INNOVATIVE TECHNIQUE TO RECOVER CONTAMINATED RIVER SEDIMENTS (CLEANSED LIFE 12 ENV/IT/000652)

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SUMMARY: Two different kinds of sediments were submitted to a landfarming process in order to convert them into a matrix suitable for environmental purpose. For nursery activity, landfarming was applied to sediments already partially recovered by phytoremediation to further ameliorate their agronomic and functional properties. Three months of process was able to stimulate microbial activities and, as a consequence, to further reduce the organic pollutant. Moreover, the absence of toxicity, and a good level in nutrient made the sediment suitable for nursery application. Instead, for road construction activity, the landfarming was carried out on fresh sediments in order to reduce water, organic matter and organic contaminant content. Five months of landfarming leaded to a great reduction in the water content even if not enough to reach the optimal level of about 15-20% for sediment reuse in this filed. Moreover, an activation of microbial biomass metabolism conducted to a relevant decrease also of organic matter and contaminants (near to zero), thus making sediments suitable for road constrction.

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1.INTRODUCTION

The continuous stream of sediments, dredged from harbors and waterways for keeping efficient the traffic of shipping, is a considerable ongoing problem recognized worldwide. On the basis of an European Sediment Network estimation, it can be assumed that around 100-200 million m^3 of contaminated sediments are dredged yearly in Europe and need to be disposed of in specific and expensive ways. The European policy encourages treatment and valorization of dredged sediments, and this will be a technological challenge in the near future. Several remediation methods for polluted sediment amelioretion are available (Rulkens et al. 1998; Thomas and Gidarakos 2001; Rulkens et al., 2005) and they deal with the removal of pollutants by means of thermal treatment, physical removal of pollutants from the sediments, chemical or (micro) biological destruction of sediment pollutants, disposal of sediments in a landfill or in confined or non-confined disposal facilities (Rulkens et al., 2005). However, remediation of the millions of cubic meters of polluted sediments in the coming years, can only be achieved if inexpensive technologies are available. Landfarming, in which external process interventions are minimized to reduce costs and use of energy, has been recognized as a promising, feasible and low cost-effective technique to remediate sediments polluted by total petroleum hydrocarbons (AKWA 2001; Bortone and Palumbo, 2007).

To carry out the landfarming process, it is necessary to dewater the dredged sediments in order to obtain the proper aerobic condition for pollutants biodegradation. In fact, sediments are in anaerobic conditions and all pores are completely filled with water, which hinders the diffusion of oxygen into sediment matrix. The partially dewatered sediment is spread out in a relatively thin layer on a specially constructed site. The microbiological activity in this layer is stimulated by I) regular ploughing of the layer, in order to maintain an adequate aeration, and by II) the addition of available nutrients (Vermeulen et al., 2003a). Moreover, landfarming will slowly change physically/chemically sediment properties, transforming it in a matrix similar to a soil (Vermeulen et al., 2003b; Lens 2005) that could be re-used in different production processes such as nursery activity and road construction, thus facing other two great environmental problems.

In fact, every year 5.2 million m^3 of soil are removed from the ground due to plant nursing activities. To prevent the risk of lowering of the ground level of about 8-10 mm/year, plant nurseries are forced to buy soils from third-party catchments, which are often of poor quality and contribute to soil exploitation elsewhere. Similar problems are met by the EU road building industry, whose yearly demand for sand, gravel and aggregates for stability and draining purposes is around 30 million m^3, for an average value of € 450 million.

In this study, two different kinds of sediments were submitted to a landfarming process in order to convert them into a matrix suitable for reusing in nursery activity and road construction.

For nursery activity, landfarming was applied to sediments already partially recovered by a phytoremediation process with the main goal of a) homogenizing the sediment after removing the plants used for their decontamination, b) reducing the eventual residual organic contamination and, c) improving biological activities in order to obtain a suitable substrate for ornamental plant growth in plant nursery sector

In road construction field, the landfarming process was carried out on fresh dredged sediments, in order to reduce water content, organic matter content and organic contaminant level.

2. Materials and methods

2.1 Experimental layout

Two different kinds of sediments were submitted to a landfarming process in order to convert them into a matrix suitable for their reusing in A) nursery activity and B) road construction.

A) For nursery activity, sediments partially recovered by a phytoremediation process previously developed in a European project (AGRIPORT ECO/08/239065/S12.532262), were used.

These sediments were decontaminated using plants (phyto-treatment) and organic amendment (compost) in a pilot scale (12 containers of about 1 m^3 each). Six different treatments, in duplicatewere carried out for about two years (2010-2012) using the following plants: a. *Nerium oleander + Paspalum v*.(O) b. *Tamarix gallica + Paspalum v*. (T) c. *Spartium junceum + Paspalum v.* (S) d. *Phragmites australis* (Ph) e. *Paspalum v*. (P) f. Control (no plants) (C) (Doni et al., 2013).

In November 2013, after plant removing, the sediments were collected and characterized (T0).

After this preliminary characterization, the sediments were submitted to three-months landfarming technology (November-January) aimed to further reduce organic contamination, improve biological activities and also homogenize the treated matrix. The landfarming treatment consisted in a periodically (twice a week) turning over the sediments inside each containers. This activity was carried out by manually moving the sediments and turning them over with a shovel.

After one and half (T1) and three months (T2) from the beginning of the landfarming process the sediments were collected. Each sediment sample consisted in a mix and homogenization of five sub-samples randomly collected in each container by vertically drilling a hole into the surface using a soil core sampler with an inner diameter of 5 cm and a length of 20 cm.

The data were reported as the mean of the results of two containers with the same treatments for each sampling time.

B) For using the sediment in road construction field, the landfarming process was carried out on fresh dredged sediments, in order to reduce water content, organic matter and organic contaminants content.

The sediments (about 800m^3) were dredged in the middle of Navicelli Canal in Pisa (nearby Tombolo's bridge), a navigable canal (length: 16 km, width: 32 m, depth:3 m). which connects Pisa to the sea at the Port of Livorno.

The dredged sediments were spread in a Navicelli basin (normally used for sediment storage), in a layer of about 50 cm, covering a surface of about 1500m^2 and dewatered for 1 month; the layer was reduced to about 40 cm after dewatering.

After the dewatering process, the fresh sediments were randomly collected into the basin in 8 different points (T0) in order to cover the overall sediment surface. The sampling point coordinates were recordered with GPS instrument in order to exactly identify the sampling points in the next sampling campaigns.

The landfarming treatment, carried out for 5 months (April-August), consisted in the periodically (twice a week) aeration by mechanically moving the sediments and turn them over by a scraper. After 2,5 (T1) and 5 (T2) months from the beginning, the sediments were collected again in the same 8 selected points. The samples were collected through the use of a shovel. Around each of the 8 selected sampling points, 5 sub-samples were collected, homogenized and mixed together in order to obtain one sediment sample for each point at each sampling campaign.

The sedimen samples (in both experimentations) were brought to the laboratory on the same day of the collection and split in two aliquots: one was air-dried and stored at room temperature for chemical analyses, the other one was stored at 4°C for TPH, PAHs, PCBs and biological analysis, which were carried out 4-5 days after sampling.

2.2 Methods

Electric conductivity (EC) and pH was determined in distilled water (sediment:H_2O ratio 1:5). with a conductimeter and pH meter. Total organic carbon (TOC) and total organic nitrogen (TN) were determined by dry combustion with a multiphase carbon and a protein/nitrogen determinator, respectively. Total P was determined in the nitric–perchloric digestion extract by colorimetry (Olsen and Sommers, 1982). A water extract was obtained by shaking for 2 h a mixture of soil and distilled water in a 1:10 (w/v) sediment:water ratio, centrifuging and filtering. In this extract, WSC and NO_3^- was determined by a C analyzer for liquid samples and by selective electrode, respectively. The total petroleum hydrocarbons (TPH) were determined by the gravimetric method according to Ceccanti et al. (2006). The extraction of polychlorobiphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) was performed according to pressurized fluid extraction (PFE) (EPA, 1995). Subsequently, the extract was cleaned-up by gel permeation according to EPA method 3630 (EPA, 1997). Finally, the PCBs and PAHs concentration was determined by a gas chromatography/electron capture detector (GC/ECD) and gas chromatography/mass spectrometry (GC/MS), respectively.

The hydrolytic enzyme activities were determined with microplate assay and fluorogenic substrates, according to the method described by Marx et al. (2001) and Vepsäläinen et al. (2001), based on the use of fluorogenic methylumbelliferyl (MUF)- substrates. The sediments were analyzed for β-glucosidase, acid phosphatase and protease using 4-MUF-β-D-glucoside, 4-MUF-phosphate and 4-MUF-protease as substrates, respectively. Fluorescence (excitation 360 nm, emission 450 nm) was measured with an automatic fluorimetric plate-reader after 0, 30, 60, 120 and 180 min of incubation at 30 °C.

Dehydrogenase activity was estimated according to Masciandaro et al. (2000) method. A phyto-test with barley (*Ordeum Vulgare*) was carried out on water extracts (1:10 w/v) following the method reported by Zucconi et al. (1981). The growth index, calculated after 72 h, was expressed by the following formula: GI% = P(T/C), where P is the mean percentage of seed germination with respect to the mean value of the control prepared with distilled water assumed to be 100 %; T and C are the length of shoot in the treatment and in the control, respectively.

The STATISTICA 7.0 software (StatSoft Inc., Tulsa, Oklahoma,USA) was used for the statistical analysis. Differences among the times and treatments were tested by analysis of variance (one way ANOVA). The means were compared using HSD Tukey's test ($P<0.05$). The results were also studied using principal component analysis (PCA). The PCA is a multivariate statistical data analysis technique, which reduces a set of raw data to a number of principal components that retain the most variance within the original data in order to identify possible patterns or clusters between objects and variables (Carroll et al., 2004).

3. Results and discussion

3.1 Phytoremediated sediments

Phytoremediated sediments were decontaminated using plants and organic amendment. Six different treatments were carried out for about two years using the following plants: a. *Nerium oleander* + *Paspalum v.*(O) b. *Tamarix gallica* + *Paspalum v.* (T) c. *Spartium junceum* + *Paspalum v.* (S) d. *Phragmites australis* (Ph) e. *Paspalum v.* (P) f. Control (no plants) (C) (Doni et al., 2013).

The preliminary characterization (Table 1) showed that the phytoremediated sediments had properties quite idoneous for their reuse in plant nursery activity; however, the landfarming

process has been carried out with the aim to increase the microbial metabolism, further reduce the organic contamination, and homogenize the substrate.

In the different treatments some differences in the chemico-agronomical properties were observed at T0 (Table 1). In particular, a higher C and, in particular, N contents (both in total and soluble forms) was observed in the planted sediments with respect to the control suggesting the contribution of plants to organic matter incorporation in the sediment matrix. Moreover, the maintenance of a vegetation cover exerts a positive influence on the C sequestration by means of root exudates and plant remains, as widely discussed in several agro-soil ecosystems (Garcia et al., 1997; Doni et al., 2013). Among the plants a lower content in C and N was found in *Tamarix* treatment.

Contrarily, little variation was observed for pH and EC in the different treatments (Table 1). The pH showed basic values (about 8), assuring no passage of toxic elements from the sediment to the plant, while the relatively low content in salt (lower than 1,2 dS m^{-1}) was no dangerous for plants. High levels of soluble salts in the root zone may affect water and nutrient uptake and adversely affect plant growth. Similarly, TP not showed great difference among planted and no planted treatments (Table 1).

Instead, all plant systems were able to greatly improve the microbial metabolism in the sediments (higher dehydrogenase, β-glucosidase, protease and phosphatase activities) with respect to the control treatment (Table 1). Comparing the different plants, the *T. gallica* and *S. junceum* treatments generally induced the highest microbial activity.

The same plant species, together with *Phragmites australis*, were the more effective in promoting hydrocarbon (TPH) degradation; a reduction averagely of 40-50% with respect to the control sediment was, in fact, measured in these treatments (Figure 1).

The results related to three months of landfarming process showed a lower but significant increase in the pH and a more relevant decrease in EC (Table 1) in every containers. The EC reduction was probably due to the further lost of salts in the leachate favored by the mixing of the sediments and the intensive rains during the experimental period (November-January). In all the containers, the EC reached values of about 200 µS/cm, considered ideal for plant germination and growth.

It was to be expected that carbon compounds would be degraded during the landfarming because of the aeration carried out, which should favor the mineralization of the organic matter and provoke the degradation of hydrocarbons. Even though, not significant decrease was generally observed for C, N and P during the landfarming process, the great increase in WSC and nitrate over time in all the containers, suggested that the organic matter mineralization was in act, and in particular that of pollutant compounds. A little, but generally significant hydrocarbon reduction was, in fact, found in all containers (Figure 1). The lower pollutant reduction measured in the control and in the *Oleander* treatment, could be related to the lower total microbial activity (lower dehydrogenase activity) (Table 1). In these treatments a hydrocarbon reduction of only 6% was measured, while in the other treatments the decrease ranged from 14% in S*partium* to 23% in *Phragmites* and *Tamarix.*

However, the landfarming treatment was able to stimulate the microbial activities in each container, as showed by the increase in both oxidoreductase activity (dehydrogenase, Dhase) and hydrolytic enzyme activities (lower increase in protease activity) (Table 1), in particular at the end of the process (T2). As observed for Dhase, lower β-glucosidase and phosphatase activities were measured in the control (Table 1), probably due to the lower nutrient content and a general worse environmental condition for microorganisms. As discussed above, this lower metabolic activity was probably the main cause of the lower hydrocarbon degradation observed in control treatment.

During the landfarming process, in order to further evaluate the reduction in toxicity and the suitability of the sediment in reuse them in the nursery activities, a phyto-test with barley seeds was carried out. The use of bioindicators (plants) provides a direct, inexpensive and integrated estimate of contaminant bioavailability and toxicity (Anastasi et al., 2009).

With the only exception of *Spartium*, a germination index greater than 100% was already measured before the landfarming process (Table 1). This result confirmed that the sediment was not toxic and already idoneous for nursery reuse before the treatment. However, the landfarming was carried out to improve biological activity and hydrocarbon degradation; goals reached as discussed above. Anyway, the landfarming led to a general increase in GI% after 1 month and half (T1), until 140%, suggesting an improvement of sediment characteristics, such as increase in nutrients (great increase in nitrate at T1), able to stimulate seed germination. Probably, also the great reduction in EC could have contributed to this enhancement.

At the end of the process, values similar or greater to the initial was measured in each treatment, with the exception of control where a significant decrease in GI% was observed. This results together with the general lower content in nutrient and biological properties make this treatment less suitable for the reuse in nursery activity.

Table 1. Chemical and biological properties in the dfferent treatment at different sampling times (T0-T1-T2). Different lowercase letters indicate statistically different values (time effect) within point according to HSD Tukey's test (P<0.05). Different uppercase letters indicate statistically different values (treatment effect) within time according to HSD Tukey's test (P<0.05)

	pH			Electrical Conductivity			Total Organic Carbon			Total Nitrogen		
				ds m^{-1}			%			%		
	T0	T1	T2	T0	T1	T2	T0	T1	T2	T0	T1	T2
P	$8,01^{aB}$	$8,27^{bD}$	$8,52^{cC}$	$0,98^{cA}$	$0,29^{bA}$	$0,20^{aB}$	$2,59^{aA}$	$2,73^{aA}$	$2,78^{aA}$	$0,197^{aC}$	$0,199^{aBC}$	$0,205^{aC}$
C	$7,96^{aB}$	$7,95^{aB}$	$8,43^{bB}$	$0,95^{cA}$	$0,78^{bC}$	$0,22^{aB}$	$2,46^{aA}$	$2,35^{aA}$	$2,64^{aA}$	$0,133^{aC}$	$0,123^{aA}$	$0,132^{aA}$
T	$8,05^{aB}$	$8,09^{aC}$	$8,46^{bBC}$	$0,99^{cA}$	$0,56^{bB}$	$0,26^{aB}$	$2,36^{aA}$	$2,33^{aA}$	$2,59^{aA}$	$0,178^{aBC}$	$0,180^{aB}$	$0,161^{aAB}$
S	$8,11^{aC}$	$8,08^{aC}$	$8,38^{bB}$	$1,01^{cAB}$	$0,47^{bB}$	$0,13^{aA}$	$3,27^{aC}$	$3,14^{aB}$	$3,32^{aB}$	$0,175^{aBC}$	$0,169^{aB}$	$0,180^{aAB}$
Ph	$7,99^{aAB}$	$8,10^{aC}$	$8,54^{bC}$	$1,09^{cB}$	$0,48^{bB}$	$0,13^{aA}$	$3,20^{aBC}$	$3,37^{aB}$	$3,18^{aB}$	$0,187^{aB}$	$0,165^{aBC}$	$0,183^{aB}$
O	$7,89^{aA}$	$7,84^{aA}$	$8,20^{bA}$	$1,01^{acAB}$	$0,83^{bC}$	$0,13^{aA}$	$2,81^{aB}$	$3,07^{aB}$	$3,03^{aB}$	$0,197^{aC}$	$0,203^{aC}$	$0,202^{aC}$

	Total Phosphorus			Water Soluble Carbon			$NO3^-$			Germination Index		
	%			mg kg^{-1}			mg kg^{-1}			%		
	T0	T1	T2	T0	T1	T2	T0	T1	T2	T0	T1	T2
P	$0,083^{aA}$	$0,072^{aB}$	$0,071^{aAB}$	1150^{aB}	1412^{bBC}	2095^{cB}	77^{aB}	96^{bB}	107^{cB}	107^{bB}	87^{aA}	101^{bB}
C	$0,087^{aA}$	$0,081^{aB}$	$0,079^{aAB}$	900^{aA}	804^{aA}	1812^{bA}	119^{bD}	58^{aA}	103^{bB}	130^{cD}	97^{bA}	74^{aA}
T	$0,090^{bA}$	$0,074^{abB}$	$0,075^{aA}$	1050^{aAB}	1413^{bBC}	2494^{cD}	99^{aCD}	167^{cD}	128^{bC}	101^{aAB}	142^{cD}	121^{bB}
S	$0,094^{bA}$	$0,082^{abB}$	$0,077^{aAB}$	1030^{aAB}	1309^{bB}	2478^{cD}	50^{aA}	198^{cD}	109^{bB}	96^{aA}	143^{cD}	126^{bB}
Ph	$0,096^{aA}$	$0,082^{aB}$	$0,090^{aB}$	1180^{aAB}	1633^{bC}	1876^{bA}	74^{aB}	131^{cC}	92^{bA}	128^{aD}	126^{aB}	112^{aC}
O	$0,094^{bA}$	$0,091^{abB}$	$0,080^{aAB}$	1160^{aB}	1485^{bBC}	2267^{cC}	98^{aC}	187^{cD}	155^{bD}	118^{aC}	134^{bC}	107^{aBC}

	Dehydrogenase			β-glucosidase			Phosphatase			Protease		
	(mg INTF kg^{-1} h^{-1})			(mmol $kg^{-1}h^{-1}$)			(mmol $kg^{-1}h^{-1}$)			(mmol $kg^{-1}h^{-1}$)		
	T0	T1	T2	T0	T1	T2	T0	T1	T2	T0	T1	T2
P	$0,72^{aC}$	$2,04^{bC}$	$2,48^{cD}$	203^{aF}	192^{aD}	249^{bC}	121^{aB}	143^{bB}	160^{cB}	$18,9^{aB}$	$19,0^{aB}$	$21,0^{bB}$
C	$0,17^{aA}$	$0,57^{bA}$	$0,89^{cA}$	125^{aA}	109^{aA}	177^{bA}	114^{aA}	122^{aA}	143^{bA}	$24,9^{aE}$	$25,0^{aE}$	$26,0^{bD}$
T	$1,64^{aD}$	$1,76^{aB}$	$1,95^{aC}$	141^{bB}	126^{aB}	258^{cC}	146^{aC}	156^{bC}	184^{cC}	$22,4^{bD}$	$21,0^{aC}$	$24,5^{cC}$
S	$1,49^{aD}$	$1,70^{abB}$	$1,91^{bC}$	169^{bE}	147^{aC}	302^{cD}	163^{aD}	175^{bD}	216^{cD}	$20,9^{bC}$	$19,4^{aB}$	$21,6^{cB}$
Ph	$0,73^{aC}$	$1,64^{bB}$	$1,52^{bB}$	149^{aC}	153^{aC}	198^{bB}	114^{aA}	131^{bA}	190^{cC}	$17,8^{bA}$	$17,0^{aA}$	$18,0^{bA}$
O	$0,61^{aB}$	$0,74^{bA}$	$1,06^{cA}$	158^{aD}	285^{bE}	297^{bD}	124^{aB}	160^{bC}	205^{cD}	$21,3^{aC}$	$22,0^{bD}$	$24,0^{cC}$

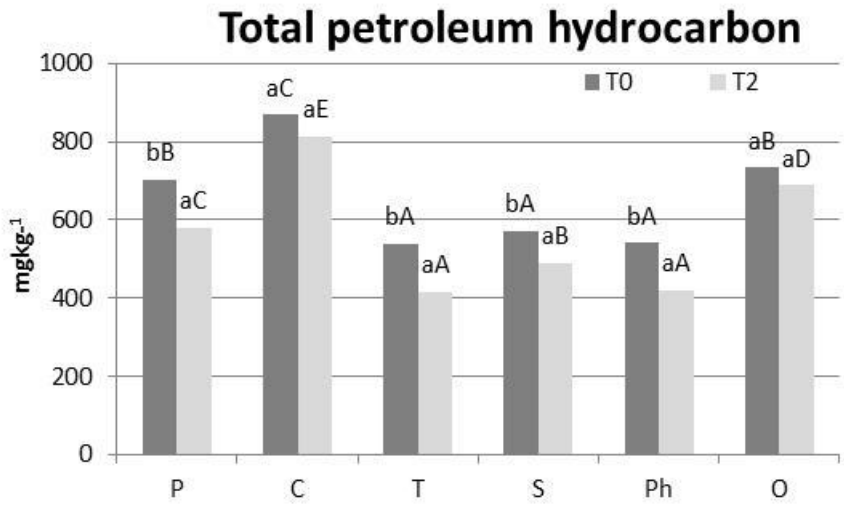

Figura 1. Total petroleum hydrocarbon in the dfferent treatment at T0 and T2. Different lowercase letters indicate statistically different values (time effect) within point according to HSD Tukey's test (P<0.05). Different uppercase letters indicate statistically different values (treatment effect) within time according to HSD Tukey's test (P<0.05)

3.2 Fresh sediments

The results (Table 2 and 3) from the Navicelli basin, showed a great variability in the chemical and biochemical parameters among the eight samples analysed, as expected by the great amount of sediment collected. However, with the exception of samples 4 and 8, a good level of C, N and P was observed, with a content higher than 1,5%, 0,15% and 0,6%, respectively. As a consequence, the C/N ratio was in a quite good range (from 8 to 13), thus ensuring a good level of microbial activity responsible for organic substrate degradation (included contaminants). Also the electrical conductivity (EC) showed very different values among the 8 sampling points with values extremely high in points 1, 2 and 3.

The Dhase activity, indicative of the whole microbial metabolism (Masciandaro et al., 2000), reflects the trend of the chemical parameters, with a significant variability among the sampling points and the lowest values in samples 4 and 8 (Table 2 and 3). Unexpectedly, concerning chemical results, also the sample 1 showed a very low dehydrogenase activity, that together with the low values of the other enzymatic activities (β-glucosidase, protease and phosphatase) suggested a sort of microbial inhibition in this sample (Table 3). The hydrolytic enzyme activities, linked to the C, N and P cycles (β-glucosidase, phosphatase and protease, respectively), were particularly low also in samples 2-3 and 4, and protease was not detected in them, while in samples 5-6-7-8 a good level of Dhase and hydrolytic enzyme activities (with the exception of protease, very low in every sample) was found, suggesting a better environmental condition for microbial activities in this points.

Concerning the organic contamination, PCBs was not detected in any sample analyzed, while a slight PAHs contamination was observed in the most of the samples (Table 4). However, the PAHs concentration resulted always lower than the legal limit concentration for soil civil reuse (10 mg k^{-1}, D.lgs. 152/2006). The highest values observed in sample 1, 2 and 3 should be the main cause of the lowest enzyme activities detected in these samples. It is well known, in fact, that contaminants could have an inhibitory effect on enzyme activities (Speir and Ross, 2002; Gianfreda et al., 2005; Iannelli et al., 2012). Moreover, also the elevated EC in the same points could have negatively affected the microbial metabolism (Besalatpour et al., 2011).

The landfarming process leaded to a great decrease in the water content that reached a value

of averagely of about 40% after 5 months. Despite this remarkable reduction, the water amount was still too high to allow the sediment reuse in road construction, since the optimum value is about 15-20%. For this reason, in order to further reduce the water content and the dewatering process time, the partially dewatered sediments have been mixed with lime (15%) before their reuse in road construction.

The loss of water as leachate, together with the washing of sediment due to the intensive rains, in particular in the first two months of treatment (April and May), leaded to a significant decrease in EC in each sampling point. Conversely, in the hottest season (June-August) the water evaporation was probably the main cause of salt concentration and then of a little, but significant, increase in EC in the most of the points (Table 2).

On the other hand, no many variations were observed for pH over time, with final values ranging from 8 and 8.3 (Table 2). Values of about 8, were reported as optimal in mineralization of hydrocarbons and in microbial growth and activity (Marin et al., 2005; Besalatpour et al., 2011).

The organic C showed a significant reduction with the treatment (averagely 15%) (Table 2), reaching values of organic matter near to 2%, considered the optimum value for sediment reuse in road construction as reported in the "Technical Specifications for road embankments" document. However, similar percentage of TOC reduction was reported by Petavy et al., (2009) in a 8 months landfarming process carried out at laboratory scale.

Similarly, the organic N and total P content (Table 2) showed a clear decrease with the landfarming process, suggesting an activation of sediment microbial biomass, which has a significant role in the organic matter mineralization (included organic contaminants). These hypothesis was confirmed by the greater increase in the dehydrogenase activity (Table 3) and also by the general increase in WSC and nitrate, products deriving from organic substrate degradation. The general increase in nitrates, albeit with large variations between sampling points, indicates a good level of oxygenation due to the landfarming process, which enabled the activation of nitrification processes (Table 2).

The decrease in WSC at T2 (Table 2) was probably due to the rapid consumption of this easily degradable substrate, that represents the most labile fraction of the organic matter used as carbon and energy sources by soil microorganism (Ghani et al., 2003). In agreement with this and with the Dhase trend, also all the other hydrolytic enzyme activities, greatly increased over time, regardless the point and initial chemical sediment characteristics (Table 3). This results suggested that, even though with a considerable variability, unavoidable in field situation, the landfarming process created suitable environmental condition for microorganisms in carrying out their metabolic activity, included organic contaminant degradation. In fact, the content of PAHs was lower than 0.5 (limit of quantification) in all sampling points at the end of the landfarming process (Table 4), suggesting that the landfarming can be considered as a relatively simple and inexpensive biological treatment technique to clean up contaminated sediments.

In order to further evaluate the reduction in toxicity, also in this experimentation, a phytotest with barley seeds was conducted.

At the start of the experiment, a germination index (GI%) ranging from 70% to 100% was observed in the 8 sampling points (Table 2), suggesting a low toxicity of the sediments, as expected by the low organic pollution (absence of PCBs and low PAHs content). However, during the landfarming process, the general increase in GI %, always higher than 90%, indicated a decrease in phytotoxicity and a stimulation of plant growth, due to the reduction in contamination and improvement of sediment characteristics (decrease in EC, increase in nitrates), as confirmed by the extremely high increase in the biological activities (Table 2 and 3).

Table 2. Chemical properties and germination index in the 8 sampling points at different sampling times (T0-T1-T2). Different lowercase letters indicate statistically different values (time effect) within point according to HSD Tukey's test (P<0.05). Different uppercase letters indicate statistically different values (treatment effect) within time according to HSD Tukey's test (P<0.05)

	pH			Electrical Conductivity			Total Organic Carbon			Total Nitrogen		
				ds m^{-1}			%			%		
	T0	T1	T2	T0	T1	T2	T0	T1	T2	T0	T1	T2
1	$8,11^{aA}$	$8,36^{bB}$	$8,30^{bBC}$	$12,6^{cF}$	$4,32^{bDC}$	$2,64^{aA}$	$2,21^{abC}$	$2,31^{bD}$	$2,11^{aD}$	$0,194^{bD}$	$0,193^{bD}$	$0,162^{aC}$
2	$8,22^{bB}$	$8,28^{bA}$	$8,14^{aAB}$	$8,94^{cD}$	$6,85^{bD}$	$2,90^{aB}$	$1,74^{aB}$	$2,00^{aD}$	$1,89^{aCD}$	$0,187^{bD}$	$0,199^{bD}$	$0,158^{aC}$
3	$8,13^{aA}$	$8,47^{cC}$	$8,35^{bC}$	$11,5^{cE}$	$3,92^{bC}$	$3,32^{aBC}$	$2,17^{bC}$	$2,35^{bD}$	$1,59^{aB}$	$0,216^{bD}$	$0,232^{bD}$	$0,175^{aC}$
4	$8,21^{aB}$	$8,56^{bD}$	$8,25^{aB}$	$7,24^{cBC}$	$2,22^{aA}$	$3,12^{bBC}$	$0,89^{abA}$	$0,97^{bB}$	$0,84^{aA}$	$0,114^{aB}$	$0,104^{aB}$	$0,110^{aB}$
5	$8,24^{bB}$	$8,56^{cCD}$	$8,04^{aA}$	$6,93^{cB}$	$2,94^{aB}$	$5,34^{bD}$	$1,80^{cB}$	$1,48^{bC}$	$1,36^{aB}$	$0,150^{bC}$	$0,114^{aB}$	$0,115^{aB}$
6	$8,10^{aA}$	$8,29^{bA}$	$8,00^{aA}$	$5,36^{cA}$	$2,73^{aB}$	$3,86^{bC}$	$2,12^{cC}$	$1,71^{bC}$	$1,46^{aB}$	$0,160^{bC}$	$0,146^{bC}$	$0,124^{aB}$
7	$8,23^{aB}$	$8,37^{bB}$	$8,24^{aB}$	$7,90^{bC}$	$4,12^{aC}$	$3,54^{aC}$	$1,67^{aB}$	$1,57^{aC}$	$1,75^{aC}$	$0,158^{bC}$	$0,151^{bC}$	$0,128^{aB}$
8	$8,24^{aB}$	$8,48^{bC}$	$8,23^{aB}$	$5,41^{bA}$	$2,94^{aB}$	$4,71^{bD}$	$0,93^{bA}$	$0,73^{aA}$	$0,70^{aA}$	$0,080^{bA}$	$0,063^{aA}$	$0,072^{abA}$
	Total Phosphorus			Water Soluble Carbon			$NO3^-$			Germination Index		
	%			mg kg^{-1}			mg kg^{-1}			%		
	T0	T1	T2	T0	T1	T2	T0	T1	T2	T0	T1	T2
1	$0,07^{2bAB}$	$0,071^{bAB}$	$0,053^{aBC}$	2399^{bD}	3153^{cC}	1393^{aBC}	$3,21^{aC}$	$6,04^{bB}$	$9,51^{cC}$	68^{aA}	92^{bBC}	108^{cB}
2	$0,060^{bA}$	$0,066^{bAB}$	$0,051^{aB}$	1942^{aC}	2747^{bBC}	1939^{aE}	$3,30^{aC}$	$5,52^{bB}$	$5,23^{bA}$	88^{aCD}	92^{aBC}	107^{bB}
3	$0,071^{bAB}$	$0,070^{bAB}$	$0,054^{aBC}$	2511^{bD}	2736^{bBC}	1342^{aC}	$2,7^{aB}$	$7,34^{bC}$	$8,53^{bB}$	94^{aD}	87^{aB}	124^{bC}
4	$0,082^{bB}$	$0,060^{aA}$	$0,060^{aBC}$	1717^{bB}	2483^{cB}	1489^{aD}	$2,41^{aAB}$	$4,41^{bA}$	$8,82^{cB}$	86^{aC}	108^{cD}	97^{cB}
5	$0,075^{bB}$	$0,082^{bB}$	$0,059^{aC}$	2046^{bC}	2569^{cB}	1172^{aB}	$1,72^{aA}$	$6,21^{bBC}$	$24,1^{cE}$	77^{aB}	99^{bC}	107^{bB}
6	$0,060^{bA}$	$0,072^{bAB}$	$0,057^{aC}$	1980^{bC}	2304^{bB}	1216^{aB}	$5,11^{aD}$	$6,28^{bBC}$	$9,71^{cC}$	83^{bBC}	73^{aA}	86^{bA}
7	$0,093^{bC}$	$0,100^{bC}$	$0,070^{aD}$	2500^{bD}	2999^{cC}	1390^{aBC}	$2,34^{aB}$	$6,57^{bBC}$	$8,20^{bB}$	95^{bD}	83^{aB}	89^{abA}
8	$0,054^{bA}$	$0,060^{bA}$	$0,040^{aA}$	1526^{aA}	1742^{bA}	1017^{aA}	$3,23^{aC}$	$4,49^{aA}$	$14,6^{bD}$	97^{aD}	99^{aC}	108^{bB}

Table 3. Biochemical properties in the 8 sampling points at different sampling times (T0-T1-T2). Different lowercase letters indicate statistically different values (time effect) within point according to HSD Tukey's test (P<0.05). Different uppercase letters indicate statistically different values (treatment effect) within time according to HSD Tukey's test (P<0.05)

	Dehydrogenase (mg INTF kg^{-1} h^{-1})			β-glucosidase (mmol $kg^{-1}h^{-1}$)			Phosphatase (mmol $kg^{-1}h^{-1}$)			Protease (mmol $kg^{-1}h^{-1}$)		
	T0	T1	T2	T0	T1	T2	T0	T1	T2	T0	T1	T2
1	$0,04^{aA}$	$0,20^{bA}$	$1,19^{cAB}$	$6,8^{aA}$	67^{bA}	132^{cF}	$15,9^{aB}$	32^{bB}	162^{cB}	$0,00^{aA}$	$16,6^{bA}$	100^{cB}
2	$0,16^{aB}$	$0,77^{bC}$	$2,61^{cE}$	$9,1^{aA}$	112^{bCD}	96^{bD}	$7,4^{aA}$	16^{bA}	171^{cB}	$0,00^{aA}$	$21,8^{bA}$	143^{cC}
3	$0,42^{aD}$	$0,54^{bB}$	$3,12^{bF}$	$8,1^{aA}$	104^{bC}	100^{bD}	$10,2^{aAB}$	23^{bAB}	194^{cC}	$0,00^{aA}$	$47,9^{bC}$	64^{cA}
4	$0,03^{aA}$	$1,21^{bE}$	$1,07^{bA}$	$16,8^{aB}$	87^{bB}	77^{bC}	$32,2^{aC}$	44^{bC}	255^{cD}	$0,00^{aA}$	$93,7^{aE}$	208^{cE}
5	$0,65^{aE}$	$1,23^{bE}$	$1,21^{bAB}$	$58,5^{aE}$	102^{bC}	54^{aA}	$45,0^{aD}$	67^{bD}	295^{cE}	$2,09^{aB}$	$29,0^{bAB}$	197^{cE}
6	$0,43^{aD}$	$1,41^{bF}$	$1,34^{bB}$	$31,5^{aC}$	80^{bB}	140^{cF}	$114,1^{aF}$	145^{bF}	312^{cF}	$3,91^{aB}$	$53,9^{bC}$	159^{cD}
7	$0,30^{aC}$	$1,92^{bG}$	$2,69^{cE}$	$9,7^{aA}$	123^{bD}	116^{bE}	$76,7^{aE}$	88^{aE}	170^{bB}	$5,23^{aB}$	$36,4^{bB}$	141^{cC}
8	$0,01^{aA}$	$0,94^{bD}$	$2,32^{cD}$	$38,9^{aD}$	84^{cB}	68^{bB}	$30,4^{aC}$	43^{bC}	135^{cA}	$12,00^{aC}$	$62,5^{bD}$	139^{cC}

Table 4. Polychlorobiphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) in the 8 sampling points at T0 and T2.

		1	2	3	4	5	6	7	8
PCBs mg kg^{-1}	T0	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
PAHs mg kg^{-1}	T0	3.05	1.45	3.2	0.54	0.86	<0.5	0.75	<0.5
	T2	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5

3.3 Principal component analysis

The PCA multivariate statistical analysis was carried out using data at T0 and T2 of both experimentations (fresh and phytoremediated sediments) in order to evaluate the main parameters affected by landfarming process. The principal component analysis resulted in 76,5% of the data variance being contained in the first three components. Therefore, the first three principal components (PC) were retained (Table 5). The PC loadings showed that the 1st PC (33.8% of the total variance) was closely associated with all the enzyme activities, suggesting the paramount importance of the landfarming process in affecting biological metabolism of sediments.

The 2nd PC (27,9% of the total variance) was more closely associated with nutrient (TOC, TN, TP) and electrical conductivity. pH and WSC were included in the 3rd PC with 14.80 % of the total variance.

Scatter plot of the first two principal components (Figure 2), providing a graphical representation of the landfarming treatment over the time for both fresh and phytoremediated sediments. The two experimentations were clearly divided in the graph, even though phytoremediated sediments were closely clustered together, probably for the more intensive transformation occurred in fresh sediments under the landfarming process.

However, in both the experiments, even if greater in fresh sediment, T2 were shifted with respect to the T0 towards positive values of PC1, which was associated with enzyme activities, thus indicating the strong increase in sediment metabolism. Moreover, for fresh sediments the clear shift of T2 towards negative values of PC2 demonstrated the activation of organic matter mineralization (decrease in nutrients). The closeness of fresh samples at the end of landfarming process also indicated that the samples reached characteristics more similar between them with respect to the starting material.

On the other hand, the landfarming of phytoremediated sediments cause only a little change in the chemical nutritional sediment characteristics.

Table 5. Principal components (PC) and component loadings. EC, Electrical conductivity; TOC, total organic carbon; TN, total nitrogen; TP, total phosphorus; WSC, water soluble carbon; Contaminants %, % of contaminants with respect to the starting (100%) (TPH for phytoremediated sediments, PAHs for fresh sediments); GI, germination index, DHase, dehydrogenase. *variables with a significant level >0.7.

	PC 1	PC 2	PC 3
pH	0,131	-0,003	-0,781*
EC	0,253	0,883*	0,291
TOC	0,197	0,879*	-0,257
TN	-0,078	0,752*	-0,386
TP	-0,097	0,871*	0,161
NO_3^-	0,646	0,655	0,099
WSC	-0,475	0,124	-0,769*
Contaminants%	-0,433	0,384	0,434
GI	0,610	0,174	0,264
DHase	0,772*	0,076	-0,339
β-glucosidase	0,874*	0,325	-0,034
Protease	0,919*	-0,156	0,093
Phosphatase	0,921*	-0,009	-0,011
Var. Sp.	4,392	3,634	1,920
Prp.Tot.	0,338	0,279	0,148

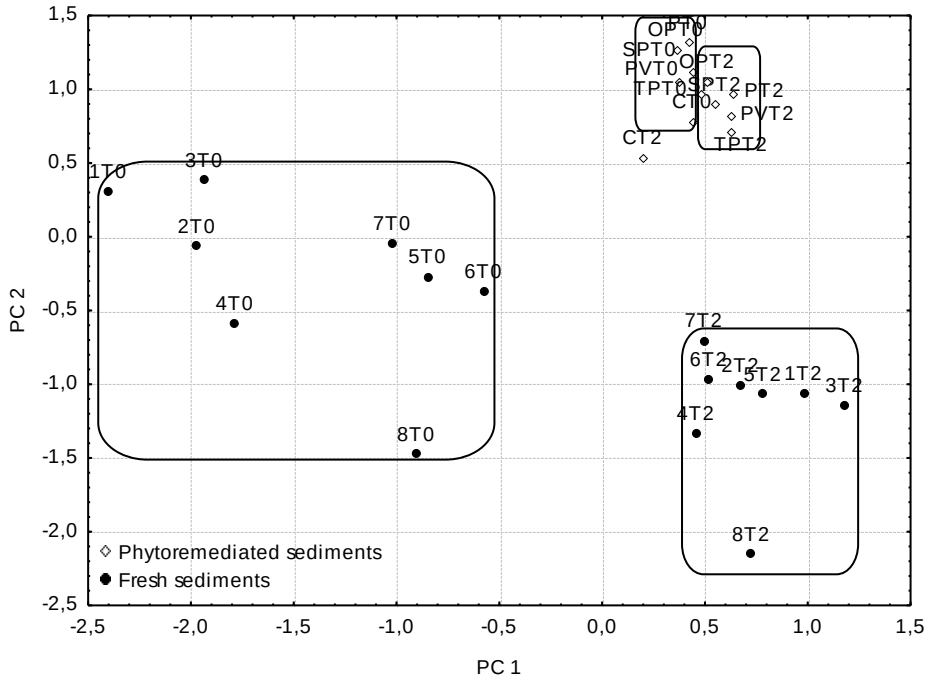

Figure 2. Scatterplot of factor scores of sediment chemical and biochemical parameters in the two different landfarming process: phytoremediated sediments and fresh sediments.

4. CONCLUSIONS

This study demonstrated that landfarming process was a rapid and low cost-effective technology to turn polluted sediments in matrices suitable for environmental purpose.

In sediment already partially recovered by a phytoremediation process, three months of landfarming permitted to reach all the objective pursued: a) activation of microbial biomass (increase in biochemical activities), b) further reduction in the residual organic contamination (15%), and c) homogenization of the substrate. These characteristics, together with the absence of toxicity (germination index greater than 100%) and a good nutrient level, made this sediment suitable for their reuse in nursery activity.

On the other hand, the direct application of five months landfarming process on fresh dredged sediments was able to transform them in a matrix with characteristics idoneous for their use in road construction.

The organic matter content decreased greatly during the process (averagely 15%) due to the activation of the sediment microbial biomass (increase in enzyme activities), responsible also of organic contaminants degradation (near to zero at the end of landfarming). This reduction permitted to reach organic matter values near to 2%, considered the optimum value for sediment reuse in road construction as reported in the "Technical Specifications for road embankments" document. Concerning the sediment water content, a great reduction (40% of water content) was achieved; however, to reach the optimal content of about 15-20%, the addition of lime (15%) was necessary.

By comparing the efficiency of landfarming process in already phytoremediated sediments and in fresh dredged sediments, it is possible to highlight that higher evolution in chemical and biochemical aspects have been observed in the fresh sediments, with respect to the phytoremediated one that probably had a more stable and balanced biological picture.

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