

STUDY OF THE CONDITIONS FOR MOVILIZATION OF COPPER IN CALCAREOUS AGRICULTURAL SOILS

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Introduction.

A study on the mobility of copper in calcareous agricultural soils near an old mining site in semi-aridic conditions (S.E. Spain) is presented. The process governing copper transfer from the element-rich zone to the neighbouring soils is strongly influenced by the semi-aridic climate and torrential rainfalls. The soils studied are calcaric fluvisols developed from Quaternary alluvial sediments from the surrounding hills, some areas of which are dedicated to mining. Seasonal crops are cultivated, mostly tomatoes and melons, using traditional forms of irrigation and, more recently, drip irrigation systems.

Materials and Methods.

Ten soil samples were obtained from a 5 km² sampling zone (1). The total metal content was determined by electrothermal atomization atomic absorption spectrometry (ETAAS) or flame atomic absorption spectrometry (FAAS). For this, the samples were slurried in a dilute hydrofluoric acid solution and the suspensions were directly introduced into the flame (2) or the electrothermal atomizer (3).

The selective extractants used were: water; 1M ammonium acetate at pH 7.0 (4); 0.5 M ammonium acetate + 0.02 M EDTA + acetic acid at pH 4.65; 0.1 M sodium pyrophosphate, oxalic acid-oxalate (5); DTPA (6); sodium dithionite + sodium citrate (7). The metal content in each fraction was analyzed by ETAAS or FAAS.

The mineralogical composition of the samples was determined by XRD analysis using radiation Cu-K α . Using the diffraction intensities obtained and the values for the same phases given in the bibliography, a semiquantitative analysis was made of the treated and untreated samples.

Results and Discussion

The extraction values in H₂O (metal extracted \times 100 / total content) point to the natural immobilization of copper when it is incorporated in carbonated soils, although these values diminish as we move further from the source.

Copper is mainly found associated with oxides and oxihydroxides as we can deduce from the values obtained in the Citrate-Ditionite extraction y oxalate, even though presence of carbonates must be also taken into account. The oxalic acid-oxalate (pH 3) extraction provides information about the metals which are associated to inorganic amorphous forms. This extractant also acts on active calcium carbonate since, due to its very small particle

size, the compound is partially dissolved. Citrate-Ditionite release metals from amorphous forms or those of low crystallinity by reduction, this fraction being often the most abundant. Several carbonates are also solubilized in this extraction. Sodium pyrophosphate is a reagent which extracts forms bound to humic substances. In our case, because of the scarcity of humic matter content in the soils studied, it acts as a carbonate complexer and extractor.

The results obtained by using the selective extractants agreed with the data obtained from the XRD studies of both the original samples and the residues remaining after each extraction stage. A reliable assessment of metal availability in these highly calcareous soils must take into account the mineral phase in which the copper is present.

In accordance with the above, the behaviour of the metals with each reagent used reveals which phases in the soil they are associated with then. Thus, 40% (maximum value) of the Cu is associated to active calcium carbonate and inorganic amorphous materials and the rest is included in the network of silicates

EDTA acts by complexing metals which seem to be associated to inorganic forms of Fe and Mn with low crystallinity and fine granulometry. Both the soluble metal and the metal associated to the exchange complex and to finely divided forms are affected by complexation with DTPA.

Table 1 Values obtained for the soil samples using the selective extractions (soluble x100/total)

	NH₄Ac	EDTA	DTPA	Oxal.	Cit.-Dit.	Pyroph.	Total (ppm)
Min	0.5	1.0	3.0	10.0	6.0	2.0	95
max	2.5	3.0	18.0	41.0	40.0	10.0	240
average	1.2	1.9	14.0	28.0	23.0	4.4	130

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