# RISKS OF HEAVY METAL TRANSFER TO *BETA VULGARIS* CULTIVATED IN A CONTAMINATED SOIL AND AMENDED WITH ORGANIC WASTES

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## ABSTRACT

Heavy metal pollution of agricultural soils is a problem in areas near to the former sites of mining activity in La Unión (Murcia). The effect of two wastes, used as soil amendments, on the bioavailability of heavy metals in a polluted soil and on their accumulation in *Beta vulgaris* was studied in a field experiment. The soil was a calcareous Xeric Torriorthent and the total metal levels were (mg $kg^{-1}$): 2706 Zn, 3235 Pb, 39 Cu, 3 Cd, and 22 Ni. The treatments were: fresh cow manure, olive husk and inorganic fertiliser as a control. Two harvests of *B. vulgaris* var. Nomonta were performed: two and three months from planting, respectively. The soil was sampled before planting and after the second harvest. The high concentrations of heavy metals in plants of all treatments indicated a health risk for human and livestock consumption. Cow manure reduced the metal absorption by plants, but olive husks favoured solubility and phytotoxicity of metals in soils and their accumulation in plants.

## INTRODUCTION

The mining activity carried out in La Unión (Murcia) since Roman times has transformed completely the landscape of the mine site and adjacent land (24.55 $km^2$), due to the accumulation of metalliferous mine wastes. The transport of fine particles by wind (dry deposition) has caused heavy metal pollution of agricultural soils in nearby areas. Mining and industrial activities, waste accumulation, road traffic and chemicals used in agriculture (fertilisers and pesticides) are recognised as the main sources of metal pollution of soils. Phytoremediation strategies are being developed for heavy metal-contaminated soils (Salt et al., 1998). These technologies are based on the use of plants, with agronomical practices for reclamation of soils. Different soil amendments have been used for reclamation of contaminated soils, including organic matter such as peat, sewage sludge, pig slurry, cow manure and compost (Luo and Christie, 1998; Ye et al., 1999; Gaweda, 1991; Walker et al., 2003). The transfer of metals to the food chain is a recognised risk and, in order to reduce it, the European Union has established limits for contaminants in foodstuffs, which include metals such as Cd and Pb (Commission of the European Communities, 2001). The aim of this work was to determine the effect of two organic wastes (cow manure and olive husk) on the bioavailability of heavy metals and their accumulation in a *Beta vulgaris* crop, in a soil affected by the mining activity.

## MATERIALS AND METHODS

A field experiment was designed in a calcareous Xeric Torriorthent soil with 3.66 g $kg^{-1}$ organic-C, 0.63 % of organic matter (OM), 15 % $CaCO_3$ and total metal concentrations (mg $kg^{-1}$) of

2706 Zn, 3235 Pb, 39 Cu, 3 Cd and 22 Ni. Three treatments, in a randomised design with three replicates per treatment, were established in experimental plots of 2x3 $m^2$. The treatments were: fresh cow manure, olive husk from a two-phase centrifugation system (both added at a rate of 30 kg fresh weight per plot, providing 9 kg OM per plot), and inorganic fertiliser N:P:K (15:15:15) at a rate of 0.8 kg per plot. Nitrogen (179 g $NH_4NO_3$ per plot) was supplied to the olive husk treatment because its concentration in this waste (15.3 g $kg^{-1}$) was lower than in the manure (28.6 g $kg^{-1}$). Five weeks after waste application, 48 plantlets (4 leaves) of *Beta vulgaris* var. Nomonta were planted in each plot. Two harvests were performed: two and three months from planting, respectively. The soil was sampled before planting and after the second harvest. Total heavy metals were analysed in plant material and soils were analysed for available heavy metals (DTPA-extractable), pH, electrical conductivity, organic carbon and cation exchange capacity.

## RESULTS AND DISCUSION

The most relevant results with respect to the soil characteristics which can affect the heavy metal availability were (Table 1): the increase in the organic C concentration in treatments with olive husk with respect to control; the increase of available P in manure-treated soil with respect to the initial control and husk-treated soils; and the decrease in soil pH due to the olive husk treatment. Nogales et al. (1997) also reported the acidifying effect of olive mill wastewater in soils. Although the OM was supplied in the same proportion by both amendments to the soil, the organic C in olive husk was higher than for cow manure (562 and 412 g $kg^{-1}$ dw, respectively). Also, the organic matter from olive husk may be more resistant to microbial degradation than that of the cow manure. Riffaldi et al. (1997) found that the potentially mineralisable organic C of olive mill wastewater sludge was 8.9-12.0 % of organic C in low organic matter calcareous soils, while an average of 47 % of organic C from cow manure can be mineralised after 30 days (Ajwa and Tabatabai, 1994). The high metal concentrations of the soil should have negative effects on microbial activities (Dai et al., 2004), provoking a low organic matter mineralization during the plant growth.

***Table 1**. Characteristics of the soil at transplanting (T1) and at harvesting (T2).*

| Treatments | Sampling | pH | Organic C (g $kg^{-1}$) | Total N (g $kg^{-1}$) | Available P (mg $kg^{-1}$) | CEC ($cmol_{(+)} kg^{-1}$) |
|---|---|---|---|---|---|---|
| Control | T1 | 7.82 b | 3.4 a | 0.64 | 2 a | 15.5 |
| | T2 | 7.65 b | 4.0 a | 0.68 | 34 d | 17.1 |
| Manure | T1 | 7.75 b | 6.4 a | 0.69 | 15 bc | 17.3 |
| | T2 | 7.73 b | 5.6 a | 0.70 | 20 c | 17.6 |
| Olive husks | T1 | 7.45 a | 9.2 b | 0.71 | 5 ab | 17.4 |
| | T2 | 7.62 b | 11.2 b | 0.85 | 5 ab | 18.0 |

*Values followed by the same letter are not statistically significant according to the Tukey test, at $P<0.05$.*

The biomass production decreased in the order: manure (15.66 tm $ha^{-1}$) > control (10.62 tm $ha^{-1}$) >> olive husks (1.54 tm $ha^{-1}$). The results indicate that the cow manure initially decreased the Pb bioavailability in soil (Fig. 1), and the Zn, Pb and Cu concentrations in plants (Fig. 2), leading to the highest plant biomass production. Similar findings were reported by Walker et al. (2003), indicating that both soluble salts and phosphate concentrations may be responsible for the reduced metal availability. However, olive husks increased the availability of metals (Fig. 1), which produced phytotoxicity and very scarce plant biomass. At harvesting, the concentration of available Mn had decreased in the husk treatment, but was still the highest value of the three treatments. The decrease in soil pH caused by the olive husks may have contributed to the increase in metal solubility and therefore plant metal uptake. Also the formation of soluble metal-OM complexes could be a relevant factor in metal solubility.

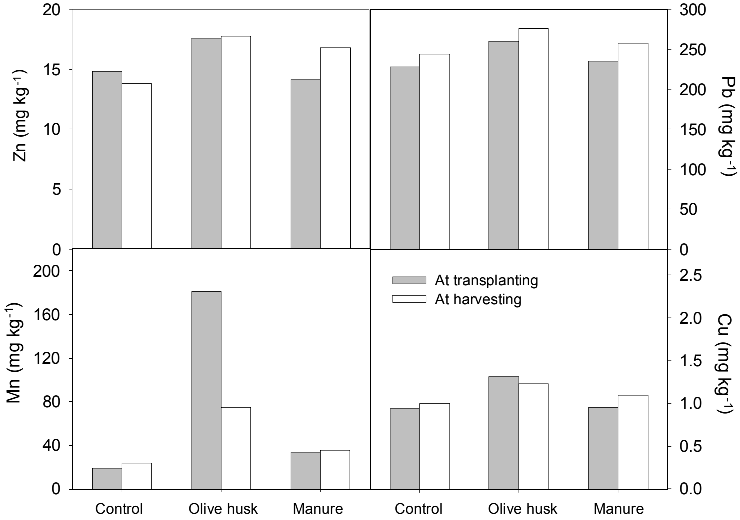


***Figure 1***. *DTPA-extractable metals in soils at transplanting and at harvesting of B. vulgaris.*

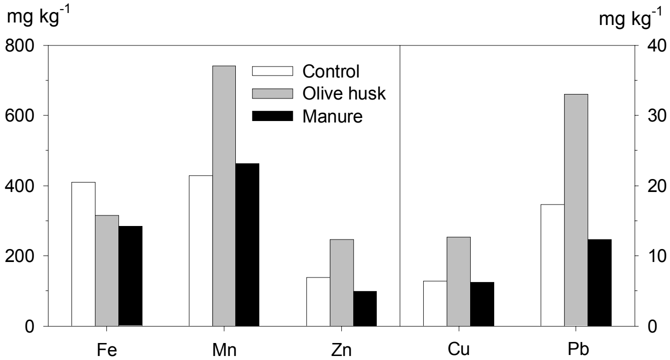


***Figure 2***. *Heavy metal concentrations in plants of B. vulgaris, in different soil organic treatments.*

The concentration of Fe in *B. vulgaris* was within the normal range of values of this crop (321-385 mg $kg^{-1}$) in manure and olive husks treatments, with excess values in control (Food Composition and Nutrition Tables, 1987). The excess of available Mn in the soil with olive husks treatment could have caused antagonism between Fe and Mn with respect to plant uptake (Kabata-Pendias, 2001). Elevated Mn concentrations in plants were found in all treatments. The Mn/Fe ratio increased from control (1.05) to manure (1.62) and olive husks treatment (2.34), a symptom of increasing Mn toxicity (Poschenrieder and Barceló, 1981). Cu concentrations in *B. vulgaris* were close to the normal values for this crop (10 mg $kg^{-1}$; Food Composition and Nutrition Tables, 1987) and were lower than the toxicity limit (20 mg $kg^{-1}$; Kabata-Pendias, 2001). However the levels of Zn were in excess of the normal values (45 mg $kg^{-1}$; Food Composition and Nutrition Tables, 1987). The concentration found in the olive husks-treated plants can be considered toxic (100-400 mg $kg^{-1}$; Kabata-Pendias, 2001). The Pb concentration in plants grown in the olive husks treatment was equivalent to 3.63 mg $kg^{-1}$ fresh weight, which is higher than the limit established by the EU for leaf vegetables (0.3 mg $kg^{-1}$, Commission of the European Communities, 2001). The limit was also exceeded by control and manure-treated plants (2.16 and 1.53 mg $kg^{-1}$, respectively). Therefore, this crop could not be commercialised or consumed, due to its health risk.

## CONCLUSIONS

The use of agricultural soils located in areas close to old mining activities should be avoided due to the high health risk of metal pollution in plants. Although cow manure reduces plant-available metals and phytotoxicity, high metal concentrations in vegetables can still occur. So, a remediation programme for these areas is required. For developing a bioremediation programme in heavy metal-contaminated soil, manure can be very useful for phytostabilisation strategies; reducing the availability of metals and their plant absorption, and improving both plant biomass and soil properties. Olive husk could be useful in phytoextraction strategies with accumulator plant species, as it increases plant absorption and available metals.

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