Geophysical Research Abstracts
Vol. 12, EGU2010-12926-1, 2010
EGU General Assembly 2010

Effects of organic and inorganic amendments on heavy metal fractionation in soils from the "Cartagena-La Union" mining site (Spain)

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The intensive mining activity carried out in the "Cartagena-La Union" district has led to the contamination with heavy metals of the surrounding area. Our aim was to evaluate the heavy metal solubility in soils from this area, in order to optimize the use of different soil amendments for the improvement of soil conditions that would favour plant establishment.

Soils collected from abandoned mine sites (n = 8) showed a high heterogeneity in both soil pH (2.5-7.7) and electrical conductivity (1.2-3.1 dS m^{-1}) and they presented low organic matter contents (0.2-2.0%). These soils showed high pseudo-total concentrations of heavy metals, especially Zn and Pb (Zn: 966-10103, Pb: 1572-11426, Cd: <0.1-60 and Cu: 27-334 mg kg^{-1}) and arsenic (150-892 mg kg^{-1}). Lower pseudo-total concentrations of heavy metals were found in the soils collected from the agricultural surrounding areas (n = 6) of the abandoned mine site (Zn: 16-1826, Pb: 298-2345, Cd: <0.1-0.6, Cu: 22-38 and As: 17-65 mg kg^{-1}). These soils showed higher soil pH values and $CaCO_3$ content (pH: 7.6-7.9; $CaCO_3$: 15-41%), lower electrical conductivity (0.1-0.2 dS m^{-1}) and generally higher levels of organic matter (0.7-3.9%) than those found in the soils collected from the abandoned mine sites.

Five representative soils collected from the different sampled areas were analysed for heavy metal fractionation after sequential extraction. Heavy metals were mainly found (>80% of the pseudo-total concentration) in the less soluble fractions (EDTA and Aqua regia-extractable) due to the neutral or slightly alkaline soil pH values and the calcareous character of these soils. Only two soils showed significant concentrations of Zn, Pb and Cd and in the most soluble fraction ($CaCl_2$-extractable), due to their slightly acidic character and the higher cation exchange capacity related to the clay and organic matter content.

In addition, field and lab-scale (aerobic incubations) studies were carried out with different soils to evaluate the effect of inorganic and organic amendments on the fractionation of heavy metals and on soil microbial biomass parameters. The organic amendments applied were: cow manure, pig slurry, solid olive mill waste, composts of olive mill wastes and humic acids from compost and from peat. Elemental sulphur and lime ($Ca(OH)_2$) were applied as inorganic amendments. Compost, cow manure, solid olive mill waste and pig slurry showed the most relevant effects on soil heavy metal fractionation and soil microbial biomass parameters.

According to the obtained results, compost and cow manure were shown as the most suitable organic amendments for these soils, since they constitutes an important source of easily biodegradable organic matter and nutrients, which led to an increase in the soil microbial biomass C and reduced microbial stress (CO_2-C/biomass C). Precipitation of heavy metals as inorganic salts, such as phosphate, due to the mineralization of fresh organic matter from the cow manure, and the input of partially humified organic matter from the compost, which can chelate heavy metals keeping them as less-soluble fractions, are key factors for their usefulness as organic amendments in immobilization strategies.

The suitability of fresh solid olive mill waste for its use as organic amendment in these soils is limited. This waste showed, in the short term, microbial toxicity and increased Mn solubility, due to the presence of phenolic compounds in this waste. Composted solid olive mill waste seems to be more appropriate than the fresh waste for the development of remediation strategies.

Although pig slurry did not produce significant effects on the fractionation of heavy metals in soil. It showed to be an important source of plant and soil microorganisms nutrients, especially nitrogen which is generally low in these soils. Thus, pig slurry could be useful in remediation strategies (especially immobilisation), it meaning, in

addition, an environmentally friendly way to manage this waste.