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Mobilization and plant uptake of chromium after application of tannery sludge derived fertilizers: 2-year trials in north Italy

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Introduction

Tanneries are widespread in northern Italy and are well-known for high quality leather products. National Directives don't allow any more the disposal of tannery sludges to landfill and recommend an alternative use as energy sources. The tannery sludge contains high contents of organic substances and nitrogen from hide material processing other than variable and unpredictable concentrations of pollutants, depending on wastewater treatment technologies. Heavy metals contamination, in particular, makes monitoring and regulation necessary in view of a potential use in fertilisers manufacture.

In tannery sludges chromium is in the non-toxic trivalent form (Rutland, 1991), which is considered to have very low solubility in soils and a strong soil-plant barrier. Nevertheless it is recognized that Cr(III) forms soluble organic complexes with organic ligands derived from skin working (Walsh and O'Halloran, 1996a,b). Accordingly, attention should be paid to the phytoavailability of Cr(III) during organic matter mineralization and to the risk of oxidation to Cr(VI), a very toxic form, in soils (James and Bartlett, 1983). Soil oxidation-reduction conditions also influence transformations of metals between chemical forms and, as a result, trace and toxic metals tend to be retained more strongly in wetland soils compared with upland soils (Gambrell, 1994). In this regard, less attention was given to how redox changes, which undergo oxidized soils after flooding, might affect the mobility and leaching to groundwater of chromium.

A novel use of tannery by-products such as hair and epithelial tissues and sewage sludges was addressed to the production of an organo-mineral fertiliser, whose environmental aspects were evaluated by two-years trials cropping corn, wheat and rice.

The achievement of the objectives of the present investigation has required: (a) to obtain data on the uptake of Cr and its distribution in plant parts, (b) Cr accumulation in the 0-20 cm topsoil and soil Cr potentially soluble or available fraction, (c) total dissolved Cr in leaching waters under flooding conditions.

1 Core

An organo-mineral fertilizer containing both mineral NP and organic N materials, the last one prepared by composting sewage sludges and skins residues from a leather processing industry, was compared with a mineral NP fertilizer and a control without added N. Field (wheat, maize and rice) and lysimeter (rice) trials were performed on the same randomised complete block design.

Cr(VI) concentration in the organo-mineral fertilizer was $<$0.4 μmoles, in accordance to Italian Rules, and before and after cropping Cr(VI) content of experimental soils was $<$1 μmoles, threshold law limit, beyond which the oxidation of Cr(III) to Cr(VI) most likely occurs. It's believed that pH and OM are the main factors affecting the fate of chemical forms of Cr in the soil-plant system, shifting the equilibrium of Cr reactions in the soil to the more reduced and insoluble form.

Throughout the 2-year experiment, total Cr concentration in the soils did not exceed the controls, but it was observed a significant ($p<0,01$) increase of the soil available Cr fraction (extracted by $K_2HC_6H_5O_7)$ after wheat and maize cultivation, probably due to the more acid conditions of the rhizosphere in the upland than in the wetland soils.

Cr concentrations $\leq$1 ppm were observed in wheat plants, as Pratt (1966), with no correlation of plant Cr with soil Cr both as total (Adriano, 2001) and potentially soluble forms; significant differences ($p<0.05$) were observed for Cr between straw and grain, the former higher than the latter, irrespective of the treatment. A multivariate analysis (two-tails SKN with Pearson coefficients) showed an inverse correlation straw/grain ($p<0.05$; r = -0.592, fd = 8), which can be regarded as a “barrier effect”, as stated by Smith and Huyck (1999). In maize grain Cr concentration was less than the instrumental detection limit and in stalks no significant difference was observed between treatments, suggesting the presence of a “barrier effect” too.

The evaluation of Cr mobility in the soil-plant system, as measured by soil-plant transfer factors, gave very low values (0.002-0.003 for wheat and 0.006-0.009 for maize) irrespective of the treatments, confirming the very low mobility of this metal as stated by Sauerbeck (1989).

In rice plants the tannery sludge derived fertilizer determined a consistent and significant ($p<0.01$) increase of Cr concentration in roots, showing that total and potentially soluble Cr(III) in the flooded soil was not correlated with root accumulation. In spite of this, Cr was not significantly translocated to the straw and the grain, indicative of a transport barrier through the upper parts of the rice plant. Accordingly, soil to plant transfer factors of chromium were similar to those of the comparing treatments, ranging from 0.003 to 0.01, throughout the 2-year experiment. Only the values obtained for Cr total uptake (g ha^{-1}) in the upper part (grain + straw) were similar or greater than those of the mineral NP treatment.

In the lysimeter study, when the heavy metal distribution was expressed as a percentage in plant parts, the main accumulation was found in the roots, i.e. 80% of total plant Cr, and only about 7% in the grain, independent of Cr treated and untreated tanks. Lysimeter study also showed that total dissolved Cr in leachate samples, collected during the growing season, was unaffected by the application of the tannery sludge derived fertilizer.

Although Cr uptake by grain crops, such as wheat, maize and rice, seems to be unaffected after 2-years application of the tannery sludge derived fertilizer and the relatively inert nature of Cr(III) in soil chemistry, showed by the very low solubility and strong soil-plant barrier, longer-term field studies are recommended to verify if bound chromium could be released to soluble forms and becoming a threat for water quality through potential leaching.

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