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Remediation of a Sandy Soil Contaminated with Cadmium, Nickel, and Zinc using an Insoluble Polyacrylate Polymer

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Abstract: This study was carried out to investigate whether an insoluble polyacrylate polymer could be used to remediate a sandy soil contaminated with cadmium (Cd) (30 and 60 mg Cd kg⁻¹ of soil), nickel (Ni) (50 and 100 mg Ni kg⁻¹ of soil), zinc (Zn) (250 and 400 mg Zn kg⁻¹ of soil), or the three elements together (30 mg Cd, 50 mg Ni, and 250 mg Zn kg⁻¹ of soil). Growth of perennial ryegrass was stimulated in the polymer-amended soil contaminated with the greatest amounts of Ni or Zn, and when the three metals were present, compared with the unamended soil with the same levels of contamination. Shoots of plants cultivated in the amended soil had concentrations of the metals that were 24–67% of those in plants from the unamended contaminated soil. After ryegrass had been growing for 87 days, the amounts of water-extractable metals present in the amended soil varied from 8 to 53% of those in the unamended

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soil. The results are consistent with soil remediation being achieved through removal of the metals from soil solution.

Keywords: Cadmium, contamination, nickel, polyacrylate polymers, soil remediation, zinc

INTRODUCTION

Polyacrylate polymers are based on acrylic acid and are composed of chains with regularly distributed carboxylic groups: $(-\text{CH}_2\text{CHCOOH}-)_n$. The degree of ionization of these groups depends on pH, and the negative charges formed are neutralized by counter ions, usually Na^+ , but K^+ and NH_4^+ can also be used.

High-molecular-weight insoluble polyacrylates swell to form gels that contain many times their weight in water. They are used in diapers, paper towels, and feminine products. It is estimated that more than 130 Gg of polyacrylates are used annually in such products (Martin 1996). Hydrophilic polymers are also marketed as superabsorbent polymers, with different trade names, for incorporation into soils and substrates when an increase in the water-holding capacity is desirable. Polyacrylates are considered nontoxic to humans and very stable (for a review on the behavior of polyacrylates in the environment, see Langbein 1996), although they can be degraded by some bacteria (Kawai et al. 1994).

Very little is known on the mobility of insoluble polyacrylate polymers in soils. In 35-cm sand columns, it was shown that a small percentage of a polyacrylate polymer moved rapidly, but this fraction seemed to represent short strands rather than degradation products (Martin 1996). The author concluded that little, if any, migration of polyacrylate polymers should be expected in soils, because of the strong retention in exchange sites present in the soil matrix.

As early as 1954, it was shown that copper forms coordination bonds with the carboxylic groups of polyacrylates (Wall and Gill 1954). In free solution, the ionic species of several metals, including copper (Cu), cadmium (Cd), nickel (Ni), and zinc (Zn), were rapidly trapped within an insoluble polyacrylate polymer and were not released upon subsequent incubation of the polymer particles with water (Torres and de Varennes 1998; de Varennes and Torres 2000). This capacity to chelate metal cations suggested that these polymers could be used for in situ remediation of metal-contaminated soils.

Hydrophilic insoluble polymers can enhance plant growth in coarse-textured soils by three main processes: 1) increased water-holding capacity of the soil and an enhanced supply to plants (Boatright et al. 1997; Johnson and Piper 1997; de Varennes et al. 1999); 2) increased supply of the cation present as counter ion, usually Na^+ , K^+ , or NH_4^+ (Silberbush, Adar, and de Malach 1993; de Varennes et al. 1999); 3) decreased bioavailability of

some trace elements, as previously shown for copper (Torres and de Varennes 1998; de Varennes and Torres 1999).

In soil, the amount of metal in solution usually represents a small percentage of the total, and movement of the ions is restricted by the presence of a matrix that can remove the metal from solution and that increases the path through which diffusion can take place. Though the polymer seemed to be unable to scavenge metals from the soil matrix, it competed with plants for copper uptake, preventing the buildup of the metal both in plants and in soil solution (de Varennes and Torres 1999).

The effect of a polyacrylate polymer in a sandy soil contaminated with cadmium, nickel, and zinc was now studied to identify whether this remediation process can be extended to a broad range of metals commonly associated with contaminated sites.

Several parameters that are related to metal bioavailability can be used to monitor in situ remediation of metal-contaminated soils. In the present work, the parameters chosen to measure the effects of polymer application were plant biomass accumulation, metal concentration in plant shoots, and levels of metals in soil solution.

MATERIALS AND METHODS

A sandy soil [Cambic Arenosol (FAO 1988)], previously cropped with cereals and annual grain legumes, was used as an example of a slightly acidic coarse-textured soil. The soil had 1% organic matter, a CEC of 2.7 cmol (+) kg⁻¹, and a pH in water (1:2.5) of 5.4. The soil was passed through a 5-mm sieve. For each treatment, six replicate pots (upper diameter 16 cm, height 14 cm) were filled with 2 kg of soil. The soil received cadmium at 30 and 60 mg Cd kg⁻¹ of soil, nickel at 50 and 100 mg Ni kg⁻¹ of soil, or zinc at 250 and 400 mg Zn kg⁻¹ of soil. An uncontaminated control was included, as well as a treatment where the three metals were applied together at 30 mg Cd, 50 mg Ni, and 250 mg Zn kg⁻¹ of soil. The metals were supplied as sulphates of cadmium, nickel, and zinc, respectively. A basal dressing of 50 mg of nitrogen (N), 65 mg of phosphorus (P), and 30 mg of magnesium (Mg) kg⁻¹ of soil was carried out at the same time as contamination of the soil took place. The nutrients were supplied as ammonium nitrate, calcium dihydrogen phosphate, and magnesium sulphate. Half of the pots in each treatment also received 210 mg potassium (K) kg⁻¹ of soil, supplied as potassium sulphate, as part of the basal dressing. All salts were applied in solid form and uniformly mixed with the soil. The pots were then watered with 300 cm³ of deionized water, covered, and aged in a greenhouse for 2 months.

The polyacrylate polymer (supplied by Hoechst Marion Roussel Lda) was added at 0.1% to half of the pots from each treatment (those that had not received K in the basal dressing). The polymer used had linear chains with molecular weights of about 40 million. The chains were not cross-linked but

joined together by physical entanglements. Fifty-five percent of the particles had diameters larger than 0.5 mm, and only 1% had diameters smaller than 45 μm . The polymer had potassium as counter ion (210 mg K g^{-1} of polymer) and therefore supplied to the remaining pots an equivalent amount of the nutrient as that introduced by the basal dressing.

Perennial ryegrass (*Lolium perenne* L. cv. Victorian) was sown, and plant number was adjusted to 40 per pot 1 month later. Another 50 mg N kg^{-1} of soil, as ammonium nitrate, was added 2 months later as a top dressing.

The pots were kept in a greenhouse (minimum temperature 8°C, maximum temperature 25°C) and watered daily. All the pots were supplied with the same amount of water at each irrigation operation, to maintain 70% of the water-holding capacity of the soil.

The shoots were collected 87 days after sowing, washed with deionized water, dried at 65°C, and weighed. The samples were ground, dried at 105°C, reweighed, ashed at 450°C, twice digested in 10 cm^3 of 3 M HCl at 90°C, diluted to 100 cm^3 with deionized water, and analyzed for potassium, cadmium, nickel, and zinc by atomic absorption spectrophotometry (using a graphite furnace for cadmium and nickel). Detection limits were 0.1 $\mu\text{g Ni L}^{-3}$, 0.03 $\mu\text{g Cd L}^{-3}$, and 20 $\mu\text{g Zn L}^{-3}$. Quality control showed that duplicated samples differed less than 10%.

At the end of the experiment, the soil from each pot was airdried, passed through a 2-mm sieve, and analyzed for pH in water (1:2.5). Soil samples (50 g) were shaken with 75 cm^3 of deionized water for 3 h. The extract was filtered through Whatman No. 6 paper and analyzed for Cd, Ni, and Zn by atomic absorption spectrophotometry as before.

All plant and soil data were subject to ANOVA. When the variances were not homogeneous, data were $\ln$ transformed. The Newman–Keul test at a level of 0.05 was used to compare mean values.

RESULTS AND DISCUSSION

Biomass accumulation was influenced by the treatments applied (levels of metals and amendment) according to the ANOVA. To examine the use of the polymer for soil remediation, it was important to differentiate its effect on metal bioavailability from its other properties that might also stimulate plant growth. We excluded the possibility of enhanced plant growth in amended soil being explained by additional water supply by the polymer, because all the pots were supplied with the same amount of water throughout the experiment to keep soil moisture adequate in all pots.

The polymer used had potassium as the counter ion. To make sure that plant growth would not be stimulated by an increased supply of this nutrient, the same amount of potassium was applied to the unamended soil as present in the polymer added to the amended soil. It was assumed that the nutrient in the polymer had the same bioavailability as that directly

applied to soil. The results show that plant growth in uncontaminated soil was the same, regardless of whether polymer was applied (Table 1). Furthermore, when plant growth was not impaired because of the presence of excessive amounts of metals, there were no significant differences between the potassium concentrations of plants from amended versus unamended soil with the same level of contamination (Table 1). It is reasonable to assume that the supply of K was not responsible for the differences in plant growth observed, and that these derived from the effect of the polymer on the bioavailability of Cd, Ni, and Zn applied to the soil.

When the mean values for biomass accumulation were compared, perennial ryegrass tolerated both levels of Cd and the smallest amounts of Zn and Ni applied, when the metal ions were presented separately, because plant growth was not affected in these cases. In contrast, plant growth was impaired at the higher levels of applied Ni and Zn, or when all three metals were presented together (Table 1). In fact, biomass accumulation was reduced to 15 and 30% of controls when the soil was contaminated with

Table 1. Dry weight and potassium concentration (mean and standard error) in the shoots of perennial ryegrass grown in a sandy soil contaminated with different levels of cadmium, nickel, and zinc, with or without polymer

Treatment	Polymer	Dry weight (g pot ⁻¹)	K (g kg ⁻¹)
Control	—	7.4 ± 0.1 abcd	20 ± 0 cd
	+	7.6 ± 0.0 abcd	24 ± 0 bc
Cd 1	—	7.1 ± 0.1 bcd	22 ± 0 bcd
	+	7.8 ± 0.1 abc	23 ± 0 bcd
Cd 2	—	7.1 ± 0.0 bcd	23 ± 0 bcd
	+	6.8 ± 0.0 cd	24 ± 0 bc
Ni 1	—	7.5 ± 0.1 abcd	20 ± 1 cd
	+	8.0 ± 0.1 abc	19 ± 0 d
Ni 2	—	2.2 ± 0.1 e	36 ± 0 a
	+	6.3 ± 0.1 d	23 ± 0 bcd
Zn 1	—	8.4 ± 0.1 ab	24 ± 0 bc
	+	8.7 ± 0.1 a	21 ± 1 bcd
Zn 2	—	1.1 ± 0.0 f	35 ± 0 a
	+	8.4 ± 0.0 ab	24 ± 0 bc
Cd + Ni + Zn	—	1.4 ± 0.1 f	37 ± 0 a
	+	6.9 ± 0.0 cd	25 ± 1 b

Notes: Control—no added metals; Cd 1—30 mg Cd kg⁻¹ of soil; Cd 2—60 mg Cd kg⁻¹ of soil; Ni 1—50 mg Ni kg⁻¹ of soil; Ni 2—100 mg Ni kg⁻¹ of soil; Zn 1—250 mg Zn kg⁻¹ of soil; Zn 2—400 mg Zn kg⁻¹ of soil; Cd + Ni + Zn—30 mg Cd, 50 mg Ni and 250 mg Zn kg⁻¹ of soil.

Means in a column followed by the same letter are not significantly different as judged by the Newman-Keul test at a level of 0.05.

400 mg Zn or 100 mg Ni kg⁻¹ of soil, respectively, and to 19% when Cd, Ni, and Zn were added together.

The incorporation of the polymer in the soil protected the plant from excessive levels of the metals. As a result, plant growth in amended soil was never significantly different from controls (Table 1). Soil remediation, as quantified by plant growth, was therefore achieved for nickel, and zinc-contaminated soil. However, because in this study the levels of Cd used did not reach the toxicity threshold, the effect of the polymer on cadmium could not be evaluated by using plant growth.

The concept of soil remediation can also be considered to include situations when only a decrease in the concentration of metals in plants is sought. A major advantage would be enhanced quality of the ecosystem, even if the plants were only used by wildlife and soil organisms. In this study, the concentrations of Cd, Ni, and Zn in the shoots increased with the rate of applied metal, but in every case the mean values for plants from amended soil were smaller than those of plants from unamended soil with the same level of contamination. Soil amendment led to levels of Cd in the shoots between 28 and 44% of those of plants from unamended soil (Figure 1), while the levels of Ni and Zn were reduced to 27–50% (Figure 2) and 24–67% (Figure 3), respectively. This was also true when plant growth was not impaired, suggesting that even in less contaminated soils this remediation process can be useful to prevent buildup of metals in plants.

The effect of the polymer on metal concentration in plants was similar to the impact on the levels of metals in soil solution; that is, the water-extractable Cd, Ni, and Zn were smaller in amended soil than in unamended soil with the same level of contamination. Soil amendment led to levels of extractable cadmium 8 and 25% of those in unamended soil (Figure 4), whereas the levels of Ni and Zn were reduced to 25–50% (Figure 5) and 40–53%

Figure 1. Cadmium concentration in the shoots of perennial ryegrass grown in a sandy soil contaminated with different levels of cadmium, or cadmium, nickel, and zinc, with or without polymer. Control—no added metals; Cd 1—30 mg Cd kg⁻¹ of soil; Cd 2—60 mg Cd kg⁻¹ of soil; all—30 mg Cd, 50 mg Ni, and 250 mg Zn kg⁻¹ of soil. Columns with the same letter are not significantly different as judged by the Newman-Keul test at a level of 0.05.

Figure 2. Nickel concentration in the shoots of perennial ryegrass grown in a sandy soil contaminated with different levels of nickel, or nickel, cadmium, and zinc, with or without polymer. Control—no added metals; Ni 1—50 mg Ni kg⁻¹ of soil; Ni 2—100 mg Ni kg⁻¹ of soil; all—30 mg Cd, 50 mg Ni, and 250 mg Zn kg⁻¹ of soil. Columns with the same letter are not significantly different as judged by the Newman–Keul test at a level of 0.05.

(Figure 6), respectively. Therefore, the smaller uptake of metals by plants in amended soil was due to removal of the metal from soil solution by the polymer.

Many sites that are candidates for remediation are contaminated with a broad range of metals. It was therefore important to examine the effectiveness of the polymer when Cd, Ni, and Zn were present simultaneously in the soil and to compare the results with those of treatments where the same metals were applied separately. Enhanced plant growth and decreased levels of the three metals in plant shoots and soil solution in amended soil compared with unamended soil contaminated with the same amounts of the three metals showed that remediation was also achieved when the three metals were applied simultaneously.

Figure 3. Zinc concentration in the shoots of perennial ryegrass grown in a sandy soil contaminated with different levels of zinc, or zinc, cadmium, and nickel, with or without polymer. Control—no added metals; Zn 1—250 mg Zn kg⁻¹ of soil; Zn 2—400 mg Zn kg⁻¹ of soil; all—30 mg Cd, 50 mg Ni, and 250 mg Zn kg⁻¹ of soil. Columns with the same letter are not significantly different as judged by the Newman–Keul test at a level of 0.05.

Figure 4. Water-extractable cadmium in a sandy soil 87 days after growing ryegrass with different levels of cadmium, or cadmium, nickel and zinc, with or without polymer. Control—no added metals; Cd 1—30 mg Cd kg⁻¹ of soil; Cd 2—60 mg Cd kg⁻¹ of soil; all—30 mg Cd, 50 mg Ni, and 250 mg Zn kg⁻¹ of soil. Columns with the same letter are not significantly different as judged by the Newman–Keul test at a level of 0.05.

However, there were some differences between the treatments corresponding to single metal or multimetal contaminations. The concentrations of cadmium, nickel, and zinc in ryegrass were considerably greater in the latter case than in the former (Figures 1–3). In unamended soil, this resulted partly from impaired growth; that is, there was a concentration effect, because the levels applied (30 mg Cd, 50 mg Ni, and 250 mg Zn kg⁻¹ of soil) separately did not reach the toxicity threshold but became phytotoxic if present simultaneously. A second reason could be the existence of interactions at the root surface between metals for plant uptake. Lastly, there was probably a competition between metals for sorption to soil matrix. In fact, water-extractable levels of the three metals were greater in

Figure 5. Water-extractable nickel in a sandy soil 87 days after growing ryegrass with different levels of nickel, or nickel, cadmium, and zinc, with or without polymer. Control—no added metals; Ni 1—50 mg Ni kg⁻¹ of soil; Ni 2—100 mg Ni kg⁻¹ of soil; all—30 mg Cd, 50 mg Ni, and 250 mg Zn kg⁻¹ of soil. Columns with the same letter are not significantly different as judged by the Newman–Keul test at a level of 0.05.

Figure 6. Water-extractable zinc in a sandy soil 87 days after growing ryegrass with different levels of zinc, or zinc, cadmium and nickel, with or without polymer. Control—no added metals; Zn 1—250 mg Zn kg⁻¹ of soil; Zn 2—400 mg Zn kg⁻¹ of soil; all—30 mg Cd, 50 mg Ni, and 250 mg Zn kg⁻¹ of soil. Columns with the same letter are not significantly different as judged by the Newman–Keul test at a level of 0.05.

unamended soil contaminated with all three metals than when each metal was present separately, which would be expected to result in enhanced uptake by plants in the first case.

In plants from amended soil contaminated with all three metals, the concentrations of cadmium and nickel, though smaller than those of plants from unamended multicontaminated soil, were still greater than those from amended soil contaminated with each metal on its own (Figures 1 and 2). In this case, growth was not impaired, which means that uptake of Cd and Ni was greater when applied together than when applied alone. Compared with unamended soil, the presence of the polymer represents additional sites for metal sorption. Saturation of sorption sites, both in the soil matrix and polymer, would result in competition between metals. In fact, the levels of water-extractable Cd and Ni were greater when all three were present together than in soil contaminated with just one metal. This suggests the need to readjust the amount of polymer applied to soils contaminated with several trace elements.

The use of hydrophilic insoluble polyacrylate polymers for in situ remediation of metal-contaminated soil presents several advantages:

1. It is a fast, simple, and relatively economic method. The polymer can be easily incorporated into the plow layer (though dust masks should be used to prevent inhalation of polymer particles), and its cost is only about 3 Euros per kg.
2. It is effective with several metal ions, as shown in the present work.
3. The polymers enhance plant growth as a result of the additional water and nutrients provided, as well as through remediation, helping the establishment of plants in severely contaminated soils, especially if the soil is acidic, infertile, or in arid or semiarid regions.

CONCLUSIONS

The application of insoluble polyacrylate polymers could be used to remediate a sandy soil severely contaminated with Cd, Ni, and Zn, both when present together or separately. Together with previous results dealing with Cu, it was demonstrated that the application of insoluble polyacrylate polymers provides a new method for in situ remediation of metal-contaminated coarse-textured soils. However, several questions remain to be answered. The duration of the remediation is unknown so far. With copper, it was shown that the polymer was stable in the soil for at least a 2-year period (de Varennes and Torres 2000). There is no data on the downward migration of insoluble polyacrylate polymers in soil layers. Most of the particles have a size similar to sand and would not be expected to move to any great extent, but breakdown products could migrate, though they will be sorbed in exchange sites (Martin 1996). The experience available with the application to soils of sewage sludges containing polyacrylates suggests that movement to deep layers or groundwater is not to be expected (Langbein 1996). Experiments to answer these questions still need to be carried out under field conditions.

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REFERENCES

- Boatright, J.L., Balint, D.E., Mackay, W.A., and Zajicek, J.M. (1997) Incorporation of a hydrophilic polymer into annual landscape beds. *Journal of Environmental Horticulture*, 15: 37–40.
- de Varennes, A. and Torres, M.O. (1999) Remediation of a long-term copper-contaminated soil using a polyacrylate polymer. *Soil Use and Management*, 15: 230–232.
- de Varennes, A. and Torres, M.O. (2000) Soil remediation with insoluble polyacrylate polymers: an overview. *Revista de Ciências Agrárias*, 23: 13–22.
- de Varennes, A., Torres, M.O., Conceição, E., and Vasconcelos, E. (1999) Effect of polyacrylate polymers with different counter ions on the growth and mineral composition of perennial ryegrass. *Journal of Plant Nutrition*, 22: 33–43.
- FAO. (1988) *Revised Legend of the FAO-Unesco Soil Map of the World*. World Resources Report no. 60, FAO: Rome, Italy.
- Johnson, M.S. and Piper, C.D. (1997) Cross-linked, water-storing polymers as aids to drought tolerance of tomatoes in growing media. *Journal of Agronomy and Crop Science*, 178: 23–27.

- Kawai, F., Igarashi, K., Kasuya, F., and Fukui, M. (1994) Proposed mechanism for bacterial metabolism of polyacrylate. *Journal of Environmental Polymer Degradation*, 2: 59–65.
- Langbein, I. (1996) Biological and physicochemical aspects of polyacrylate behavior in the environment. In *Detergents in the Environment*. Schwuger, M.J. (ed.); Marcel Dekker: New York, 225–245.
- Martin, E. (1996) Environmental impact studies of the disposal of polyacrylate polymers used in consumer products. *Science of the Total Environment*, 191: 225–234.
- Torres, M.O. and de Varennes, A. (1998) Remediation of a sandy soil artificially contaminated with copper using a polyacrylate polymer. *Soil Use and Management*, 14: 106–110.
- Silberbush, M., Adar, E., and de Malach, Y. (1993) Use of a hydrophilic polymer to improve water storage and availability to crops grown in sand dunes. I. Corn irrigated by trickling. *Agricultural Water Management*, 23: 303–313.
- Wall, F.T. and Gill, S.J. (1954) Interaction of cupric ions with polyacrylic acid. *Journal of Physical Chemistry*, 58: 1128–1130.