

# Fate of nanoparticulate zinc oxide fertilisers in soil: solubility, diffusion and solid phase speciation

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## Abstract

Zinc (Zn) deficiency has been recognised as one of the main problems limiting agricultural productivity in alkaline calcareous soils. Application of Zn fertilisers is a common procedure in these soils to provide plant Zn requirements. Nanomaterials can be used in producing more soluble and diffusible sources of Zn fertilisers. Higher specific surface area and reactivity of zinc oxide (ZnO) nanoparticles compared to bulk ZnO may affect Zn solubility, diffusion in soil and hence Zn availability to plants. We applied synchrotron-based X-ray fluorescence mapping and X-ray absorption spectroscopy to examine diffusion and solid phase speciation of Zn in an alkaline calcareous soil to which nanoparticulate and bulk ZnO associated with two fertiliser products (monoammonium phosphate (MAP) and urea) were applied. Dissolution kinetics of ZnO coated fertiliser treatments and Zn standard compounds were also evaluated in sand columns. Results showed that there were no significant differences in Zn solubility from bulk and nanoparticulate ZnO coatings of MAP or urea granules. Micro-XRF maps of Zn also revealed that most of the applied Zn remained on or close to the fertiliser granules after 5 weeks of incubation. Coating of MAP granules with nanoparticulate/bulk ZnO transformed all the applied ZnO to zinc ammonium phosphate species. Aggregation of ZnO nanoparticles as well as high pH around urea granules inhibited the Zn dissolution in coated urea treatments.

## Key Words

ZnO nanoparticles, dissolution, solid phase speciation, X-ray absorption spectroscopy (XAS), X-ray fluorescence (XRF), alkaline calcareous soil.

## Introduction

Micronutrient deficiencies such as limited zinc (Zn) availability are one of the main problems limiting agricultural productivity, especially in alkaline calcareous soils. Therefore, Zn is often included in macronutrient fertilisers to improve crop quality and productivity. Following the addition of Zn fertilisers to soil, Zn transforms gradually from more active and available fractions into less available species such as precipitates (i.e. ZnCO<sub>3</sub>) and adsorbs to oxide phases (e.g. Fe-, Al-oxides)(Ma and Uren 2006). It has been well established that higher Zn fertiliser efficiency can be achieved through sources of Zn in fertilisers with higher solubility (Mortvedt and Giordano 1969; Shaver *et al.* 2007). Moreover, availability of Zn to plants in calcareous soils mainly depends on the diffusion of Zn from fertiliser granules to the plant root (Shuman 1998).

Nanomaterials could be applied in designing more soluble and diffusible sources of Zn fertiliser for increased plant productivity. The smaller size, higher specific surface area and reactivity of nanoparticulate ZnO compared to bulk ZnO may affect Zn solubility, diffusion and hence availability to plants. However, the unique properties of nanoparticles that make them useful as sources of nutrients could also pose environmental risks. Therefore, it is important to develop a thorough understanding of the fundamental reaction pathways of these emerging materials in the soil to ensure safer and more sustainable use of nanoparticulate materials in agriculture. Therefore, we applied synchrotron-based x-ray fluorescence ( $\mu$ -XRF) mapping and X-ray absorption spectroscopy ( $\mu$ -XAS) to examine diffusion and solid phase speciation of Zn in an alkaline calcareous soil to which nanoparticulate and bulk zinc oxide (ZnO) associated with two fertiliser products (monoammonium phosphate (MAP) and urea) were applied. Dissolution kinetics of ZnO coated fertiliser treatments and Zn standard compounds were also evaluated in sand columns.

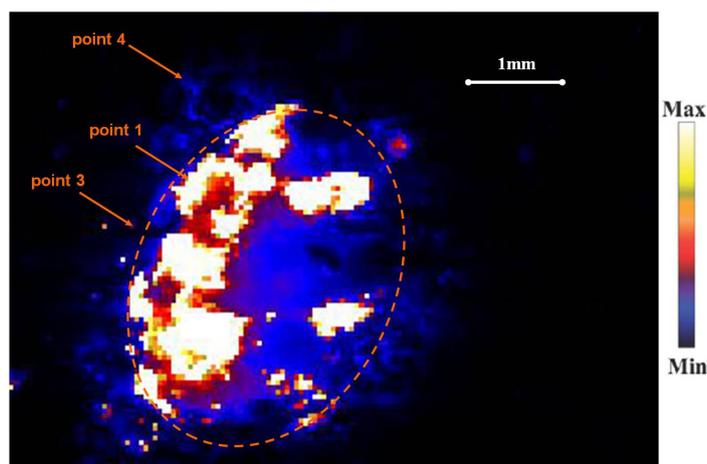
## Materials and methods

Fertiliser treatments were prepared by coating of two commercially available fertiliser products (MAP and urea) with nanoparticulate ZnO (~20 nm) (NanoAmore Inc., USA) and bulk ZnO (<1 µm) (Sigma-Aldrich, ReagentPlus®). A moist (at 60% of the water holding capacity) calcareous sandy loam soil with the pH 8.4 (1:5 soil/water) was placed in Plexiglass holders (with Kapton windows). Fertiliser treatments were placed in the centre close to the Kapton window and were incubated for five weeks. Micro-XRF maps were collected in fluorescence mode at beamline 13-BM at the Advanced Photon Source, Argonne National Laboratory, Argonne, IL. Micro-XAS spectra of three points of interest (POIs) in each treatment as well as standard Zn compounds were also collected.

Zinc oxide coated fertiliser treatments; nanoparticulate/bulk ZnO powders and standard Zn compounds were placed in columns packed with acid-washed sand to evaluate their solubility kinetics. Flow of leaching solution (0.01M CaCl<sub>2</sub>, pH=4) was introduced at a velocity of 10ml/hr using a peristaltic pump from the bottom of the sand column and effluents from the columns collected for 48 hours using a fraction collector (SuperFrac™, Pharmacia). Zinc concentrations in each fraction were measured using ICP-OES following 0.2 µm filtration.

## Results and discussion

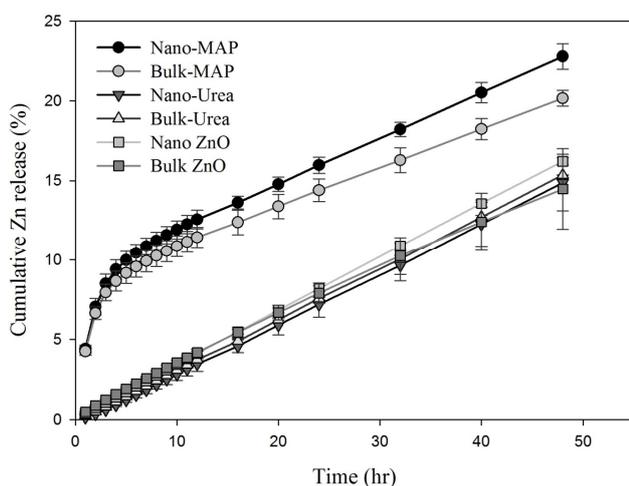
Micro-XRF maps of Zn for fertiliser treatments in the soil samples showed the spatial distribution of Zn on and around the granules. The µ-XRF maps of MAP granules coated with nanoparticulate or bulk ZnO revealed that most of the fertiliser Zn remained on the granule after 5 weeks of incubation (Figure 1). Only a small amount of Zn diffused and localized in the soil just away from the granule. Linear combination fittings (LCF) of XANES spectra of POIs in MAP treatments showed that the dominant Zn species on MAP granules and away from them was zinc ammonium phosphate. Only a small fraction of Zn dissolved and formed zinc carbonate species away from the MAP granules.



**Figure 1.** Micro-XRF maps of Zn for soil incubated with MAP granules coated with nanoparticulate ZnO. The dashed area represents the location of the fertiliser granule and the marked points indicate locations µ-XAS spectra collected.

According to the µ-XRF maps of coated urea granules, Zn predominantly remained at the place of application around the granule. However, µ-XRF maps showed a slight increase in Zn diffusion for urea treatments compared to MAP treatments which may be as a result of high solubility of urea fertilisers which facilitates the movement of ZnO particles. Solid phase speciation of POIs in urea treatments showed that despite the fact that ZnO was the dominant Zn species on and around the coated urea granules, a very small amount of Zn formed Zn carbonate species away from the point of application in highly calcareous soil.

In Figure 2, the release of Zn from coated fertilisers and Zn compounds in sand columns over time are illustrated. Results showed that there were no significant differences in Zn solubility between bulk and nanoparticulate ZnO coatings of MAP/urea granules. Cumulative Zn release from ZnO coated MAP treatments was more than Zn released from ZnO coated urea treatments over the period of the experiment, which may have been due to the lower pH in the vicinity of MAP granules compared to urea granules (Lombi *et al.* 2005) facilitating Zn dissolution.



**Figure 2. Cumulative release of Zn from coated fertilisers and nanoparticulate/ bulk ZnO powders.**

In coated MAP treatments, there was no significant difference in Zn dissolution between nanoparticulate ZnO and bulk ZnO coatings which is as a result of transformation of applied bulk or nanoparticulate ZnO to zinc ammonium phosphate species in the coating procedure. Slow release of Zn was observed from coated urea treatments which may have been due to high pH around urea granules inhibited dissolution of Zn from both nanoparticulate and bulk ZnO coatings. Zn release from both coated urea treatments increased gradually over time and reached a plateau. At this point, dissolution of Zn from urea granules coated with nanoparticulate ZnO followed the same rate and trend as Zn released from bulk ZnO coated urea as well as bulk ZnO powder. Therefore, it may be concluded that ZnO nanoparticles underwent some aggregation process which reduced their solubility in the sand column.

## Conclusions

Coating of MAP granules with nanoparticulate or bulk ZnO transforms all the applied ZnO to zinc ammonium phosphate species which limits expected Zn solubility and diffusion from ZnO nanoparticles in soil. Coating of ZnO on urea granules reduced the solubility of Zn compared to coating on MAP granules, and there was little or no difference between bulk ZnO and nanoparticulate ZnO in terms of dissolution.

## Acknowledgement

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