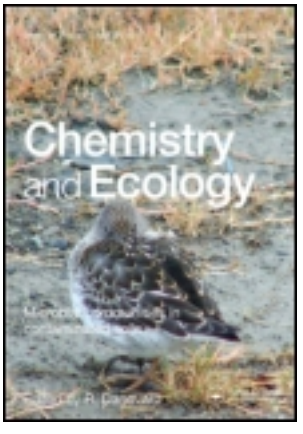

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Green remediation strategies to improve the quality of contaminated soils

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Soil contamination has been identified as an important issue requiring action for soil protection in Europe. New approaches to remediation will be required if soils are to perform their essential functions. There is a need to find new strategies of remediation which, to date, have involved rather drastic technologies or landfill disposal. The US EPA is promoting strategies (green remediation) that restore contaminated sites to productive use with great attention paid to global environmental quality, including the preservation of soil functionality. As an example of this approach, a case study is reported in which phytoremediation as a 'green remediation strategy' has been selected to clean-up sites contaminated by polycyclic aromatic hydrocarbons (PAHs). *Lupinus albus* and *Zea mays* were tested and the efficiency of the remediation was determined comparing the decrease in PAH concentration in soil with and without plants growing (32 and 22%, respectively). This is a consequence of the presence of plants that stimulated the microbial biomass involved in PAH degradation. As an index of soil quality at the end of the phytoremediation test, soil stability structure was evaluated by means of wet aggregate stability (WAS). This parameter sharply increased from 35 to 60% after cultivating selected plants.

Keywords: green remediation; phytoremediation; PAHs; plants; soil

1. Introduction

Soil is a non-renewable resource that plays a fundamental role in environment protection. Damage to soil very often means threats to other environmental media. There is a need for a comprehensive soil protection strategy to tackle the various aspects of soil degradation, including among others: erosion, organic matter decline, compaction, salinisation and pollution [1].

The increasing interest in protecting soil functionality has promoted the development of innovative remediation strategies to restore soil quality for the future use of contaminated land [2–4]. During the process of technology selection, these strategies take into account both the clean-up efficiency and minimisation of the negative effects on the environment and soil quality [5].

To this aim, less-invasive *in situ* technologies, such as bioremediation and phytoremediation, are considered as primary remedies, wherever possible, to minimise soil disturbance and restore soils of high quality. These technologies belong to 'green remediation' which is defined as the practice of considering the environmental impacts of remediation activities at every stage of the

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process in order to maximise the net environmental benefit of a clean-up. Green remediation, aimed at reducing the energy requirements of the treatment system, can also decrease the negative impacts on the environment by minimising soil disturbance such as compaction, erosion and structure depletion [6].

Phytoremediation is a viable technology both for metals [7–9] and organics [10,11]. In the latter case, plants may enhance the degradation of organic compounds, promoting an adequate substrate for microbial growth [12–14].

As an example of this approach, a case study is reported in which phytoremediation as a 'green remediation strategy' had been selected to clean-up sites contaminated by polycyclic aromatic hydrocarbons (PAH). Soil pollution by PAHs is an issue of relevance because several of these compounds are carcinogenic and/or mutagenic [15]. During the last decades, there has been considerable interest in remediating sites polluted by PAHs [16,17]. Among several technologies, phytoremediation is considered a viable environmentally friendly alternative to traditional invasive techniques [18]. One of the features of phytoremediation is the ability to degrade organic compounds in the soil around the plant roots; in the meantime, vegetation may positively affect soil properties. The aim of the study, a feasibility test, was to evaluate the effects of plants on PAH degradation and on soil quality after remediation.

2. Materials and methods

The PAH-contaminated soil was collected in a former industrial area in northern Italy, where activity began at the beginning of the last century. Different materials were produced including asphalts, naphthalene and creosote, among others.

Soil samples were air dried and ground to pass through a 2-mm sieve before laboratory analysis. Soil pH was determined using a glass electrode in a soil/water ratio of 1 : 2.5, cation-exchange capacity (CEC) was determined using barium chloride (pH 8.1), and soil texture was assessed using the pipette method according to SSSA methods of soil analysis [19].

A feasibility test, at a microcosm scale, was carried out with the aim of evaluating the efficiency of two plant species, *Lupinus albus* and *Zea mays*, in the remediation of this PAH-contaminated soil. These two plants were selected after some preliminary tests (data not reported here) for their high tolerance to the stress deriving from this kind of contamination. Moreover, these species present some special features interesting for phytoremediation. *L. albus* is a leguminous plant able to survive in the presence of a reduced nitrogen supply, as often happens in contaminated industrial soil. *Z. mays* is particularly interesting because of its high biomass and a deep rooted system able to explore a large portion of soil. Experiments were carried out by planting in 200 g of soil using five seeds per microcosm for both species.

Five replicates of vegetated microcosms for species were prepared and watered daily with tap water. Five microcosms without plants were run simultaneously as blanks. The growing period lasted three months, after which plants started to decay. Experiments were carried out in a growth chamber in controlled conditions: 14 h of light, with a temperature of 24 °C, and 10 h in the dark at 19 °C. Relative humidity was maintained at 70%. Soil samples were analysed at the beginning and end of the experiments in vegetated and non-vegetated microcosms. The efficiency of the technology was evaluated by determining the residual PAH soil concentration. The soil samples in this study were extracted using EPA method 3550, which uses sonication to extract PAH with a mixture acetone/hexane (1 : 1 v/v) from solid samples. Soil extracts were analysed by GC/MS, according to US EPA method 8270C, using a Thermofinnigan 'TRACE DSQ' GC-MS with a quadrupolar analyser and PTV injector (DB 5 ms capillary column, 30 m × 0.25 mm I.D., 0.25 μm stationary phase film thickness). All reagents were pesticide quality. Method accuracy and precision were evaluated by analysing in triplicate one certified reference soil without PAHs

which was spiked at the levels of 10 and 500 $\mu g \cdot g^{-1}$ for each compound. The relative standard deviation (RSD) of the replicates on the concentrations of individual compounds ranged from 5 to 15%. Method detection limits, estimated as three times the background noise, were similar for all analysed compounds at $<0.9\,\mu g \cdot kg^{-1}$ dry weight for all PAHs.

Aggregate stability, used as index of soil quality, was determined by the single sieve method [20–22], using soil samples of 10 g of the 1–2 mm air dry samples. The soil material retained on the sieve was oven dried, weighed and then corrected for sand content. The wet aggregate stability (WAS) was calculated as [23]:

$$\text{WAS\%} = \frac{[\text{Retained Soil Material} - \text{Sand}]}{[\text{Soil Sample} - \text{Sand}]} \times 100$$

All statistical analysis was performed using Statistica v. 6.0 (Statsoft, Inc.). Data were analysed using one-way analysis of variance. Differences among means were compared and a post-hoc analysis of variance was performed using the Tukey honestly significant differences test ($p < 0.05$).

3. Results and discussion

The original soil was characterised by a pH value of 8.63, a CEC of 16.4 $cmol \cdot kg^{-1}$, and the following texture: sand 79.0%, silt 14.7% and clay 6.3%. The soil was characterised by PAH concentrations up to $\sim$14,000 $mg \cdot kg^{-1}$. At the end of the growing cycle, in the non-vegetated microcosms, PAHs concentrations were the same as the beginning of the experiment, $13,850 \pm 423\,mg \cdot kg^{-1}$. After the growing period of *L. albus* and *Z. mays* plants, the concentration decreased to 9466 ± 396 and $10,767 \pm 402\,mg \cdot kg^{-1}$, respectively, with a reduction of 32 and 22%. These results are reported in Table 1.

The single PAHs determined by the analysis were the 16 PAHs in the US EPA list of priority pollutants: naphthalene, acenaphtylene, acenaphthene, fluorene, phenantrene, anthracene,

Table 1. Concentrations (means of five replicates) of single compounds and total concentrations found in non-vegetated soil and in microcosms vegetated with *Lupinus albus* and *Zea mays*.

	Non-vegetated microcosms	*Lupinus albus* microcosms	*Zea mays* microcosms
PAH	($mg \cdot kg^{-1}$)	($mg \cdot kg^{-1}$)	($mg \cdot kg^{-1}$)
Naphthalene	163c	116b	101a
Acenaphthylene	38b	31a	33a
Acenaphthene	94b	74a	73a
Fluorene	126b	85a	86a
Phenanthrene	1459c	856a	1139b
Anthracene	359b	204a	200a
Fluoranthene	2392c	1688a	1942b
Pyrene	1845c	1293a	1556b
Benz(a)anthracene	942c	799b	664a
Crysene	1574c	1064a	1402b
Benzo(b)fluoranthene	1133c	988a	1119b
Benzo(k)fluoranthene	1352c	478b	421a
Benzo(a)pyrene	726b	498a	537a
Indeno(1,2,3-cd)pyrene	775c	541a	661b
Dibenz(a,h)anthracene	128c	82a	116b
Benzo(g,h,i)perylene	744c	669a	717b
Total concentration	13850c	9466a	10767b

Note: Means with different letters for the same compound are significantly different from each other ($p < 0.05$) according to the Tukey test.

fluoranthene, pyrene, benzo(a)anthracene, crysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene, dibenzo(a,h)anthracene and benzo(g,h,i)perilene. The results for the single compounds obtained by the analysis are reported in Table 1.

At the end of the experiment, concentrations of each single compounds tend to decrease in vegetated pots, both with *L. albus* and with *Z. mays*. To observe the efficiency of the two plant species in the degradation of the PAHs, percentage degradation values were calculated by considering the decrease in the concentration of a single PAH in the vegetated soil, with respect to that in non-vegetated soil. Data are reported in Figure 1.

In the case of soil vegetated with *L. albus*, the lowest percentage degradation was obtained for benzo(g,h,i)perilene, ~10%. This value tended to increase for the other PAHs. The majority of them were degraded with an abatement percentage of ~30%, and in three cases the presence of plants favoured degradation to ~40% (phenantrene, anthracene) and 65% (benzo(k)fluoranthene).

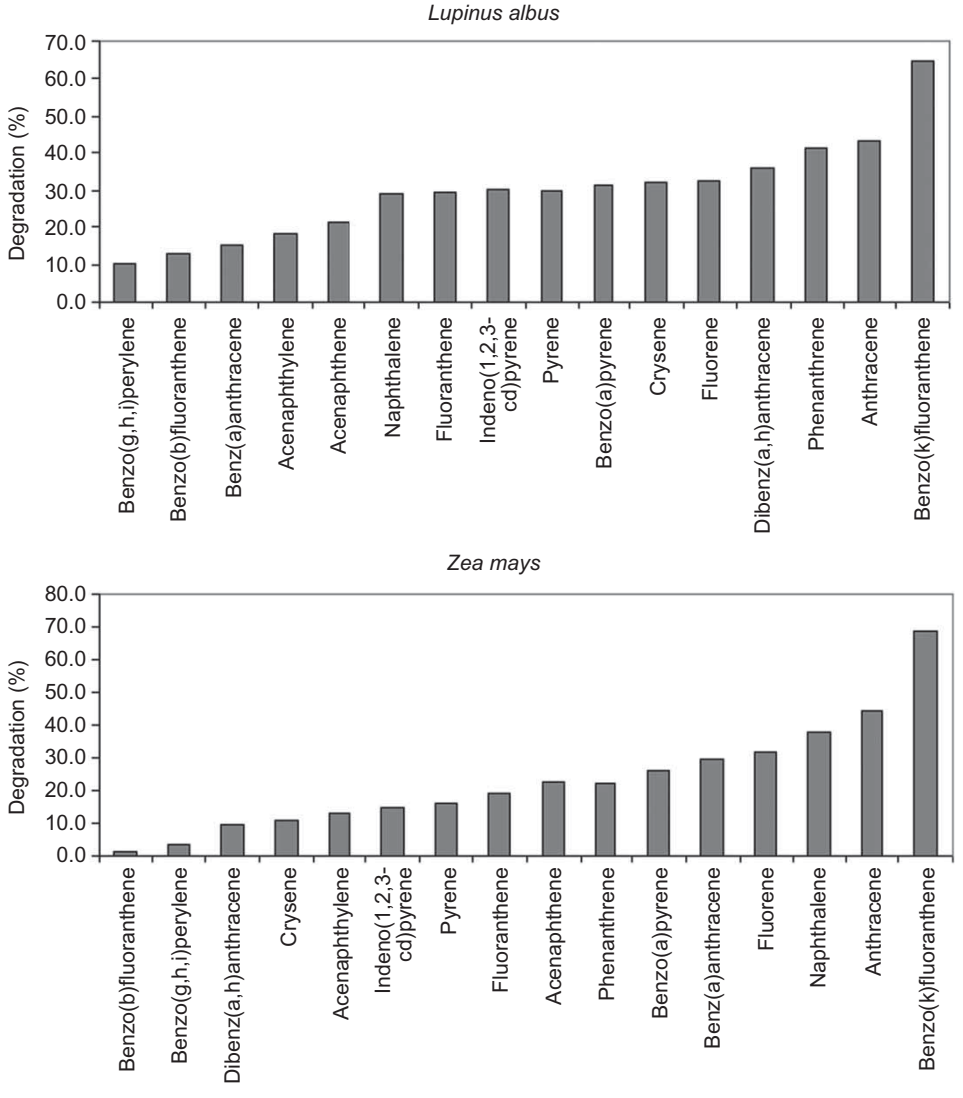

Figure 1. Percentage degradation of each single PAH in vegetated soil. Percentages were calculated using mean concentration values.

The degradation of PAHs was also favoured in soil planted with *Z. mays*, but with a lower efficiency compared with *L. albus*. Most of the PAHs degradation percentages were <30%. The lowest values were obtained for benzo(b)fluoranthene (1%) and benzo(g,h,i)perilene (4%), while the more degraded compounds were naphthalene and anthracene (both ∼40%) and benzo(k)fluoranthene (∼70%).

Thus, the presence of vegetation promoted the degradation of PAHs in the contaminated soil. The efficiency of phytoremediation was plant species dependent for most of the PAHs. In general, *L. albus* stimulated the degradation process to a greater extent.

Three different types of patterns could be identified by the observation of results obtained for each single compound. Similar degradation percentages have been obtained for PAHs like anthracene, benzo(a)pyrene, acenaphthylene, acenaphthene and fluorene with both plant species.

In the case of phenanthrene, fluoranthene, pyrene, crysene, indeno(1,2,3-cd)pyrene, benzo(b)fluoranthene, dibenz(a,h)anthracene and benzo(g,h,i)perilene, greater degradation was obtained in microcosms vegetated with *L. albus*. For naphthalene and benz(a)anthracene, there was greater abatement in pots vegetated with *Z. mays*.

From the feasibility test, both species can be suggested as effective for the treatment of the PAH-contaminated soils by phytoremediation, because plant growing stimulated the microbial biomass involved in PAHs degradation. Microbial investigation showed that most (95%) of the isolated bacterial strains belong to the phylum Proteobacteria [24]. The results obtained agree with findings showing that the introduction of plants enhances the efficiency of organics biodegradation [25–27]. The process is, however, characterised by relative complexity and the success of remediation depends on the specific site conditions [28,29]. Data obtained in this soil are of particular interest because for decades, PAH contamination, has been considered a limiting factor for microbial biodegradation of these compounds [30].

Evaluation of the physical properties of soil is very important if the the original state is to be recovered after remediation [31]. Soil stability structure is a parameter of noteworthy importance in determining soil ability to perform its essential functions. At the end of the growth cycle, wet aggregate stability was determined using a wet sieving methodology, in vegetated and non-vegetated microcosms. Compared with non-vegetated soil, the presence of plants improved soil stability structure. The growth of plants resulted in increased aggregate stability due to the effect of roots that can exude polysaccharide material which may act as a binding agent promoting the increase of larger aggregates reducing soil bulk density [32–34]. The water aggregate stability increased from ∼33 to 55% in the case of microcosms vegetated with *L. albus*, and from 37 to 62% in microcosm with *Z. mays*. Moreover plants can promote PAHs degradation through related humic compounds [35].

The increase in structure stability derived from the presence of plants highlights the enhanced soil quality following a 'green remediation' approach. Soil aggregate stability is considered an important soil-quality indicator for its positive effects contrasting soil compaction, typical of contaminated sites, and increasing available water holding capacity, properties favouring root growth and better physiological plant functions [36]. Good structural properties will better support a functioning community of PAH-degrading microbes, able to increase removal efficiency in following growing cycles.

4. Conclusions

PAH pollution had been discovered in many Italian soils. In particular, at the site of this case study, soil contamination by PAH was due to previous industrial activity. Stakeholders considered several technologies, such as thermal desorption, soil washing or solvent extraction, but phytoremediation appeared particularly attractive in order to preserve an acceptable soil quality. The selection of

technology for site remediation is a fundamental step with a potentially significant impact on soil quality throughout the course of a clean-up project. Incorporating soil quality considerations into the remedy-selection process can offer increased sustainability and long-term cost savings. It should be considered that in Italy, >70% of the soil remediation work completed can be described as 'excavation and off-site landfill'. Many sites are located very near or in an urban environment where it is essential that the remediation strategy be both protective of human health and achieve community acceptance.

Results from the reported case study showed that compared with non-vegetated soil, the efficiency of PAHs degradation was significantly stimulated by used plants, with a particular reduction over 40 and 60% in the concentration of anthracene and benzo(k)fluoranthene, respectively. Thus, it would be possible to use '*in situ*' passive energy technologies such as phytoremediation that increased PAHs degradation, ameliorating, in the meantime, soil quality, as described by the increase in water aggregate stability. In contaminated soils, biological activity is generally very low and this might result in a decline in aggregate stability and soil physical conditions. From our results, it appears that phytoremediation increased aggregate stability by growing a plant with an extensive root system, which is particularly efficient in a microcosm experiment where roots are restricted to a definite volume of soil. The increase in aggregate stability can be ascribed to the root action which promoted a larger microbial biomass in the rizosphere that, in turn, produces more binding agents and therefore increases aggregate stability.

The use of green remediation will avoid invasive soil excavation, increasing carbon sequestration, while decreasing loss of soil by run-off and the dispersion of dust due to increase in soil structure stability.

For successful phytoremediation, both plants and microorganisms must survive and grow in PAHs-contaminated soil. Obviously, specific site conditions such as climate and moisture will influence phytoremediation efficiency. Appropriate agronomic practices and amendments will result in increased plant biomass production and greater reductions in PAH. These can also be used to improve soil physical and chemical conditions to enhance plant and microbial growth.

The issue of considering the environmental effects of a remedial strategy should be tackled from the initial phases of site characterisation, to include options that maximise the environmental benefit. Soil should be considered in each phase of the remediation process, in particular, in the selection of different possible technologies, to obtain the best possible soil quality at the end of the clean-up process.

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