

COMPARISON OF HUMIC ACIDS FROM COMPOST AND PEAT AS AMENDMENTS OF HEAVY METAL POLLUTED SOILS.

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ABSTRACT

The effects of humic acids extracted from two different organic materials on the distribution of heavy metals and organic-C mineralisation in two contaminated soils were studied in an incubation experiment (26 °C, 24 weeks). Humic acids isolated from a mature compost (HAC) and a commercial *Spaghnum* peat (HAP) were added to an acid soil (pH 3.4; 966 mg kg⁻¹ Zn; 9229 mg kg⁻¹ Pb) and a calcareous soil (pH 7.7; 2602 mg kg⁻¹ Zn; 1572 mg kg⁻¹ Pb) at a rate of 1 g organic-C added per 100 g soil. After 24 weeks of incubation, the mineralisation of the organic-C added was rather low in the soils studied (< 6 % of TOC in the acid soil; < 9 % of TOC in the calcareous soil). Both humic acids caused Zn and Pb significant immobilisation (increased proportion extractable only with aqua regia) in the acid soil, while Cu and Fe were slightly mobilised (extractable with 0.1 M CaCl₂ and/or 0.5 NaOH). In the calcareous soil there were lesser effects, and at the end of the experiment Zn, Fe and Pb (with HAP) were slightly mobilised while Cu and Pb (with HAC) were immobilised, their residual fraction increasing. These results indicate the usefulness of humic acid-rich materials in soil remediation involving phytostabilisation.

INTRODUCTION

Chemical amelioration, using acids, lime or organic matter, alters soil chemical conditions (pH, Eh) and the concentrations of chelating and complexing agents in the soil solution and in the solid phase (Iskandar and Adriano, 1997). Some organic materials, like compost and peat, have been recently employed in different experiments on the bioremediation of soils contaminated with heavy metals (Clemente et al., 2003; Narwal and Singh, 1998; Walker et al., 2003, 2004). These materials improve soil fertility and generally increase plant production and can also change heavy metals availability. Humic acids are present in high concentrations in stabilised organic materials. These humic acids can affect the mobility and therefore the bioavailability of heavy metals when these materials are used as organic amendments in soils. Organic amendments such as mature compost, which contain a high proportion of humified organic matter (OM), can decrease the bioavailability of heavy metals in soil by adsorption and by forming stable complexes with humic substances (Takamatsu and Yoshida, 1978), permitting the re-establishment of vegetation on contaminated sites (Tordoff et al., 2000).

The aim of this work is to study the effect of humic acids on the availability of soil heavy metals, and the stability of these substances in soils, in an incubation experiment.

MATERIALS AND METHODS

An acid soil (pH = 3.4) and a calcareous soil (pH = 7.7) from a former Pb-Zn mine area at La Unión (Murcia, SE Spain) were selected. The soils have high Zn-Pb concentrations and low organic matter (OM) content (Table 1). The humic acids were isolated as a solid fraction by acidifying the NaOH extracts of a mature compost, prepared from a mixture of olive leaves and the

solid fraction of olive-mill wastewater (total composting time, including maturation period, was 9 months) (García-Gómez et al., 2003), and a commercial *Sphagnum* peat. These humic acids were chemically characterised and their content of functional groups was determined (Table 2).

Table 1. Characteristics of the studied soils.

	Acid Soil	Calcareous Soil
pH	3.4	7.7
CE (dS m ⁻¹)	1.2	1.9
MO (%)	0.8	0.7
TOC (g kg ⁻¹)	4.9	3.8
N _T (g kg ⁻¹)	0.3	0.3
CaCO ₃ (%)	<0.5	30
Zn (mg kg ⁻¹)	966	2602
Cu (mg kg ⁻¹)	27	42
Pb (mg kg ⁻¹)	9229	1572

An incubation experiment (26 °C, 60 % water-holding capacity) was carried out using humic acids from compost (HAC) and from peat (HAP) (1 g organic-C per 100 g soil), and one control with no amendment. After 2, 8 and 24 weeks, the soils were sampled and different fractions of heavy metals (Zn, Cu, Pb and Fe) were determined by AAS after sequential extraction (McGrath and Cegarra, 1992). The sequential extraction procedure had the following steps: 1. 0.1 M CaCl₂, metals in soil solution and in exchangeable forms; 2. 0.5 M NaOH, metals associated with OM; 3. 0.05 M Na₂H₂EDTA, metals mainly in the carbonate fraction; 4. digestion with aqua regia, residual metals. The dynamic of C-mineralisation was determined by measuring the CO₂ evolved during the incubation time, trapping it in a NaOH solution.

Table 2. Elemental and functional group composition of the humic acids.

	Humic acids from compost	Humic acids from peat
C (%)	58.8	60.6
N (%)	5.2	2.9
H (%)	6.2	6.6
S (%)	0.5	0.2
O (%)	29.3	29.7
Total acidity (meq g ⁻¹)	3.68	6.32
Carboxylic groups (meq g ⁻¹)	2.63	2.59
Phenolic groups (meq g ⁻¹)	1.05	3.73
Carbonyl groups (meq g ⁻¹)	1.68	1.27

RESULTS AND DISCUSSION

The mineralisation of the humic acids in the acid soil was < 6 % of TOC with a constant mineralisation rate after 80 days of incubation. In the calcareous soil, the NaOH traps were saturated, suggesting carbonate decomposition due to soil acidification after addition of humic acids. In a separate experiment, total organic-C content was measured in control and HAP-treated cal-

careous soil, showing low mineralisation (< 10 % of TOC) of the humic acids added. These results show the high microbiological stability of these substances in soils.

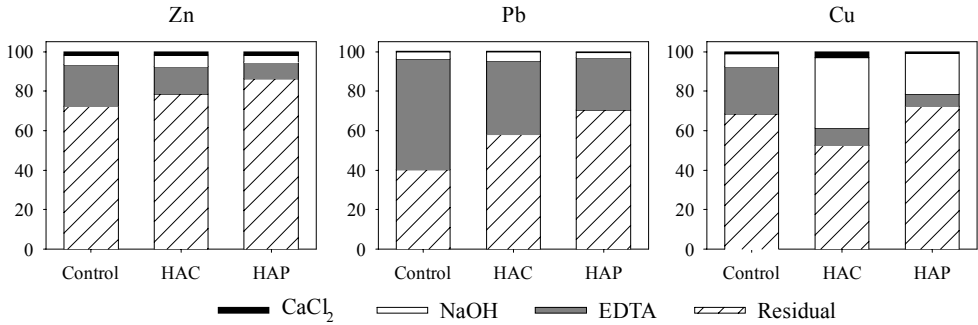


Figure 1. Sequential extraction in acid soil samples after six months of incubation. Control: soil without treatment; HAC: humic acids from compost; HAP: humic acids from peat.

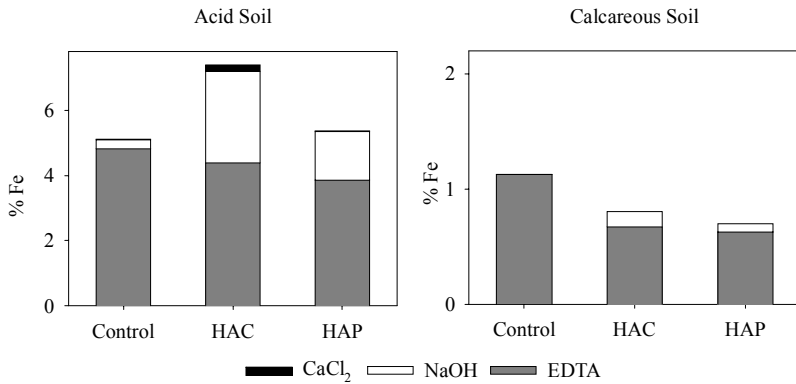


Figure 2. Extractable fractions of the sequential extraction in soil samples after six months of incubation. Control: soil without treatment; HAC: humic acids from compost; HAP: humic acids from peat.

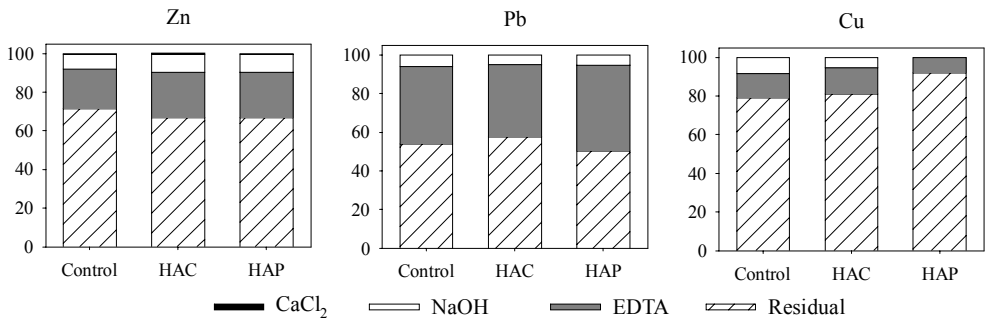


Figure 3. Sequential extraction in calcareous soil samples after six months of incubation. Control: soil without treatment; HAC: humic acids from compost; HAP: humic acids from peat.

In the acid soil, humic acids caused the immobilisation of Zn and Pb, increasing their concentrations in the residual fraction at the expense of the EDTA-extractable fraction, especially in HAP-treated soil (Figure 1). In this soil, Cu and Fe were slightly mobilised by the humic acids (Figures 1,2), the concentrations of these elements increasing in the NaOH-extractable fraction

and decreasing in both the EDTA-extractable and residual fractions. This mobilisation confirms how Cu easily bonds to the OM of the soils, by adsorption with colloids or by functional groups complexation (Ross, 1994). The contribution of exchange sites and functional groups able to chelate Fe with the humic acids facilitated the mobilisation of this element. In the calcareous soil, there were lesser effects. At the end of the experiment, Zn and Pb concentrations in the residual fraction of HAP-treated soils were slightly lower than in control soil, showing a certain metal mobilisation (Figure 3) which may be due to a pH effect. NaOH-extractable Fe increased at the expense of the EDTA-extractable fraction, although Fe availability in the calcareous soil was very low (Figure 2). Cu, in both HA-treated soils, and Pb, in HAC-treated soil, were immobilised at the end of the experiment, their concentrations increasing in the residual fraction.

CONCLUSIONS

The addition of humic acids to the acid soil caused Zn and Pb immobilisation (decreased availability to plants), while Cu and Fe availability increased in the HA-treated soils, as they were linked with the soluble organic matter added. In the calcareous soil, only slight increases in Zn, Pb and Cu bioavailabilities were observed, as humic acids addition did not affect greatly the distribution of the metals in the different soil fractions.

The use of organic materials with a high content of humic acids as soil amendments will be successful in immobilising heavy metals in acid soils, whereas their use in calcareous soils is expected to be less effective, this being related to the effect on soil pH.

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