Zinc oxide nanoparticles in the soil environment: dissolution, speciation, retention and bioavailability

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In God, the Greatest

To my beloved parents

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Abstract

Zinc oxide nanoparticles (ZnO NPs) have unique physical and chemical characteristics which deviate from larger particles of the same material, due to their extremely small size, higher specific surface area and surface reactivity. The peculiar properties of ZnO NPs could potentially improve zinc (Zn) fertilizers for sustainable agriculture. This is based on the assumption that ZnO NPs provide a more soluble and bioavailable source of Zn in soil compared to micron- or millimetre- sized (bulk) ZnO particles currently used for Zn fertilizers in Zn deficient soils. However, a thorough understanding of the fate and reactions in soils and interactions of nanoparticles with plants of ZnO NPs is required prior to the recommendation for use of these novel materials. Therefore, there is a need to investigate dissolution, diffusion, transformation, partitioning and availability of manufactured ZnO NPs in soil to ensure safer and more sustainable application of ZnO NPs as a new source of Zn fertilisers for plants, and better management of their potential risks.

Given inclusion of Zn in macronutrient fertilizers is the common procedure for their field application, ZnO NPs and bulk ZnO were coated onto macronutrient fertilizers (monoammonium phosphate (MAP) and urea) and dissolution kinetics, diffusion and solid phase speciation of Zn from coated fertilizers were evaluated. Coating of ZnO on macronutrient fertilizers significantly affected solubility and dissolution kinetics of the ZnO sources, but nano-sized ZnO did not show any enhanced solubility over bulk ZnO. The low pH value of ZnO-coated MAP granules resulted in greater and faster dissolution of ZnO compared to ZnO-coated urea granules. However, interactions of ZnO particles with phosphate in MAP granules likely resulted in precipitation of Zn-phosphate species. The high pH and ionic strength of the dissolving

solution resultant from hydrolysis of urea likely promoted aggregation of any ZnO NPs released from coated urea granules and also hindered dissolution of ZnO.

To evaluate changes in Zn speciation with coating of the ZnO sources and after incorporation of the coated-fertilizers into an alkaline calcareous soil, synchrotron-based micro X-ray absorption fine structure (μ-XAFS) method was used. The findings confirmed precipitation of Zn-phosphate species at the surface of MAP fertilizer granules irrespective of the size of ZnO particles used for coating. For coated urea, the Zn remained as ZnO species for both nano-sized and bulk ZnO coatings. Solid phase speciation in the fertilized soil varied with distance from the point of fertilizer application. Significant amounts of $Zn(OH)_2$ and $ZnCO_3$ species were identified in the soil some distance from coated urea and MAP, respectively, indicating dissolution/precipitation processes were active. Moreover, limited and comparable diffusion of Zn from coated fertilizers with nanoparticulate or bulk ZnO into soil was observed using micro x-ray fluorescence mapping (μ-XRF). Transformation of Zn at the surface of MAP granules, mass flow of water towards the hygroscopic fertilizer granules or strong aggregation of ZnO nanoparticles released from urea granules could have been the mechanisms which restricted Zn diffusion. Given that coating of ZnO on macronutrient fertilizers markedly reduced Zn solubility, reactions of ZnO NPs and bulk ZnO in soil were studied when applied as the pure oxides.

Availability of Zn for durum wheat (*Triticum durum*) plants from nanoparticulate and bulk sources of ZnO was evaluated in an acidic and an alkaline soil using an isotopic dilution procedure (L value). Significant dissolution and plant acquisition of Zn from ZnO was observed (ca. 50 – 100 % of added), even with limited pre-incubation of soils with the Zn sources. However, no significant effect of particle size was observed on plant acquisition of Zn from the ZnO.

Retention and dissolution of ZnO NPs and dissolved Zn species from ZnO NPs was further investigated in five soils with diverse physical and chemical properties. Strong retention of ZnO NPs and/or dissolved Zn species from ZnO NPs was found in all soils especially in alkaline and calcareous soils. The adsorption affinity of ZnO NPs was generally greater than that of soluble Zn, which suggested ZnO NPs were retained more strongly than soluble Zn in soils. Soil pH and clay content of soil were the most important soil properties affecting retention, although the number of soils used was too small to draw firm conclusions as soil parameters co-varied.

Generally, nanoparticulate forms of ZnO appear to offer little advantage over bulk-sized ZnO as a source of fertilizer Zn to crops. Rapid dissolution of ZnO NPs and partitioning of dissolved Zn species derived from ZnO NPs and/or high retention of ZnO NPs in soils suggested that soil application of manufactured ZnO NPs would not appear to offer any benefits over bulk ZnO, whether applied in pure form or along with macronutrient fertilisers. However, from an ecotoxicological point of view, ZnO NPs would not be persistent in soil systems and hence their mobility in soil would be limited. Therefore the risks associated with application of ZnO NPs in soil would be similar to that of soluble Zn.

Declaration

This work contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution to Narges Milani and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text.

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Narges Milani _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ **Date** _ _ _ _ _ _ _ _ _ _

List of Publications

Milani, N., M.J. McLaughlin, S.P. Stacey, J. Kirby, G. M. Hettiarachchi, D. Beak and G. Cornelis. 2012. Dissolution kinetics of macronutrient fertilisers coated with manufactured zinc oxide nanoparticles. Journal of Agricultural and Food Chemistry. 60: 3991-3998.

Milani, N., M.J. McLaughlin, G.M. Hettiarachchi, D.G. Beak, J.K. Kirby and S.P. Stacey. 2012. Fate of nanoparticulate zinc oxide fertilisers in an alkaline calcareous soil. Soil Science Society of America Journal. Submitted.

Milani, N., M.J. McLaughlin, J.K. Kirby, G. Cornelis and S. P. Stacey. 2012. Retention and lability of manufactured zinc oxide nanoparticles in natural soils. To be submitted

Milani, N., M.J. McLaughlin, G.M. Hettiarachchi, , D.G. Beak, J.K. Kirby and S.P. Stacey. 2010. Fate of nanoparticulate zinc oxide fertilisers in soil: Solubility, diffusion and solid phase speciation. *19th World Congress of Soil Science*, Brisbane, Australia, 1-6 August 2010 *(oral presentation)*

Milani, N., M.J. McLaughlin, G.M. Hettiarachchi, D.G. Beak, J.K. Kirby and S.P. Stacey. 2009. Zinc diffusion and speciation in an alkaline-calcareous soil treated with fertilisers coated with bulk and nanoparticulate zinc. *13th Australasian Society for Ecotoxicology Conference.* Adelaide, Australia, 20-23 Sep 2009 *(oral presentation)*

Thesis structure

The experimental chapters in this thesis have been written in manuscript format. Given manuscripts must be self-contained, there is some degree of repetition in this thesis.

Chapter 1 outlines the specific physical and chemical properties of manufactured nanoparticles. A review of the current literature is provided in this chapter on the fate and behaviour of manufactured nanoparticles in aquatic and terrestrial environments and uptake and interactions of nanoparticles with soil organisms and plants. This chapter highlights the need for new sources of Zn in fertilizers and the potential benefits of using ZnO NPs for Zn nutrition of plants .

Chapters 2 and 3 present the results of investigations on dissolution kinetics of Zn from ZnO NPs and bulk ZnO coated onto macronutrient fertilizers in sand columns as well as diffusion and solid phase speciation of Zn from coated fertilizers in an alkaline calcareous soil. The results presented in these chapters provide a good understanding of possible benefits of application of nanoparticulate source of ZnO over bulk ZnO in the coating of macronutrient fertilizers on Zn availability.

Given the reactions which reduced Zn availability when Zn was coated onto macronutrient fertilisers, Chapter 4 presents the data on application of pure ZnO NPs and bulk ZnO in soils (i.e. not associated with macronutrient fertilizers). The results of dissolution, partitioning of dissolved Zn and / or retention of ZnO NPs was compared to soluble Zn in 5 Australian soils with diverse chemical and physical properties. This chapter also compares lability of ZnO NPs for durum wheat (*Triticum durum*) plants in 2 soils with bulk ZnO and soluble Zn.

Chapter 5 summarizes and discusses the findings from this thesis and makes suggestions for future research arising from the experimental work presented.