USE OF HYDROPHILIC POLYMERS FROM DISPOSABLE DIAPERS TO RESTORE METAL-CONTAMINATED SOILS

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1 INTRODUCTION

Hydrophilic polymers swell to form gels that contain many times their dry weight in water. They are marketed as 'superabsorbent polymers', with different trade names, for incorporation into soils and substrates. YunKai et al. (2002) reviewed the effects of these polymers on agricultural soils and crops. Another use of hydrophilic polymers is in disposable diapers and similar products. A layer of polyacrylate polymer is located between cellulose fibres, and the whole contained by a plastic cover.

Effects of metals on ecosystems and biological resources are increasingly recognised (Izquierdo et al., 2005; Pérez-de-Mora et al., 2006). It is too expensive to remove metals from severely contaminated soils, and the restoration of these sites does not imply a decrease in the total contents of toxic metals, but rather a change in their availability. Factors that influence the flow of metals from solid phases towards soil solution govern their bioavailability. In this manuscript, the emphasis is set on the effect of polyacrylate polymers on plant growth and quality of metal-contaminated soils, deriving from their effect on metal availability.

2 MATERIALS AND METHODS

Several experiments with metal-contaminated soils were carried out. The Cu-contaminated soil came from a vineyard that received copper sulphate as fungicide over several years; the Cd-contaminated soil became enriched with the metal because it was used for Cd-related studies for more than a year; the remaining soils came from a sulphide mine in the Iberian Pyrite Belt.

In all studies, parameters were measured in unamended soil and in polymer-amended soil. The level of polymer applied varied between 0.2 and 0.3% (m/m). Plant growth was evaluated based on dry weight of aboveground tissues. Soil enzymatic activities were measured as described elsewhere (Qu et al., 2010b).

3 BIOAVAILABILITY OF TOXIC METALS

Exposure of polyacrylates to metals such as Cu, Ni, Cd and Zn leads to an irreversible collapse of the polymer particles as these metals form ionic cross-links and coordination bonds with carboxylic groups present that prevent re-expansion of the polymer.

The sorption of cations in free solution is a fast process taking place within a few minutes. This process is much slower when polymers are applied to soils, as the amount of the metal in solution is small, and the movement of metals is hindered by the solid phase. In consequence, the time taken for the polymers to collapse is extended over a large period of time, but the process can still be followed, as the maximum water-holding capacity of the amended soil slowly declines, so that at each irrigation operation the weight of the wet soil becomes smaller. In contrast, the maximum water-holding capacity of unamended soil remains constant (Figure 1).

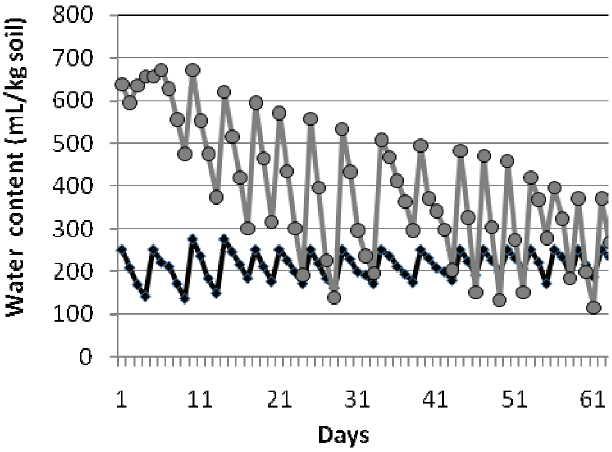

FIGURE 1 **Changes in the water content of a mine soil without (black line) or with 0.4% polyacrylates (grey line)**

The extractable level of toxic metals in soils decreases following polymer application (Table 1). Depending on the extracting solution, metal and soil type a decrease between 11 and 64% of the content of the unamended soil was observed.

TABLE 1 **Extractable levels of metals in contaminated soils**

Metal	Extracting solution	Level of metal (% of control)	Reference
Cu	Water	11	de Varennes and Torres, 1999
Pb	0.01 M $CaCl_2$	63	Guiwei et al., 2008
Pb, Cu and Zn	Water	64, 50 and 50	de Varennes et al., 2009
Cd	0.01 M $CaCl_2$	57	Qu et al., 2010c

4 QUALITY OF RESTORED SOILS

The activity of several soil enzymes increases in polymer-amended soils (Table 2).

TABLE 2 **Enzymatic activity of polymer-amended metal-contaminated soils**

Metal	Soil enzyme	Enzyme activity (×activity in unamended soil	Reference
Cu	Acid phosphatase	1.7	de Varennes and Queda, 2005
Cu	β-glucosidase	1.8	
Pb	Dehydrogenase	3.3	Guiwei et al., 2008
Pb	Protease	11	
Pb	Acid phosphatase	1.9	
Pb	β-glucosidase	3.3	
Pb	Cellulase	11	
Pb, Cu and Zn	Dehydrogenase	1.6	de Varennes et al., 2009
Pb, Cu and Zn	β-glucosidase	1.5	
Cd	Protease	1.5	Qu et al., 2010c
Cd	Acid phosphatase	1.1	
Cd	β-glucosidase	1.4	
Cd	Cellulase	2.9	

Heavy metals interact with hydroxyl and sulfydryl groups and with nitrogen-containing ligands of enzymes, inhibiting their activity (Huang and Shindo, 2000; Gil-Sotres et al., 2005). The decrease in the levels of metals in soil solution may thus be responsible for the stimulation of the activity of soil enzymes. Re-vegetation of metal-contaminated soils also leads to enhanced activity of several soil enzymes (Izquierdo et al., 2005; Pérez-de-

Mora et al., 2006). This may result from indirect effects on enzymatic activity due to the stimulation of microbial activity by greater plant growth and consequent increases in the amount of root exudates and plant residues reaching the soil.

Enhanced growth of several plant species has been shown in metal-contaminated soils following application of polyacrylate polymers, including cultivated species such as perennial ryegrass (Lollium perenne L.), annual medic (*Medicago polymorpha* L.) and orchardgrass (*Dactylis glomerata* L.) or native species present in mine soils such as *Chaetopogon fasciculatus* (Link) Hayek, *Spergularia purpurea* (Persoon) G. Don fil. and *Andryala integrifolia* L. (Table 3). Depending on soil and plant species, the increase in plant growth varied between 4 and 3000 times that of plants grown in unamended soil.

TABLE 3 **Relative growth of several species grown in soils contaminated with metals**

Metal	Plant species	Growth (× growth in unamended soil)	Reference
Cu	Perennial ryegrass	11	de Varennes and Torres, 1999
Cu	Annual medic	4	de Varennes and Queda, 2005
Pb	Orchardgrass	3000	Guiwei et al., 2008
Pb, Cu and Zn	Perennial ryegrass	21	de Varennes et al., 2009
Cd	Orchardgrass	6	Qu et al., 2010c
Pb	Native species	2	Qu et al., 2010b

At present, polyacrylates in disposable diapers contain Na^+ as counter ion. This represents a limitation for the use of these products as soil amendments. Either natrophylic plants have to be chosen or enough precipitation has to occur to wash the soil profile before sowing takes place. Nevertheless, in a recent experiment (Qu et al., 2010a) it was shown that *S. purpurea* (an halophyte) greatly responded to application of polymers to a sulfide mine soil, and even shredded diapers containing polyacrylate could promote the growth of this native species (Figure 2).

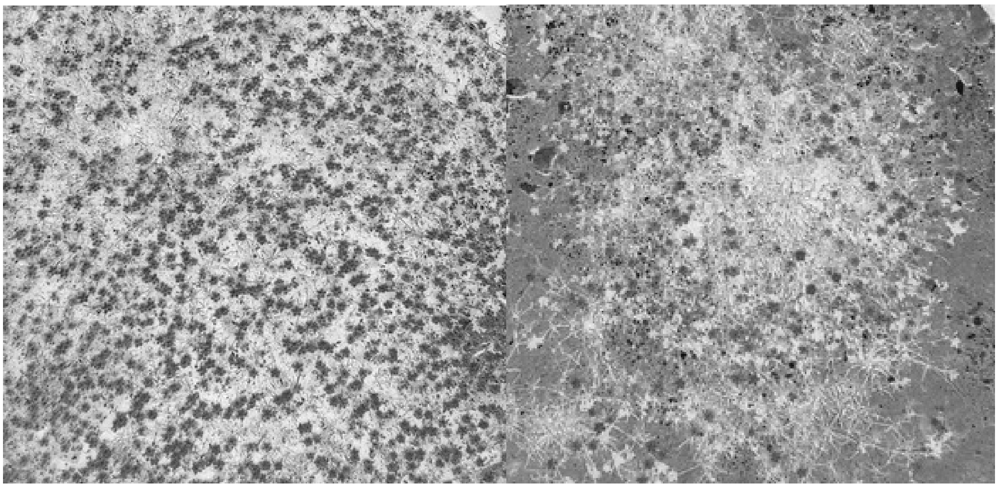

FIGURE 2 **Growth of *Spergularia purpurea* in a soil derived from a sulfide mine. Mine soil received 0.3 shredded diapers per kg of soil (left) or was left unamended (right).**

5 CONCLUSIONS

In conclusion, the application of insoluble hydrophilic polymers promotes plant growth due to increased water-holding capacity of the soil and decreased bioavailability of toxic metals. The establishment of a plant cover in metal-contaminated soils is faster in amended soils and provides full soil coverage that stabilizes the soil and enhance its quality.

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