



## **Assessment of different methods to estimate heavy metal bioavailability in 30 contrasting Spanish and New Zealand soils**

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The accumulation of heavy metals in soil from different sources (atmospheric deposition, agricultural practices, urban-industrial activities, etc.) is of a great environmental concern because of metal persistence and toxicity. In this sense, there is a consensus in the literature that the estimation of the bioavailable heavy metals in soil is a preferable tool to determine potential risks from soil contamination than the total contents. However, controversy exists around the definition of an accurate and universal bioavailability estimator that is useful for soils with different properties, since many factors control this parameter. Thus, the main objective of this work was to compare the effectiveness of different methods to predict heavy metals plant uptake from soils with different properties and heavy metal contents.

For the development of the present work, 30 contrasting soils from New Zealand and Spain were selected. Apart from the analysis of the basic soil properties, different methods to estimate heavy metal bioavailability were performed: total heavy metals, DTPA-extractable soil metals, diffusive gradient technique (DGT), and total heavy metals in soil solution. In these soils, a bioassay using wheat (*Triticum aestivum*) was carried out in a constant environment room for 25 days (12 hours photoperiod, day and night temperature of 20°C and 15°C respectively). After this time, the plants were divided in roots and shoots and heavy metal content was analysed in each part. Simple correlations were performed comparing the phytoavailable contents with the bioavailability estimated by the different methods.

As expected, higher heavy metal concentrations were found in roots compared with shoots. Comparing the theoretical available heavy metals estimated by the different methods with the root and shoot uptake, better correlations were found with the root contents, thus, the discussion is based in the comparisons with the uptake by this part of the plant. According to the results, DTPA seemed to be the extractant that best estimated plant uptake (except for Cd, not estimated by any of the methods used). Similar good results were found using the total heavy metal contents, except for Ni and Zn. DGT also worked well, but its use for Pb is not advisable, since many values were below the detection level. The heavy metals in soil solution were less successful for predicting plant uptake. In general, the good results obtained for Cr and Zn seemed to be influenced by a few high values found in some soils. Taking this point into account, the soils with very high levels of these heavy metals were removed from the analysis and simple correlations were done again with the remaining soils having a lower range of these metals. For the case of Cr, four soils were removed (soils with ten times or more total Cr than the average of the others 26 samples) and three for the case of Zn (soils with two times or more total Zn than the average of the others 27 samples). After this, the correlations with total heavy metals and DTPA became very weak, being the heavy metals in soil solution for Cr, and DGT for Zn, the methods that best estimated the plant uptake of these metals.

This work has proved the importance of careful revision of the data distribution, since good results can be influenced by just few samples with high values. In this sense and as a conclusion, DTPA and total heavy metals followed similar patterns and were good predictors of Cu and Pb uptake, and useful to distinguish between low and high values for Cr and Zn. On the other hand, DGT and heavy metals in soil solution showed a similar effectiveness to estimate Cu, Ni, Pb, Zn and Cr, but DGT presented, in general, higher correlation levels (except for Cr). Taking all of the results together, it seems that the most robust and efficient estimator for all metals studied (except Cd, impossible to predict with any of the methods used) was the DGT.

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