its higher interior metal mobility in the plant tissues.

In addition, bioaccumulation factor (BAF), which has been used in previous studies to categorize plants as hyper-accumulator, accumulator and excluder on the basis of their ability to accumulate metals (Ma et al., 2001; Cluis, 2004), was in accordance with the TF, being generally higher in roots with respect to aboveground tissues in both *S. junceum* and *T. gallica* (Figure 5-b, 5b). According to the results of metal fractionation, the BAF of Cd was the higher in the two shrub plants, thus confirming its higher plant availability. The selected shrub species showed a different ability in accumulating heavy metals, with *S. junceum* more efficient in the case of Zn and Ni and *T. gallica* in the case of Cu and Pb. Also *P. vaginatum Sw.* was able to relatively accumulate metals showing, in fact, BAF values higher (for Cu and Zn) or not significantly different (for Cd, Ni and Pb) from that of *T. gallica* root.

3.5 Heavy metal mass balance

At each sediment sampling, the leachate derived from each treatment, collected separately into a drain well, was measured and analyzed to determine the total amount of metal eliminated through percolation (Table 4). Similarly, at the end of the experimentation, the aboveground parts and roots of all plants were collected in order to measure the biomass production and determine the total amount of metal absorbed by plant tissues (Table 5). At this sampling time, also the rhizosphere, defined as the volume of soil that is influenced by the roots of plants (Kumar and Dubey, 2012) (Table 6), and gravel and sand samples derived from the draining layers (Table 7) were analyzed for metal content.

Table 4 Concentration of heavy metals in leachates.

	Total volume of leachate $\text{CuCdNiZnPbLmg l}^{-1}$ (l)	Cu (mg l ⁻¹)	Cd (mg l ⁻¹)	Ni (mg l ⁻¹)	Zn (mg l ⁻¹)	Pb (mg l ⁻¹)
P	128028	0.007	0.011	0.023	0.039	0.010
C	25462	0.008	0.010	0.016	0.051	0.005
P \pm S	98794	0.007	0.013	0.024	0.050	0.007
P \pm T	87969	0.008	0.026	0.014	0.077	0.010

The coefficients of variation ranged from 3% to 10%.

Table 5 Concentration of heavy metals in plant tissues.

	Total dry weight $\text{CuCdNiZnPbkgmg kg}^{-1}$ (kg)	Cu (mg kg ⁻¹)	Cd (mg kg ⁻¹)	Ni (mg kg ⁻¹)	Zn (mg kg ⁻¹)	Pb (mg kg ⁻¹)
<i>Spartium junceum</i> L.						
aAboveground	11.96	12.7	1.0	2.2	53.8	1.0
rRoot	3.66	17.4	1.1	9.4	53.1	3.1
<i>Tamarix gallica</i> L.						
aAboveground	7.69	15.1	0.9	3.0	38.0	0.7
rRoot	4.64	27.5	1.3	4.8	37.2	7.1
<i>Paspalum vaginatum</i> Sw.						
aboveground + Aboveground \pm root	270	38.4	1.2	4.6	113.5	10.2

The coefficients of variation ranged from 3% to 10%.

Table 6 Concentration of heavy metals in the rhizosphere.

	rhizosphere $\text{CuCdNiZnPbkgmg kg}^{-1}$ Rhizosphere (kg)	Cu (mg kg ⁻¹)	Cd (mg kg ⁻¹)	Ni (mg kg ⁻¹)	Zn (mg kg ⁻¹)	Pb (mg kg ⁻¹)
<i>Spartium junceum</i> L.	1947	83	2.32	86	324	84
<i>Tamarix gallica</i> L.	2281	128	2.74	69	304	82
<i>Paspalum vaginatum</i> Sw.	12319	81	2.31	68	245	66

The coefficients of variation ranged from 3% to 10%.

Table 7 Concentration of heavy metals in the draining layer.

	Total weight $\text{CuCdNiZnPbkgmg kg}^{-1s}$ (kg)	Cu (mg kg ⁻¹)	Cd (mg kg ⁻¹)	Ni (mg kg ⁻¹)	Zn (mg kg ⁻¹)	Pb (mg kg ⁻¹)
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Sand	20300	14.9	0.2	10.5	5.5	1.6
Gravel	32700	11.8	0.4	6.4	2.2	0.5

The coefficients of variation ranged from 3% to 10%.

The calculation of heavy metal mass-balance was carried out independently for the four treatments (Table 8). In order to elaborate the mass balance, several assumptions have to be made and some result averages have to be calculated, making approximate the balance values. The results indicated that, at the end of the experimentation, the higher content of metals are still found in the sediment (Table 8). Generally, the content of heavy metals were lower in plant treated sediments compared to the control; this ~~is-eould-be~~ could be due to the accelerated mineralization process in control sediment causing metal concentration. However, the presence of plants could exert a positive role on carbon sequestration by means of root exudates and plant remains (Garcia et al., 1997b; Doni et al., 2013). In addition, such a discrepancy between control and plant treated sediments is especially pertinent, being the metal concentrations in the different compartments (plant tissues, leachate, etc.) near or under low background concentrations. Expressed in percentage distribution, leachate and plant tissues constituted the minor fractions of the total metal removal, whereas, the greatest contribution was attributed to rhizosphere stabilization followed by gravel and sand adsorption.

Table 8 Heavy metal mass balance (%) in the different compartments.

		Sediment	rhizospheregravel-sandleachateRhizosphere	Gravel-sand	Leachate	Pplant tissues
Cu	P	81.0	12.4	6.43	0.034	0.129
	C	94.3	-5.650.007-P+	5.65	0.007	
	P + S	70.4	21.8	7.61	0.031	0.163
	P + T	66.1	26.4	7.28	0.030	0.157
Cd	P	71.7	17.1	8.54	2.53	0.194
	C	91.1	-8.490.45-P+	8.49	0.45	
	P + S	60.4	27.5	9.33	2.52	0.243
	P + T	57.1	29.5	8.90	4.28	0.226
Ni	P	84.2	11.4	4.34	<0.01	0.017
	C	96.0	-4.02<0.01-P+	4.02	<0.01	
	P + S	74.4	20.7	4.89	<0.01	0.022
	P + T	74.9	20.2	4.88	<0.01	0.021
Zn	P	93.1	6.4	0.46	0.051	<0.01
	C	99.6	-0.410.012-P+	0.41	0.012	
	P + S	79.0	20.3	0.57	0.061	<0.01
	P + T	80.2	19.2	0.51	0.076	<0.01
Pb	P	85.6	13.7	0.60	0.065	<0.01
	C	99.4	-0.55<0.01-P+	0.55	<0.01	
	P + S	75.9	23.4	0.64	0.037	<0.01
	P + T	75.5	23.9	0.62	0.046	<0.01

P: *Paspalum vaginatum* Sw.; C: control; P + S: *P. vaginatum* Sw. + *Spartium junceum* L.; and P + T: *P. vaginatum* Sw. + *Tamarix gallica* L.

The leachates showed relatively low concentrations of heavy metals (Table 4). The lower volume of leachate in the control sediment is probably the reason of the lower percentage of metals in the leachate with respect to the other compartments of the system (Table 8). The high percentage of Cd exchangeable fraction in the initial sediment may account for the dynamic interactions of this element in rhizosphere and for its higher removal by leaching and root plant stabilization (Sahuquillo et al., 2003). In greater detail, the dispersion of Cd due to percolation accounted for 2.5% in P and P+S and for 4.3% in P+S and for 4.3% in P+S+T treatment, while the dispersion due to rhizosphere stabilization accounted for 17%, 28% and 29% in P, P+S and P+S+T treatments, respectively. For the other metals very little amounts, lower than 0.1%, seems to be leached.

3.6 Principal Component Analysis

The PCA multivariate statistical analysis painted a clear picture to distinguish between the sediment samples as a function of the layer (0-20, 20-40 and 40-60 cm), time (initial and final) and treatment (P, C, P+S and P+S+T), and to determine the most important chemical, physical and biological sediment parameters for sediment characterization. All raw data used in the PCA analysis were subjected to pre-treatment in order to remove or reduce irrelevant sources of variation or 'noise' which may interfere in the analysis. Firstly, the raw data were log transformed to reduce data heterogeneity; following this, the transformed data were standardized.

The principal component analysis of the chemical, physical and biological data for all sediments resulted in 71% of the data variance being contained in the first two components. Therefore, the first two principal components (PC) were retained (Table 9). Figure 6 provides the biplot of the PCA analysis for all sediment treatments in all layers and at both sampling times using the first two principal components; it provides a graphical representation of clusters of sediments with similar properties. In addition, if a variable is close to a sediment sample in the biplot, it will have a high direct influence on it. Finally, the respective loadings provide an indication of the correlations between the different variables; vectors situated closely together represent variables that are highly correlated while orthogonal vectors represent variables that are uncorrelated.

Table 9 Principal components (PC) and component loadings.

	PC1	PC2
TOC	0.403	0.804 ^a
TN	-0.087	0.912 ^a
TP	0.508	0.563
E.C.	0.157	-0.797 ^a
pH	-0.836 ^a	0.136
DH-ase	-0.708 ^a	0.343
CFU	-0.328	0.837 ^a
Cd	0.886 ^a	0.155
Cu	0.851 ^a	-0.245
Ni	0.809 ^a	-0.008
Zn	0.742 ^a	-0.330
Pb	0.647	0.257
TPHs	0.897 ^a	0.023
Var. Sp.	6.42	3.55
Prp. Tot.	0.459	0.253

E.C., electrical conductivity; TOC, total organic carbon; TN, total nitrogen; TP, total phosphorus, DH-ase, dehydrogenase activity; CFU, total cultivable microbial population; TPHs, Total Petroleum Hydrocarbons. Var. Sp., explained variance; Prp. Tot., total proportionality

$$1PC_1 = 0.403TOC + 0.087TN + 0.508TP + 0.157E.C. - 0.836pH - 0.708DH-ase - 0.328CFU - 0.886Cd - 0.851Cu - 0.809Ni - 0.742Zn - 0.647Pb + 0.897TPHs + 6.42Var. Sp. + 0.459Prp. Tot.$$

$$2PC_2 = 0.804TOC + 0.912TN + 0.563TP - 0.797E.C. + 0.136pH + 0.343DH-ase + 0.837CFU + 0.155Cd - 0.245Cu - 0.008Ni - 0.330Zn + 0.257Pb + 0.023TPHs + 3.55Var. Sp. + 0.253Prp. Tot.$$

a Variables with component loadings used to interpret the PC, threshold level 0.7.

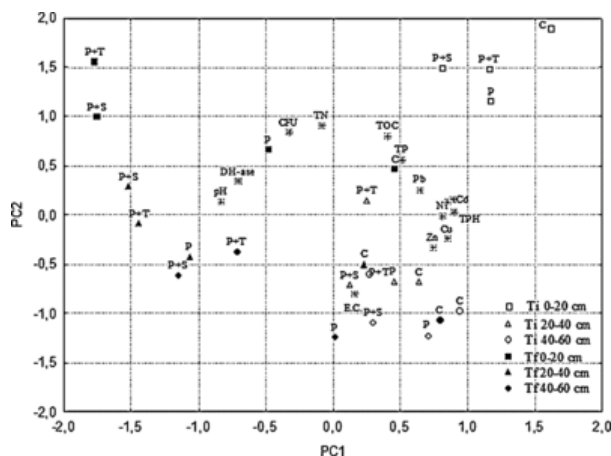


Figure 6 Biplot of factor scores and loadings the initial (Ti) and final (Tf) sampling times in the different plant treatments at the three depths (0-20, 20-40 and 40-60 cm)-20, 20-40, and 40-60 cm).

TOC: total organic carbon; TN: total nitrogen; TP: total phosphorus; E.C.: electrical conductivity; DH-ase: dehydrogenase activity; CFU, colony forming unit; and TPH: total petroleum hydrocarbons.

P: *Paspalum vaginatum* Sw.; C: control; P + S: *P. vaginatum* Sw. + *Spartium junceum* L.; and P + T: *P. vaginatum* Sw. + *Tamarix gallica* L.

The PC loadings showed that the 1st PC (46% of the total variance) is closely associated with the sediment parameters of inorganic contaminants (Cd, Cu, Ni, and Zn), organic contaminants (TPHs), pH, and dehydrogenase activity. However, the 2nd PC (25% of the total variance) is more closely associated with the chemical parameters of total organic carbon, total nitrogen, electrical conductivity, and with the biological parameter of total cultivable microbial population (CFU).

Dehydrogenase activity was negatively correlated with the organic and inorganic contaminants on the PC1, indicating a negative effect of contamination on microbial metabolism (Masciandaro et al., 2013).

Similarly, total cultivable microbial population (CFU) was positively affected by the addition of organic-C, being these parameters positively correlated with each other on the PC2 (Table 9).

In the PCA biplot, all initial sediment samples (Ti) were on the right side, while the final sediment samples (Tf), in particular P+S and P+S + S and P+T treatments, were shifted on the left side (shift towards negative values of the PC1). The only exception was the control sediment that did not show appreciable change of position over time on the PC1. Being the PC1 positively associated with organic and inorganic contaminants (heavy metals and TPHs), this shift indicated that the plant treatments positively affected the sediment decontamination.

At both initial (Ti) and final (Tf) sampling times the different layers were spread along the PC2, indicating the establishment of a profile with different nutrient content (total organic C and total N) and microorganism growth. In particular, the surface of planted sediments (0-20 cm), being more shifted towards positive values along the PC2 axis with respect to the subsurfaces (20-40 and 40-60 cm) and control sediments, were characterized by a higher stimulation of nutrient cycles, probably favored by organic matter application and plant root-microorganism interaction.

4 Conclusions

This pilot case study proved that the three selected plants (*Paspalum vaginatum* Sw., *Tamarix gallica* L. and *Spartium vaginatum* Sw., *T. gallica* L., and *S. junceum* L.) in association with the application of compost had the ability to degrade organic contaminants and to remove heavy metals (Zn, Cu, Cd, Ni, and Pb) from moderately contaminated sediments. The best plant uptake performance was observed for Cd, Zn, and Cu. According to metal fractionation results at surface layer (0-20 cm), the bioaccumulation factor (BAF) of Cd was the higher in the two shrub plants, thus confirming its higher plant bioavailability. However, Ni and Pb, being strongly associated with the residual fraction of the sediment (>50%) were the lowest translocated metals. Generally, in both shrubs, the heavy metals showed the higher concentration in the root tissues compared to the aboveground, with *S. junceum* L. more efficient with respect to *T. gallica* L. in interior metal mobility in the plant tissues.

In order to obtain a better insight in the efficiency of the phytoremediation system, metals remained in the sediments, as well as, metals removed by leaching, plant absorption, rhizosphere stabilization, and draining layer adsorption were determined, and the results were elaborated to check for the mass-balance of metals in the sediment-plant system. The capacity of rhizosphere to precipitate heavy metals, reducing their availability and toxicity in sediments, seems to be the principal mechanism contributing to heavy metal containment. This process could be considered as an alternative option to metal phytostabilization and to a lesser extent for phytoextraction, so far emphasized for the possible remediation

strategies from contaminated matrices. These results can be of great help to elucidate the metal behavior during phytoremediation of dredged sediments and to estimate the duration before remediation is completed.

In conclusion, the phytoremediation process was able to convert the dredged sediments into an uncontaminated and biologically active matrix. Therefore, the treated sediments can be re-usable for environmental purposes, including road construction, landfill cover, dune nourishment; in addition, the sediments can be considered as a sort of soil (techno-soil), and for this reason could be used in agricultural or nursery activities.

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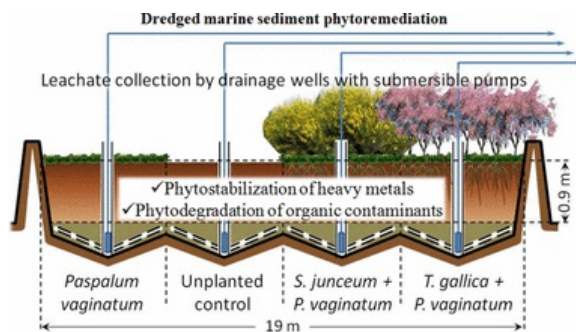
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Graphical abstract



Highlights

- Phytostabilization was suitable to recover dredged marine sediments.
- An improvement of the nutritive and biological sediment properties were obtained.
- A significant reduction in organic contaminants was measured in planted sediments.

- The great contribution in metal containment was attributed to rhizosphere stabilization.
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