Soil inorganic amendments to enhance Cu and Zn uptake by spinach and lettuce cultivated on metal contaminated soil

E.E. Golia[1], M. A. Chartodiplomenou, S. Papadimou, O.D. Kantzou and N. Tsiropoulos[2]

[1] Laboratory of Soil Science,
Department of Agriculture, Crop Production and Rural Environment
Fytokou Road, 36 446 N. Ionia Magnesias, Volos, Greece

[2]Laboratory of Analytical Chemistry and Pesticides Laboratory,
Department of Agriculture, Crop Production and Rural Environment
Fytokou Road, 36 446 N. Ionia Magnesias, Volos, Greece

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Presenting author email: egol@uth.gr

The prevention of heavy metal contamination in soils is based on controlling the sources of pollution, but also on reducing their mobility or enhancing the remediation efficiency of contaminated soils, using appropriate mechanisms (Gul *et al*, 2015). Amendments or ameliorants have long been used to improve the quality of agricultural soils. Different materials (organic, eg. compost, inorganic minerals eg. lime) have been used in order to overcome a lot of physical and chemical problems in soils (Luin *et al*, 2018). Soil with excellent structure form accepts water readily and has a broad range of water content over which water logging and excessive hardness do not limit seeding emergence or plant growth. Soil amendments have been, also, used with success to reduce heavy metals availability to plants (Kwon-Rae *et al*, 2012). The use for bioremediation technology for metals and metalloids is recognized as efficient and effective strategy (Saheen *et al*, 2015; Naser *et al*, 2018).

Spinach (*Spinacia oleracea*) and lettuce (*Lactuca sativa*) are both leafy green vegetables that are eaten raw or cooked. Vegetables cultivated in soils polluted with toxic metals take up heavy metals and accumulate them in their edible and non-edible parts in quantities high enough to cause clinical problems both to animals and human.

In order to study the heavy metal transportation from polluted soil to leafy plants a pot experiment was conducted. The soil sample (with three replicates each) was collected from the industrial area of Volos, Central Greece (Golia *et al*, 2008). Four inorganic soil amendments were used: lime ($CaCO_3$), red mud consisting of 75% hematite (Fe_2O_3), gypsum ($CaSO_4{\cdot}2H_2O$) and Al-oxide (Al_2O_3). The soil was mixed with an application rate of 7% . The pots (18 cm in diameter and 13 cm in depth) were filled with 3,5 kg of soil and the amendment. Three control pots per soil were also set up without amendment. The moisture content of each pot was maintained at 70% by weighing the pots twice a week to compensate for evapotranspiration losses. The plants were harvested 45 days for the lettuce and 53 for the spinach after their establishment in the pots.

After the end of the experiment, aerial plants were collected. They were placed in paper bags, dried at 75 °C for 12 h, and ground using a mortar and pestle. The extraction method with Aqua Regia solution was followed. Soil properties were measured while pseudo-total concentration of metals was determined using the Aqua Regia (HCl-HNO3, 3:1) (ISO/DIS 11466 1994). Lime, gypsum and aluminum oxide was obtained from Sigma–Aldrich (purity > 95%), while red mud was an industrial byproduct of "Aluminium of Greece" in "Aspra Spitia". Metals were determined by atomic absorption spectrophotometry (AAS) using flame (F-AAS) or the Graphite Furnace (GF) technique (AOAC 1984)).

In figures 1 & 2 the concentrations of Cu and Zn in spinach and lettuce cultivated in control soil and in the soil- amendments mixtures used, are presented.

Lime is considered one of the most common and important amendment materials for metals stabilization as it plays a significant role in reducing metals availability, increasing agricultural profits and lowering the respective environmental risks. Lime applications for years increase pH and thus decrease metal uptake by crops. Liming could reduce the Zn contents by 29,5 & 18,1% and Cu contents by 21,8 & 10,3% in spinach and lettuce respectively. The acidic pH makes copper ions more mobile. Lime application caused an increase of soil reaction up to one unit, so copper available concentration reduced. It is well established that Cu concentration can be reduced also by chemisorption using carbonates, phosphates and adsorption on other clay minerals (Kabata-Pendias and Pendias 2000), using pH changes and modifications. Red mud addition reduces the total metal concentration of Zn, rather than Cu. Red mud addition generally decreases metal leachability and therefore the resultant hazard of releasing metals through adsorption and complexation of the metals on to inorganic components to different extents for the different metals. Oxides of Fe, Mn and Al also have high retention capacity for copper ions (Kabata-Pendias and Pendias 2000). The possible mechanisms for copper retention through the use of inorganic amendments are precipitation as carbonates and hyrdroxides or ion-exchange (Kumpiene et al. 2008).

Gypsum application, is a good and rather cheap option for remediating metal contaminated soils lending to an increase in the soil pH and in its sorption capacity. Spinach seemed to have a greater response to gypsum application up to 19,5 % reduction of Zn concentration.

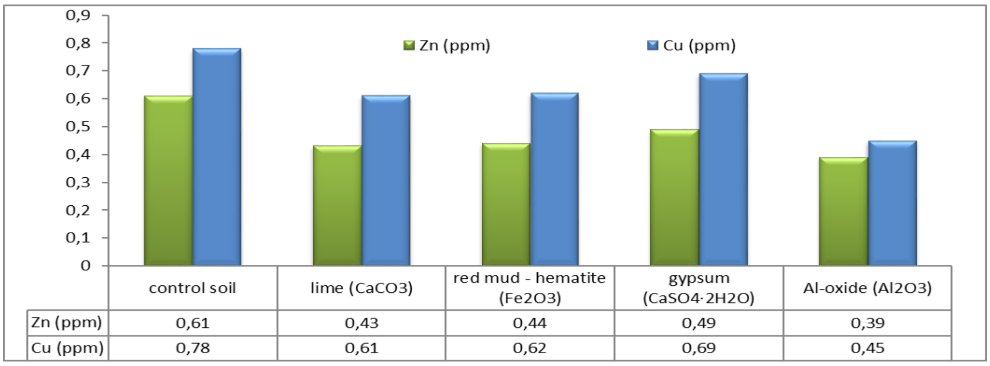

Figure 1. Cu and Zn concentrations (mg/kg dry matter) in spinach.

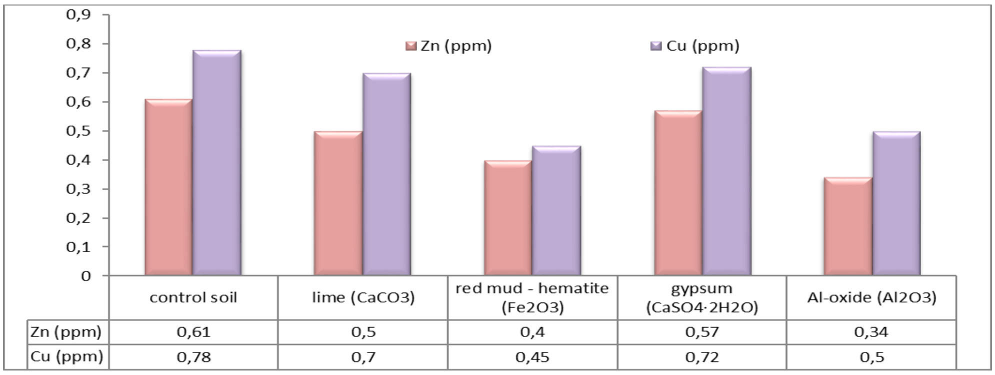

Figure 2. Cu and Zn concentrations (mg/kg dry matter) in lettuce.

Application of aluminum oxide (Al_2O_3) significantly decreased Cu concentrations both in spinach and lettuce (36 & 44,2% respectively). Cu decrease of soluble plus exchangeable Cu compared to the control has been reported (Saheen *et al*, 2015; Naser *et al*, 2018). In this respect, hydrous Al-oxide can form complexes with Cu ions by chemical bonding. The amendments used in this study seem to be suitable candidates for a chemical stabilization of metals in contaminated soils, as they are able to significantly reduce the solubility and uptake of metals by leafy vegetables.

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