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Phytoextraction of metals from a multiply contaminated soil by Indian mustard

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Abstract

The effects of nitrilotriacetate (NTA) and citric acid applications on metal extractability from a multiply metal-contaminated soil, as well as on their uptake and accumulation by Indian mustard (*Brassica juncea*) were investigated. Desorption of metals from the soil increased with chelate concentration, NTA being more effective than citric acid in solubilising the metals. Plants were grown in a sandy soil collected from a contaminated field site and polluted by Cd, Cr, Cu, Pb and Zn. After 43 days of plant growth, pots were amended with NTA or citric acid at 5 mmol kg^{-1} soil. Control pots were not treated with any chelate. Harvest of plants was performed 1 week after chelate addition. Soil water-, NH_4NO_3- and DTPA-extractable Cd, Cu, Pb and Zn fractions were enhanced only in the presence of NTA. In comparison to unamended plants, Indian mustard shoot dry weights suffered significant reductions following NTA application. NTA treatment increased shoot metal concentrations by a factor of 2–3, whereas citric acid did not induce any difference compared to the control. Chromium was detected in the above-ground tissues only after NTA amendment. Due to differences in dry matter yield, a significant enhancement of metal uptake was observed in NTA-treated plants for Cu and Zn.

Keywords: *Brassica juncea*; Chelates; Desorption; Metals; Phytoextraction; Phytoremediation

1. Introduction

Large areas of agricultural soils are contaminated by heavy metals that mainly originate from former or current mining activities, agronomic practices, industrial emissions, or the application of sewage sludge. The remediation of soils polluted with toxic metals is particularly important because metals do not degrade and thus persist almost indefinitely in the environment. Phytoextraction, which makes use of the harvestable part of plants to remove pollutants, represents a green and environmentally friendly tool for cleaning metal-polluted soils and waters in opposition to conventional chemical and physical remediation technologies that are generally too costly and often harmful to soil characteristics (i.e. texture and organic matter) (Baker et al., 1994; Luo et al., 2005).

An ideal plant for metal clean-up can be envisioned as one with high biomass production and ease of harvesting, combined with high capacity and tolerance for

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metal accumulation, translocation and uptake in the above-ground portion. Unfortunately, neither hyperaccumulators, which generally present slow growth and low biomass production, nor metal-resistant crops, that have higher dry matter yield but lower metal accumulation capacity, have been yet identified that combine these properties all together (Li et al., 2003). However, regardless of the plant used, efficient metal extraction by plants is also often limited by the availability of metals for root uptake, in particular in neutral and alkaline soils. Indeed, phytoavailability of metals is strongly influenced by soil characteristics such as pH, cation exchange capacity, or organic matter content, any of which may limit successful soil remediation (Salt et al., 1995; Kayser et al., 2000).

One promising strategy is the 'enhanced' or 'chelate-assisted' phytoextraction through the application of soil amendants to rapidly increase availability of metals in the soil for plant uptake. Both synthetic and natural chelates can desorb metals from the soil matrix to form water-soluble metal complexes into the soil solution (Blaylock et al., 1997; Schmidt, 2003; Quartacci et al., 2005). Restrictions apply, however, to the use of complexing agents. Many synthetic chelates, e.g. EDTA, show a low degree of biodegradability and the application of such chelators involves the risk of water pollution by uncontrolled metal solubilisation and leaching (Crèman et al., 2001; Jiang et al., 2003; Wu et al., 2004), and may also induce plant stress resulting from higher metal uptake (Schmidt, 2003). Some of the restrictions concerning chelate-assisted phytoextraction may be overcome by usage of easily biodegradable and low phytotoxic compounds such as nitrilotriacetate (NTA) and low molecular weight organic acids (Krishnamurti et al., 1997; Kulli et al., 1999; Kayser et al., 2000; Chen et al., 2003; Wenger et al., 2003). In agreement with the reported studies indicating a low extraction of metals by plants in contrast to a remarkable enhancement of metal solubility following chelate applications, the amendment of several Cd-contaminated soils up to 200 mg kg^{-1} with both NTA and citric acid applied at 20 mmol kg^{-1} soil caused only a 2-fold increase in metal concentration and uptake by Indian mustard (*Brassica juncea* (L.) Czern.) (Quartacci et al., 2005).

In spite of the fact that in most cases soil pollution involves the simultaneous presence of several metals at toxic concentrations, very few are the studies published on phytoextraction of multiple metal-polluted soils. In a brown soil containing several hazardous trace elements among which As, Cd, Cr, Cu, Hg, Pb and Zn, the decontamination effect by several energy plants was considered not realistic for an effective phytoremediation programme, even in the presence of EDTA or after soil acidification (Ustak and Vana, 1998). The results of a study on a multiply metal-contaminated soil (Cd, Cr, Cu, Mn, Pb and Zn) showed that the use of maize and rapeseed can be envisaged only for the phytoremediation of lightly contaminated soils (Wang et al., 2002). For a soil more heavily polluted by Cd, Cu and Zn hyperaccumulators and crops tested were not appropriate, due to the heterogeneity and depth of soil contamination (Keller et al., 2003). In a study on the behaviour of four crop-related *Brassica* species grown on the same contaminated soil used in the present experiment but mixed with sand in a 1:3 (w/w) proportion, Marchiol et al. (2004) detected in Indian mustard low concentrations of metals without significant differences among species.

Among biomass crops, which compensate lower metal accumulation by high shoot dry matter yields, Indian mustard was identified as a species able to take up and accumulate into its above-ground parts metals such as Cd, Cu, Ni, Zn, Pb and Se (Haag-Kerwer et al., 1999). It has been observed that this species concentrated Cu, Pb and Zn in its above-ground part in amounts much higher than those detected in the metal soluble fractions present in a soil contaminated by acid waters and pyritic slurry (del Rio et al., 2000).

In the present pot experiment the potential role of organic acids and NTA in the availability, accumulation and uptake of metals by Indian mustard was evaluated in order to test whether these chelates may represent a realistic and effective tool for the removal of metals from a polluted site soil containing toxic levels of Cd, Cr, Cu, Pb and Zn.

2. Materials and methods

2.1. Soil preparation and plant material

The contaminated soil used in the present study was collected from a farming area near Carpiano (Milan, Italy). The pollution source is imputable to the high metal levels present in the irrigation water used for more than a century. In particular, the fields that presented the highest metal contamination were those set aside as watered meadows, cultivation usage which utilises very high volumes of water during the whole year. As a consequence of this usage, metals accumulated in the soil in remarkable amounts.

After grass cover removal, surface soil (0–20 cm) was collected from a 10 ha irrigated meadow, air-dried, gently ground to pass through a 2-mm sieve, homogenised and stored dry. Preliminary tests showed that *B. juncea* performed poorly when sown in pots containing the polluted soil. Two weeks after germination seedlings appeared stunted as compared to plants grown on a standard soil, with leaves presenting an extensive chlorosis and necrotic areas. After a few days most seedlings died.