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Soil solution Zn and pH dynamics in non-rhizosphere soil and in the rhizosphere of *Thlaspi caerulescens* grown in a Zn/Cd-contaminated soil

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Abstract

Temporal changes in soil solution properties and metal speciation were studied in non-rhizosphere soil and in the rhizosphere of the hyperaccumulator *Thlaspi caerulescens* J. & C. Presl (population from Prayon, Belgium) grown in a Zn- and Cd-contaminated soil. This paper focuses on soil solution Zn and pH dynamics during phytoextraction. The concentration of Zn in both non-rhizosphere and rhizosphere soil solutions decreased from 23 mg/l at the beginning to 2 mg/l at the end of the experiment (84 days after transplanting of seedlings), mainly due to chemical sorption. There was no significant difference in overall Zn concentration between the planted and the unplanted soil solutions ($P > 0.05$). Soil solution pH decreased initially and then increased slightly in both planted and unplanted soil zones. From 60 to 84 days after transplanting, the pH of the rhizosphere soil solution was higher than that of non-rhizosphere soil solution ($P < 0.05$). Zn uptake by the hyperaccumulator plants was 8.8 mg per pot (each containing 1 kg oven-dry soil) on average. The data indicate that the potential of *T. caerulescens* to remove Zn from contaminated soil may not be related to acidification of the rhizosphere.

1. Introduction

Zinc is an ubiquitous contaminant. Disposal of municipal wastes, irrigation of industrial effluents, agricultural use of sewage sludge and residues from metalliferous mining and the smelting industry have contaminated large areas of cultivated land with Zn. Zinc is phytotoxic and can reduce crop yields and may represent a potential hazard to the food chain. Clean-up of Zn-contaminated soils is difficult. Existing methods such as mechanical removal and chemical engineering are expensive, and often cannot maintain soil structure and fertility. Phytoextraction using hyperaccumulator plants has been recognised as a potential technique for the decontamination of metal-polluted soils (Baker et al., 1994; Brown et al., 1995a; Huang et al., 1997).

The term 'hyperaccumulator' is used to describe a plant capable of accumulating trace metals at tissue concentrations approximately 100 times greater than those of 'normal' plant species (Baker and Brooks, 1989). *Thlaspi caerulescens* has been recorded as a Zn hyperaccumulator plant (Reeves and Brooks, 1983; Brown et al., 1995b), and much of the previous work on *T. caerulescens* has involved the uptake and transport of Zn (Baker et al., 1991; Brown et al., 1994; Brown et al., 1995b; Shen et al., 1996; Huang et al., 1997; McGrath and Dunham, 1997). The concentration of Zn in the soil solution is considered to reflect accurately the plant available concentration of Zn in the soil. Soil pH is known to be one of the most important chemical factors controlling the solubility and plant availability of Zn in soil. Although changes in soil solution Zn speciation and

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pH induced by *T. caerulescens* have been reported recently (Knight et al., 1997; McGrath et al., 1997), little is known about the temporal variation in soil solution Zn and pH in the rhizosphere of the hyperaccumulator during phytoextraction.

A pot experiment was conducted to study temporal changes in soil solution properties and chemical speciation of Zn and Cd in non-rhizosphere soil and in the rhizosphere of the hyperaccumulator *T. caerulescens* grown in a Zn- and Cd-contaminated soil. The paper focuses on soil solution Zn and pH dynamics during phytoextraction for the examination of the temporal variation in the bioavailable Zn in metal-contaminated soil.

2. Materials and methods

Plough layer soil (0–15 cm) was taken from an arable site considered typical of a large proportion of the agricultural area in Northern Ireland. The soil was a sandy loam brown earth (Typic Dystrochrept) developed from silurian shale and Triassic sandstone near Hillsborough, County Down. Freshly collected soil was passed through an 8 mm sieve and air-dried. Subsamples of the air-dried soil were ground to pass a 2 mm sieve. The clay content was 13.2%, total carbon was 2.4% and the pH (in water) was 6.2. The aqua regia soluble concentration of Zn was 43.5 mg/kg. Soil pH, total carbon and particle size were determined using routine methods (Ministry of Agriculture, Fisheries and Food 1986). Soil pH was measured in water (1:2.5 soil:water ratio) using a pH meter. Particle size analysis was performed using the pipette method and soil textural classes were determined using the textural triangle. Total carbon was determined by Dumas combustion of ball-milled subsamples using a Carlo Erba nitrogen analyser. The aqua regia soluble metal concentration was determined by a routine method (Department of the Environment, 1987).

Soil (<2 mm) was mixed with appropriate amounts of analytical grade solid $ZnCl_2$ and $Cd(NO_3)_2$ in order to add 500 mg Zn and 20 mg Cd per kg of dry soil. Basal fertilisers applied were 100 mg N/kg dry soil as ammonium nitrate, and 80 mg P/kg and 100 mg K/kg as KH_2PO_4. These were thoroughly mixed with the soil. The mixture was then adjusted with distilled water to 60% of water holding capacity (WHC) and maintained at this moisture content for two days. The soil was mixed thoroughly again and aliquots (1.0 kg oven dry weight) were transferred to acid washed plastic plant pots. One porous plastic soil moisture sampler (Rhizon SMS, Rhizosphere Research Products, Wageningen, The Netherlands) was installed in the centre of each pot to allow samples of the soil solution to be extracted. There were four replicates of each treatment in a randomised block design.

Eight seedlings of *T. caerulescens* were transplanted into each of the pots and grown with supplementary heating (temperature $18 \pm 3°C$) and lighting (12 h photoperiod) for 84 days in a glasshouse. The planted pots were used to provide 'rhizosphere' soil and unplanted pots were included to give 'non-rhizosphere' soil. All the pots were adjusted daily to 70% WHC with distilled water during plant growth. The soil solution samples were obtained on a total of eight occasions (every 10 days on average) using 20 ml sterile plastic syringes which exerted a vacuum pressure equivalent to 0.3 bar. Each soil solution sample was separated into several aliquots to allow a range of chemical analyses including Zn and pH. The plant shoots were harvested 84 days after transplanting and washed, dried, weighed, ground and digested in a mixture of concentrated HNO_3 and $HClO_4$ (4:1, v/v) (Ministry of Agriculture, Fisheries and Food 1986). The metal was determined using a Perkin Elmer model 5000 Flame atomic absorption spectrophotometer (FAAS) and soil solution pH was measured using a pH meter. Data were tested statistically by analysis of variance.

3. Results and discussion

Fig. 1 shows the temporal variation of soil solution pH in both non-rhizosphere (unplanted) and rhizosphere (planted) soils treated with inorganic Zn and Cd salts. Soil solution pH decreased initially and then increased slightly in both non-rhizosphere soil and in the rhizosphere of *T. caerulescens*. From 60 days until 84 days after transplanting, the pH of the rhizosphere soil solution was higher than that of the non-rhizosphere soil solution ($P < 0.05$). This result supports the previous work of Bernal and McGrath (1994), McGrath et al. (1997) and Knight et al. (1997). Knight et al. (1997), who also used Rhizon SMS soil moisture samplers, reported

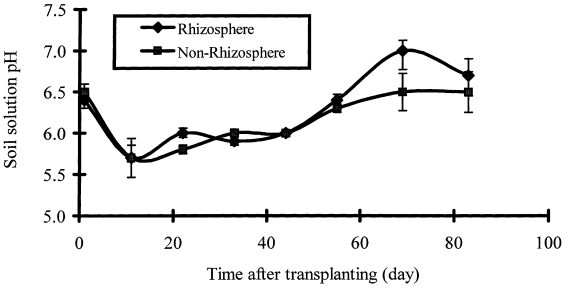

Fig. 1. Changes in soil solution pH in the non-rhizosphere and rhizosphere of *Thlaspi caerulescens* grown in a Zn/Cd-contaminated soil.

a significant increase in the solution pH of four soils of between 0.4 and 0.9 units after growth of *T. caerulescens* for 100 days. Lorenz et al. (1997) also found an increase in soil solution pH during the growth of radish plants. The increase in solution pH was probably the result of the plants taking up N predominantly in the NO_3–N form, with concurrent excretion of OH^- ions in order to maintain electrical neutrality within their roots (Hedley et al., 1982).

The soil solution Zn dynamics in non-rhizosphere soil and in the rhizosphere of *T. caerulescens* grown in the metal-contaminated soil is shown in Fig. 2. Zinc concentrations in rhizosphere soil solutions dropped from 23 to 5 mg/l during the period from 10 to 30 days after transplanting, levelled off during 30–40 day period, dropped again to 2 mg/l and remained at this concentration until the end of the experiment. The non-rhizosphere soil solution Zn concentrations showed a similar trend. The initial substantial decrease in the solution Zn concentration was probably due to chemical sorption in the soil receiving high metal loadings. Statistical analysis indicated no significant difference in overall Zn concentration between the planted and unplanted soil solutions ($P > 0.5$). However, the concentration of Zn in the rhizosphere dropped much more 45 days after transplanting and was even lower from 60 days after transplanting compared to that in the non-rhizosphere soil. This decrease in Zn concentration in the rhizosphere soil solution may have resulted from an increase in pH as mentioned above, indicating that rhizosphere acidification was not the mechanism by which the hyperaccumulator plant mobilised Zn in the soil. It was observed that the hyperaccumulator plants grew better and faster 45 days after transplanting. The *T. caerulescens* plants harvested 84 days after transplanting had, on average, a biomass of 1.5 g DM per pot, a concentration of 5800 mg Zn/kg, and therefore a calculated uptake of 8.76 mg Zn per pot. The further drop in solution Zn concentration in the rhizosphere soil 45 days after transplanting may have resulted from Zn uptake by *T. caerulescens* plants. Previous work showed that

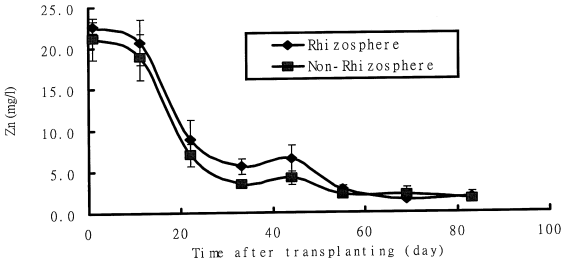

Fig. 2. Soil solution Zn dynamics in the non-rhizosphere and rhizosphere of *Thlaspi caerulescens* grown in a Zn- and Cd-contaminated soil.

T. caerulescens decreased the concentration of 1 M NH_4NO_3-extractable Zn (McGrath et al., 1997) and soil solution Zn (Knight et al., 1997). Brown et al. (1995a) suggested that this plant species may be a candidate for the phytoremediation of Zn-contaminated soils due to its hyperaccumulation of Zn.

It should be pointed out that in the present study a soil concentration of 500 mg Zn/kg was obtained by mixing the Zn into the soil as an inorganic salt in solid form. This addition gave moderate contamination of the soil on the basis of its estimated total Zn concentration and resulted in a magnitude of 23 mg/l at the start of the experiment (Fig. 2). Even at the end of the experiment (84 days after equilibrium) the Zn concentration was still as high as 2 mg/l. Luo (1997) investigated the soil solution Zn concentrations in 10 agricultural soils and found an average concentration of 0.02 mg Zn/l. Knight et al. (1997) collected soil solution using Rhizon SMS samplers from seven metal-contaminated European soils in which the total Zn concentrations ranged from 210 to 3259 mg Zn/kg and found that the solution Zn concentrations were less than 1.4 mg/l. The method and rate of application of Zn used in this study led to a very high initial concentration of Zn in the soil solution. Moreover, despite much effort to mix the soil uniformly, there was considerable variation in the initial Zn concentrations in the soil solutions. This occurred probably because the added metal salt particles were not thoroughly and uniformly mixed with the soil and also because the mixture had not been equilibrated within the experimental period. Thorough mixing and sufficient equilibration of media are necessary for studying hyperaccumulator rhizosphere effects when metal-spiked soil is used in pot experiments. Further work is needed to elucidate hyperaccumulator rhizosphere dynamics and processes of bioavailable metals in a wide range of soils in relation to metal hyper-availability.

4. Conclusions

Soil solution pH showed temporal variation in both non-rhizosphere soil and in the rhizosphere of *T. caerulescens* grown in a Zn- and Cd-contaiminated soil. An increase in soil solution pH during plant growth indicated that rhizosphere acidification was not the mechanism by which the hyperaccumulator mobilised Zn in the soil. The soil solution Zn concentrations in both non-rhizosphere and rhizosphere of the Zn-hyperaccumulator decreased substantially with time at early stages of the experiment, probably due to chemical sorption. A further decline in Zn concentration in the rhizosphere soil solution at later stages of plant growth might be accounted for by plant uptake and an increase in soil solution pH.

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