The Zn oxide nanoparticles (ZnO NPs) have been proposed as a possible Zn fertilizer to alleviate Zn deficiency in soils [1]. The NPs in the soil are subjected to chemical and biological reactions and physical processes, and they can be either retained in the solid matrix or mobilized into pore water, which have a profound impact on their availability. Using the experience gained from studies on chemical availability of trace metals in soils, similar extraction techniques are beginning to be used to assess the availability of metal-based engineered NPs in soils [2]. However, there are still no studies on the selection, comparison, and validation of these chemical extraction techniques to estimate in agricultural ecosystems the availability for plant uptake of metals from metal-based NPs in soil.

The aim of this investigation was to find effective chemical extraction methods for an effective risk assessment of crop exposure to ZnO NPs in agricultural soils. Chemical measurements in soils could estimate the risk of plant accumulation of Zn if a correlation between the resulting soil chemical values and plant metal amounts can be demonstrated.

A greenhouse pot experiment was performed with two different crops (cherry tomato and common bean), which were grown in two agricultural soils with different pH: an acidic soil (pH 5.4) and a calcareous soil (pH 8.5). The upper layer of the soil in the pots were spiked on average with 3, 20, and 225 mg Zn kg\(^{-1}\) (Zn basis) as dry powder of ZnO NPs (<100 nm, Sigma-Aldrich). The green beans and cherry tomato fruits were recollected gradually. At the end of the experiment the different vegetative parts of plants (root, stem, and leaf) were separated and soil samples were taken from the upper layer of the soil. The total Zn concentrations in soil and plant tissues were determined. The water soluble Zn in soil (Zn-WS) was extracted with double-deionized water. The Zn phytoavailability in soil was assessed by a mixture of LMWOAs (10 mM combined organic acid solution of acetic, lactic, citric, malic, and formic acids in a molar ratio of 4:2:1:1:1, respectively) (Zn-LMWOAs). The immediate mobile Zn fraction in the soil was estimated with 0.01 M CaCl\(_2\) (Zn-CaCl\(_2\)) and the potentially mobile Zn was predicted with 5 mM DTPA (Zn-DTPA). Additionally, available concentration of Zn in soil was measured using the technique of DGT (diffusive gradients in thin films). In order to find a valuable extraction method for different crops, the results obtained for common bean and cherry tomato were jointly considered.

In acidic soil, Zn bioaccumulation patterns in the different plant tissues (root, stem, leaf, or fruit) were successfully simulated by all soil chemical extraction tests used. In contrast, Zn-extractable amounts in calcareous soil were not or poorly correlated with the Zn concentration in plant. The CaCl\(_2\)-extractable Zn only weakly correlated with the Zn content in the roots and stems. The Zn amounts in plant fruits exclusively correlated with the LMWOAs-extractable Zn, suggesting that this soil extraction method is a valuable tool in order to assess Zn accumulation in edible parts of crops of Zn applied to calcareous soils as ZnO NPs. However, the DTPA-extraction method could not predict successfully the Zn accumulation in plant tissues. The results showed that in the high concentration treatments (225 mg kg\(^{-1}\)) the amounts of DTPA-extractable Zn were too high in comparison to Zn amounts in plant.

Acknowledgements
This work was financed by the Spanish projects RTA2013-00091-C02-01 and RTA2013-00091-C02-02.

References