The role of DTPA and EDDS in remediation of Se from contaminated soil by Brussels sprouts (*Brassica oleracea* var. gemmifera)

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Abstract
The use of plants to remove heavy metals from soil (phytoremediation) is emerging as a cost-effective way compared conventional methods. Because contaminants such as Se, Pb and Cd have limited bioavailability in the soil, methods to facilitate their transport to the stems and roots of plants are required for successful phytoremediation. The objective of this study was to investigate the effects of adding different rates of DTPA (0, 0.5, 1 and 5 mmol/kg of diethylene triamine penta acetate), and EDDS (0, 5, 7.5, and 10 mmol/kg of ethylene daimine dissuccinate) on Se availability in contaminated soils with 0, 5, 10 and 15 mg/kg $NaSeO_4$, on the capacity of *Brussels sprouts* plants to take up Se under a greenhouse conditions. Results indicated that DTPA and EDDS application to Se contaminated soils significantly decreased dry matter yield of plants. Most plant available fractions (water soluble and exchangeable), carbonate, metal oxide, organic matter bound fraction increased linearly with Se application with regression R^2 values of 0.90 or greater. At all DTPA and EDDS application rates, Se concentrations in leaves were about 2-3 times higher than in roots and about 3-4 times higher than in stems. Application of DTPA and EDDS over 0.5 and 7.5 mmol/kg doses significantly decreased total Se uptake in leaves, stems, and roots in plants.

Key Words
EDDS, DTPA, heavy metal availability, phytoextraction, translocation effiviency.

Introduction
Soil contamination by heavy metals is a global environmental issue due to the rapid development of intensive agriculture and industry in many parts of the world. Elevated concentrations of heavy metals not only lead to reductions in the microbial activity and fertility of the soil and in crop production (McGrath *et al.* 1997), but also threaten human health through the food chain.
The remediation of soil and water contaminated with heavy metals has become a challenging task facing regulators and scientific communities. Contaminated soils can be remediate by physical, chemical and biological techniques (McEldowney *et al.* 1993). Traditional treatments for metal contamination in soils are expensive and cost prohibitive when large areas of soils are contaminated. Treatments can be done *in situ* or *ex situ* which are both extremely expensive. These include high temperature treatments, solidifying agents and washing process (USDA and NRCS 2000). Many different remediation methods have been tried to address the rising number of heavy metal contaminated sites. Most of traditional methods are either extremely costly (i.e., excavation, solidification and burial) or simply involve the isolation of the contaminated sites. Some methods, such as soil washing, can pose an adverse effect on biological activity, soil structure and fertility, and incur significant engineering costs. Traditional treatments for metal contamination in soils are expensive and cost prohibitive when large areas of soils are contaminated. Unlike conventional methods, phytoremediation is inexpensive, effective, and can be implemented in situ, and it is environmentally friendly. A special advantage of phytoremediation is that soil functioning is maintained and life is the soil is reactivated (Trapp and Karlson 2001).

The solubility of heavy metals in soil is limited due to complexion with organic matter, sorption on clays and oxides, and precipitation as carbonates, hydroxides and phosphates (McBride 1994). Increased solubility of the heavy metal can be achieved by adding synthetic chelants, such as EDDHA [etylenediamine-di (o-hydroxyphenylacetic acid)], EDTA (ethylenediaminetetraacetic acid), and NTA (nitrilotriacetate), and they have been used to enhance the solubility of metals in soils and their subsequent uptake and translocation in plant stems (Huang *et al.* 1997, Kos and Lesˇtan 2003a). Despite the high efficiency of EDTA for inducing the extraction of metals, some concerns have been expressed regarding the enhanced mobility of metals in soil and their potential risks of spreading metal contaminants to groundwater and the surrounding environment due to its high affinity with heavy metals and its poor biodegradability in the environment. EDDS is an easily biodegradable, low-toxic chelant with a strong chemical affinity to Pb, Cu, Se and other metals. The use of this chelant in the remediation process has received much attention in the past few years (Kos and Lesˇtan 2003b, 2006a).

There is limited information on the use of EDTA and EDDS to enhance Se accumulation in plants. Therefore, this study is carried out to compare the relative efficiency of selected synthetic chelants agents in enhancing Se phytoextraction and to identify soil amendments that increase Se desorption from soil.

Materials and methods

A loamy (36.0% sand, 34.0% silt, and 30.0% clay) textured soil was sampled from Erzurum province (39^o 55' N, 41^o 61 E) of Turkey. The soil had 1.20% $CaCO_3$, 300.2 mmol/kg P_2O_5, 430.3 mmol/kg K_2O, 6.90 pH (H_2O) and 1.15 dS/m electrical conductivity.

Soil was transferred to 20 cm diameter polyethylene pots. Each soil was treated with 0, 5, 10 and 15 mg/kg $NaSeO_4$ as pollutant. The soil contamination was performed by putting the right amount of heavy metals dissolved in deionised water into each pot (3000 g soil/pot), which was first saturated and then air dried at room temperature and, during this process, the metals in water were thoroughly mixed into the soil. The wetting-drying mixing process was repeated to ensure equilibrium following 1 mo after incubation. To support optimum plant growth 350 N kg ha^{-1} (as ammonium sulfate), 92 kg ha^{-1} P (as triple superphosphate), 166 kg ha^{-1} K (as potassium sulfate) were applied before planting. Three months after the addition of Se, polluted soils were treated with the synthetic chelants agents, DPTA and EDDS, at the rates of 0, 0.5, and 5 mmol/kg of diethylene triamine penta acetate (DTPA), and 0, 5, 7.5, and mmol/kg of ethylene daimine dissuccinate (EDDS). Concentrations of synthetic chelants were based on the upper soil surface layer and were sprayed on the soil surface, following procedures used in a previous work (Vogeler *et al.* 2001).Plants were maintained in a heated greenhouse under natural light at a minimum temperature of 10-11°C and maximum of 25-30°C and a relative humidity of about 30-40%. Day length was 14 h during the experimental period. Plant seeds were germinated for 20 days at 25°C with an approximate of 20.000 plant/ha. Three seedlings were transplanted to each pot containing 3000 g soil. The pots were weighed daily and irrigated with deionised water to replace water lost throughout evapotranspiration. Water content of the soil was adjusted to 70% of field capacity. There were three replicates of each treatment giving a total of 96 pots in a randomized block design. The plants were harvested 150 days after being planted, and soil and plant analyses and Se distribution using a sequential extraction procedure were done according to AOAC (2005), Mertens (2005a), Mertens (2005b) and Tessier *et al.* (1979).

*Statistical analysis:*Each pot was considered as a replicate and all of the treatments were repeated three times. All data were subjected to a two way analysis of variance (ANOVA) and separated by LSD with SPSS 2004.

Results and discussion

Dry matter yield of plants: Application of the addition of DTPA and EDDS did not impact leaves, stem, root and total dry matter yield of plants without Se contamination in the soils. However, DTPA and EDDS application to Se contaminated soils significantly decreased dry matter yield of plants and plants showed a significant decrease in yield with increase in the DTPA and EDDS addition levels. The highest dry matter reduction was obtained from leaves and stem parts of the plant with 1.0 mmol/kg for DTPA and 7.5 mmol/kg for EDDS for both the 10 and 15 mg/kg Se contamination level in the soil (Figure 1).

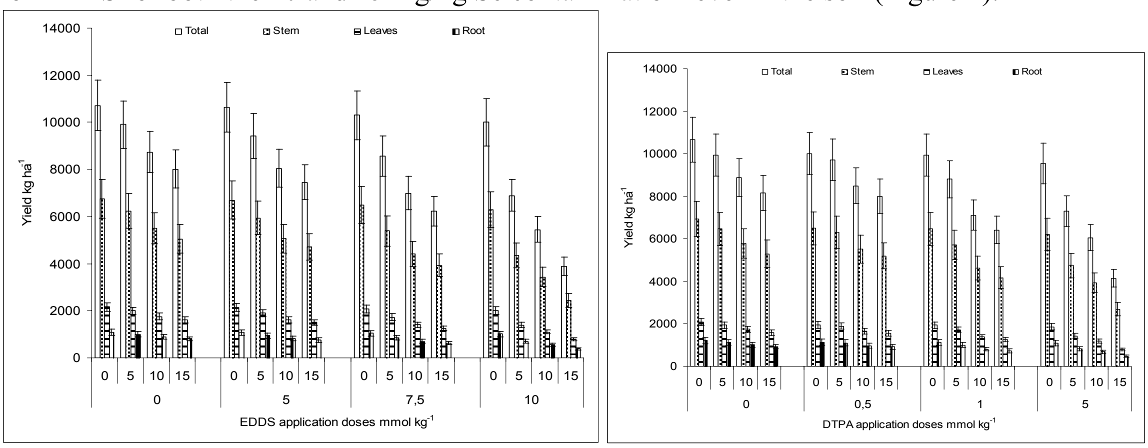

Figure 1. Effects of DTPA and EDDS synthetic chelants on dry matter weight of different plant parts of Brussels sprouts grown on soil with different Se contamination

Efficiency of Synthetic Chelants Agents in Enhancing Soil Se Desorption: All Se pools increased linearly with Se application with regression R^2 values of 0.90 or greater. Effects of synthetic chelants application significantly increased Se availability in soils. Se concentration in the soil increased with increased levels of DTPA and EDDS added to *Brussels sprouts* planted soils. The greatest increases with DTPA (5 mmol/kg) and EDDS (10 mmol/kg) addition at 15 mg/kg Se contaminated soil occurred in the most plant available fractions (water soluble and exchangeable), and followed the order of carbonate, metal oxide, organic matter bound and silicate bound fraction. Among the synthetic chelants tested, there were significant differences in their ability to stimulate total Se accumulation. Similar results were reported by Yadav *et al.* (2007), Sager and Hoesch (2006), Lu *et al.* (2006b), Wu *et al.* (2007).

Heavy Metal Concentration in Leaves, Stems and Roots: At all DTPA and EDDS application rates, Se concentrations in leaves were about 2-3 times higher than in roots and about 3-4 times higher than in stems (Figure 2). Although, leaves have the highest Se concentration, stem is more important portion of the plant to removal Se from the Se contaminated soil because of the fact that consist the biggest part of the plant. Application of DTPA and EDDS over 0.5 and 7.5 mmol/kg doses significantly decreased total Se uptake in leaves, stems and roots in plants (Figure 3). Similar increases in crop removal were reported by Ducsay and Lozek (2006), Srivastava *et al.* (2005), Yadav *et al.* (2007), Zhang *et al.* (2007), Li *et al.* (2008).

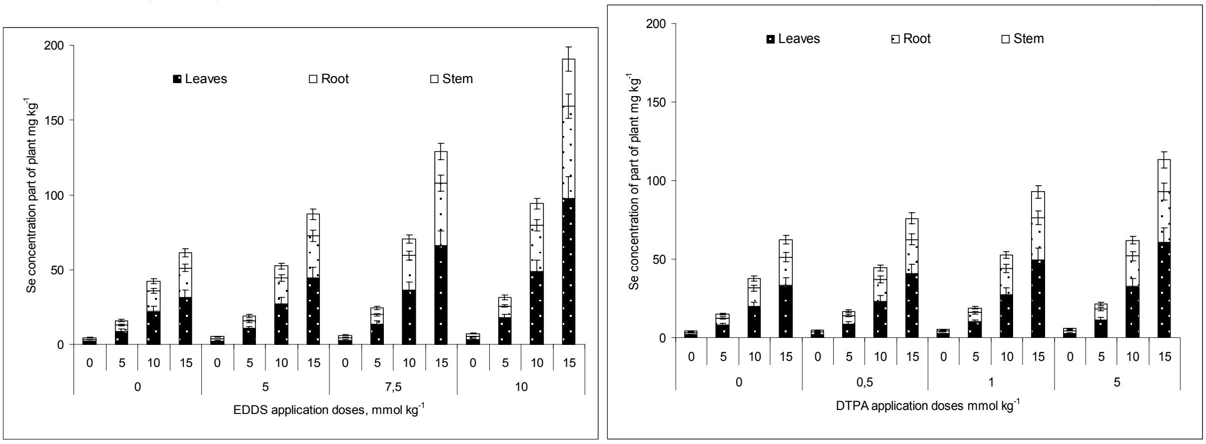

Figure 2. Effects of DTPA and EDDS synthetic chelants on Se concentration in different plant parts of the Brussels sprouts grown on soil with different Se contamination

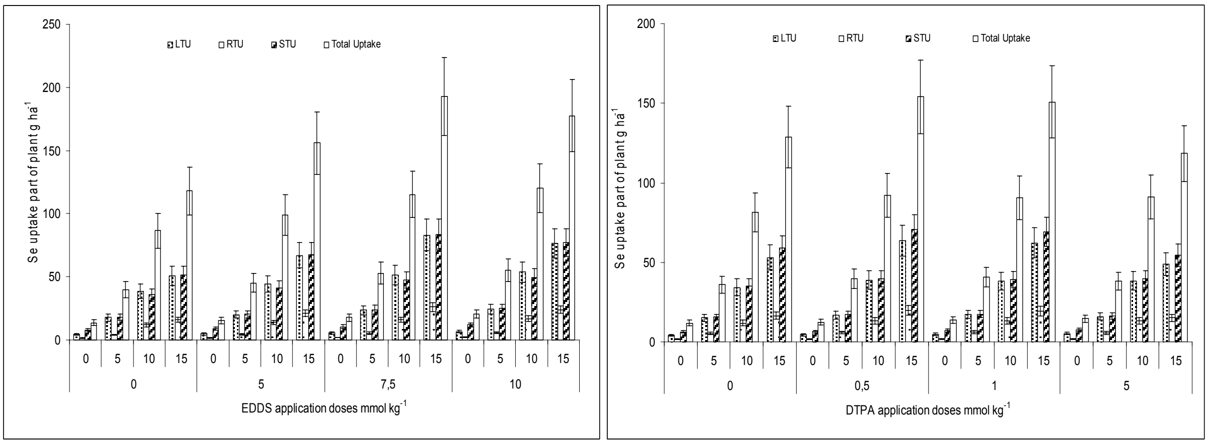

Figure 3. Effects of DTPA and EDDS synthetic chelants on Se uptake by different plant parts of the Brussels sprouts grown on soil with different Se contamination

Conclusion

Phytoremediation is widely considered as low cost and ecologically-responsible alternative to the expensive physical-chemical methods currently practiced, and an emerging bio-based and low cost alternative technology in the clean-up of contaminated soils. The ability of DTPA and EDDS to release Se in soils planted with *Brussels sprouts* followed the order of EDDS>DTPA, respectively. Among the synthetic chelants tested, EDDS was the most effective for *Brussels sprouts*. The results of this study demonstrated that EDDS is an efficient soil amendment in enhancing Se desorption from soil and for increasing Se accumulation in plants. More importantly, this chelating agent not only facilities heavy metal removal from the soil via plant uptake, but in theory means that any metal that can be chelated and solubilized can be removed in the same manner, providing the soil chemistry favors the forming of a chelate- metal complex.

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