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Comparative evaluation of phytoremediation of metal contaminated soil of firing range by four different plant species

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Abstract The phytoremediation potential of *Helianthus annuus*, *Zea maize*, *Brassica campestris* and *Pisum sativum* was studied for the soil of firing range contaminated with selected metals i.e. Cd, Cu, Co, Ni, Cr and Pb. The seedlings of the selected plants germinated in a mixture of sand and alluvial soil were transferred to the pots containing the soil of firing ranges and allowed to grow to the stage of reproductive growth. Subsequently they were harvested and then analyzed for selected metals by using AAS. Among the studied plants, *P. sativum* exhibited highest removal efficiency (i.e. 96.23%) and bioconcentration factor for Pb thereby evidencing it to be Pb hyperaccumulator from the soil of firing ranges. *Z. maize* appreciably reduced the levels of all the selected metals in the soil but the highest phytoextraction capacity was shown for Pb i.e. 66.36%, which was enhanced to approximately 74% on EDTA application. *H. annuus* represented the highest removal potential for Cd i.e. 56.03% which was further increased on EDTA application. Thus it proved to be an accumulator of Cd after EDTA application. It was therefore concluded that different plants possess different phytoremediation potentials under given set of conditions.

1. Introduction

Firing ranges are used mostly for routine practices of the armed forces with small arms and ammunitions and typically comprise of a series of metal targets placed in front of an impact berm equipped with bullet traps. The bullet moves through the target and strikes the impact berm, penetrating and smearing it. Pb is used as a chief component in bullet construction along with other metals such as antimony, arsenic and Ni. On firing, these heavy metals sputter out in the form of fine and coarse particulate and get deposited on nearby soil, thereby polluting it heavily. Mostly, these metals concentrate in the immediate vicinity of target area and the degree of contamination of target area decreases rapidly with depth (Dermatas et al., 2004).

The degree of contamination of the soil of firing ranges has also been found to increase with the increase in period of firing

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history. There is thus a dire need to remove the toxic metals from these contaminated areas in order to control the hazardous effects arising thereof due to leaching to nearby agricultural soils and groundwater. Recently phytoextraction has emerged as a cost effective technique to remediate the metal contaminated soils.

The ideal plant species for phytoextraction are those possessing the ability to accumulate and tolerate high concentrations of metals in harvestable tissue, and exhibit a rapid growth rate (Brennan and Shellay, 1999; Lee et al., 2002). Metal accumulation by the plants is governed by their growth rate and ability to translocate metals to the above ground tissue (Keller, 2004; Selvam and Wong, 2008). Large variety of plant species have been tested for their phytoextraction capacities for various metals i.e. various *Brassica* sp., clover (*Trifolium pratense* L.), panikum (*Panicum antidotal*), *Salix populas*, and *Nicotiana* sp. (Abdel-Sabour and Al-Salama, 2007; Grispen et al., 2006; Purakayastha et al., 2008; Reinhard et al., 2008).

Agronomic crops like *Cucurbita pepo*, *Amaranthus* sp., *Raphanus sativus oleiformis* and *Zea maize* have successfully been used as metal accumulators as well as translocators (Aggarwal and Goyal, 2007; Eleni et al., 2005). *Brassica napus* and *R. sativus* grown on multi contaminated soils have proved to be better to reclaim a marginally polluted soil (Marchiol et al., 2004). *Brassica juncea* (L.) Czern. showed the strongest ability to accumulate Pb in roots and then to transport it to the shoots from soils containing sulfates and phosphates as fertilizers (Kumar et al., 1995). Similarly, among the various varieties of grasses, vetiver grass was found to best tolerate the Pb contaminated soils (Annie et al., 2007; Wilde et al., 2005).

Phytoextraction duration is the main cost factor for phytoextraction. The phytoextraction duration of a specific heavy metal polluted soil is estimated by determining a linear relationship between the adsorbed heavy metal contents in the soil and the heavy metal contents in the plant shoots (Japenga et al., 2007). In most of the cases the efficient metal uptake by remediation plants is limited by low phytoavailability of the targeted metals. That is why numerous chelants like EDTA have been used to enhance the bioavailability of the metals in soil as high as 100 times by forming soluble M-chelant complexes. But these chelants may also enhance the risk of metal leaching from soil to groundwater (Blaylock, 1997; Houston, 2007).

The risk of metal leaching from the soil may be reduced by using suitable chelates in appropriate doses (Komarek et al., 2007; Sundar et al., 2007; Turgut et al., 2004). Optimum phytoextraction dose for EDTA was found to be 10 mM for 7 days for soils highly contaminated with Pb (Hovsepyan and Greipsson, 2004; Liu et al., 2008). In the poor soil, two applications of EDTA were more effective than once (Lina et al., 2009). The chelant application at different stages of plant growth generate different results. The EDTA application before seed germination significantly reduced *Helianthus annuus* seedling emergence and dry weight. Soil available Pb and Pb concentrations in plant biomass were found to increase with EDTA concentration but the actual amount of phytoextracted Pb decreased at high EDTA concentrations due to severe growth depression (Sinegani and Khalilikhah, 2008). Depending on the nature and type of Pb-contaminated soil being remediated, the bioavailability and uptake of Pb by coffeeweed were enhanced by amending the soil with suitable chelates especially after the plants have reached maximum biomass (Miller et al., 2008).

The present study thus aims at developing the remediation strategies for metal contaminated soils of firing ranges by using four different plant species i.e. *H. annuus*, *Z. maize*, *Brassica campestris* and *Pisum sativum*. The effect of EDTA application on phytoextraction potential of these plants for selected metals was also investigated.

2. Experimental methodology

2.1. Soil sampling

Soil sample was collected from 0 to 3 cm deep top layer of soil of the firing range with the help of plastic spade after removing leaves, grass and other large external objects in polythene bags and stored in refrigerator at 4 °C to minimize bacterial activity. In order to avoid any discrepancy in metal analysis, the use of metal containers for collecting, mixing and storage was avoided. The firing range was operational for more than 20 years and served as a training facility for Rangers Headquarters Lahore (Radojevic and Bashkin, 1999). The pH of soil sample was determined by preparing a 1:2 soil–water solution, that was found to be 5.8.

2.2. Quality control and quality assurance

All the glassware used during the present experimentation were of high quality, acid resistant pyrex glass. The analytical grade reagents with a certified purity of 99% and stock metal standard solution (1000 ppm) for AAS analysis were procured from E. Merck (Germany). Working standards were prepared by appropriate dilutions of stock standard solutions with double distilled water.

HITACHI AAS Z-5000 system equipped with Zeeman background correction facility was used under optimum analytical conditions for the estimation of metals. The standard calibration method was adopted for the quantification of results and triplicate samples were run to insure the precision of quantitative results.

2.3. Green house experiment

Seeds of four different plants i.e. *H. annuus*, *B. campestris*, *Z. maize* and *P. sativum* were germinated in a mixture of sand and alluvial soil. After 3–4 weeks, the seedlings were transferred to the pots containing soil (1 kg) collected from firing ranges. Plants were grown in pots in two groups i.e. control and experimental ones. The experimental pots were applied with an EDTA dose after the plants attained maximum biomass, while the control group was given no EDTA application.

Sodium salt of EDTA was applied to the plants in amounts of 1.0 g/kg of soil in the form of water solution in a single dose after the plants attained maximum biomass. The above-ground tissues were harvested 15 days after chelate amendment by cutting the stem 1 cm above the soil surface. These harvested plants were then washed with deionized water and air dried to a constant weight. Subsequently, the plants were ground in a ball mill.

2.4. Heavy metal determination

In order to estimate the metal content of plants by AAS, the plant tissues were harvested, washed thoroughly with