Safety of Nanoparticles in Agriculture

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Nanoparticles: What, where and why?

- Particles measuring less than 100 nm in two or more dimensions are classed as nanoparticles (NP).[1,2,3] Nanoparticles are found in the natural environment in forms of dust particulate and volcanic ash. They are also found in our homes as icing sugar, cornflour, and as zinc oxides in healthcare products such as sunscreen and in Band-Aids.

- For centuries nanoparticles' properties have been utilized for their ability to improve function, performance and increase cost-effectiveness in engineered materials resulting in an extremely diverse research field today.

- Many nanoparticles have unique and desirable characteristics, such as increased surface mass ratio, compared with larger particles of the same material. Reliable techniques of synthesising nanoparticles are therefore paramount, especially when scaling-up for commercial production.[3,4]

[1] S. Laurent, D. Forge, M. Port, A., C. L. . Roch, E. Vander and R. Muller, *Chemical Review,* 2008, 108, 2064-2110.
[2] R. Nair, S. H. Varghese, B. G. Nair, T. Maekawa, Y. Yoshida and D. S. Kumar, *Plant Science,* 2010, 179, 154-163 (DOI:http://dx.doi.org/10.1016/j.plantsci.2010.04.012)
[3] L. R. Khot, S. Sankaran, J. M. Maja, R. Ehsani and E. W. Schuster, *Crop Protection,* 2012, 35, 64-70 (DOI:http://dx.doi.org/10.1016/j.cropro.2012.01.007).
[4] A. Cockburn, R. Bradford, N. Buck, A. Constable, G. Edwards, B. Haber, P. Hepburn, J. Howlett, F. Kampers, C. Klein, M. Radomski, H. Stamm, S. Wijnhoven and T. Wildemann, *Food and Chemical Toxicology,* 2012, 50, 2224-2242 (DOI:http://dx.doi.org/10.1016/j.fct.2011.12.029).

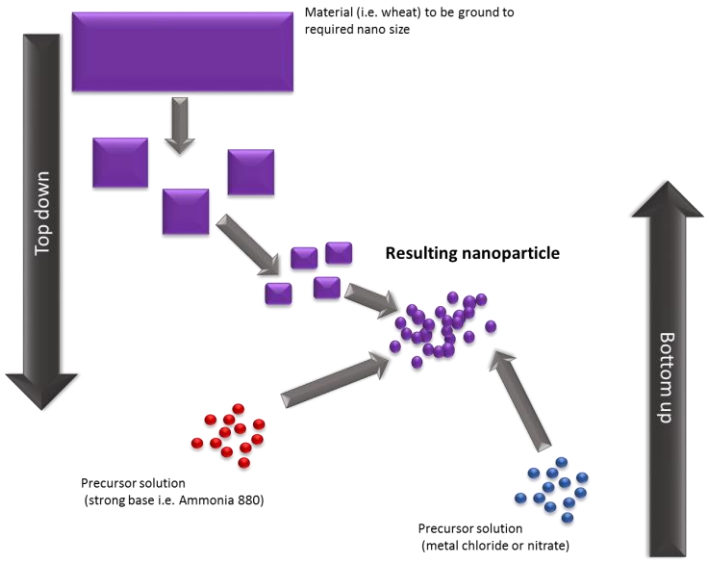
Potential problems and how we decrease the risk.

- Physicochemical properties are continually being investigated. [4]
- Some nanoscale materials can irritate skin in their powered form.
- Inhaled free flowing solid-state nanomaterials can potentially travel across internal membranes *i.e.* in the lungs→ blood, leading to irritation to mucus membranes.
- Need to differentiate the physico-chemical properties of different martials and not cluster them all as "nano". Toxicity generally occurs on the "atomic scale" not the "nano scale" *i.e.* the biological interface is with small molecules and ions (sub nano scale)

[4] A. Cockburn, R. Bradford, N. Buck, A. Constable, G. Edwards, B. Haber, P. Hepburn, J. Howlett, F. Kampers, C. Klein, M. Radomski, H. Stamm, S. Wijnhoven and T. Wildemann, *Food and Chemical Toxicology,* 2012, 50, 2224-2242 (DOI:http://dx.doi.org/10.1016/j.fct.2011.12.029).

Good product design is key to reducing the risk of inhalation

- Agricultural nanoparticles such as iron oxide and silicon dioxide can be produced using a "bottom-up" approach called **co-precipitation**. The formulation technique creates a 'ready to use' NP solution, eliminating the production of airborne NP's during manufacture.
- The process also ensures uniformity in particle size (+/- 5 nm) enabling studies to be conducted / optimized with defined particle sizes.
- Nanoparticles can be supplied to consumers in the form of a user-friendly liquid concentrate, granular premixes or effervescent tablets; reducing exposure to the user.



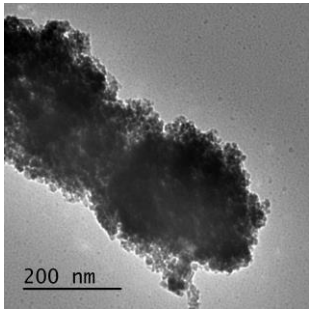
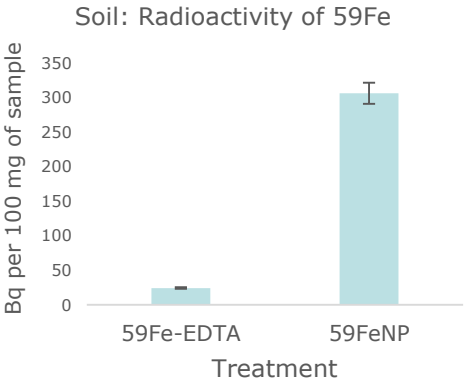


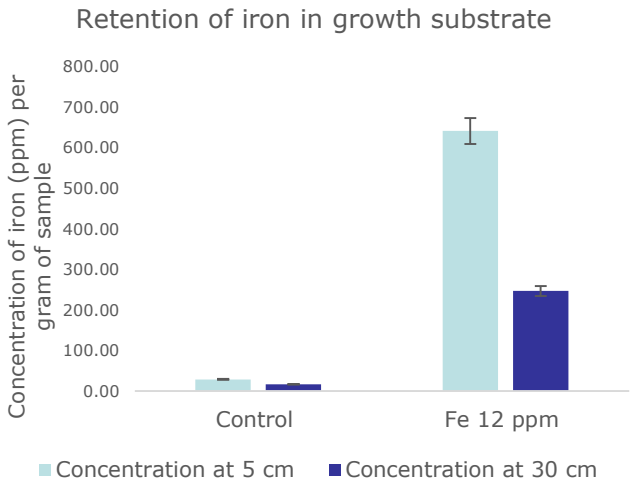
Fig. 1: Agglomerate of iron NP's, obtained via TEM.

[NB: If a nanoparticle solution dries out it forms an agglomerate, therefore no longer nanoscale.] – figure 1

Iron Oxide nanoparticle vs Fe-EDTA

- Commercially, iron is currently commonly applied as a soluble fertilizer in the form of a chelated salt of, for example, ethylenediaminetetraacetic acid (EDTA) or other variant. The chelate aids the dispersion of iron in a solution by attaching to all six valent bonding sites of the metal ion to form an octahedral complex.
- In 2016 a head-to-head trial using the radioisotope 59-Fe was used to produce Fe-EDTA and FeNP, applied at the same rate and concentration.*



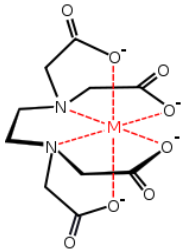


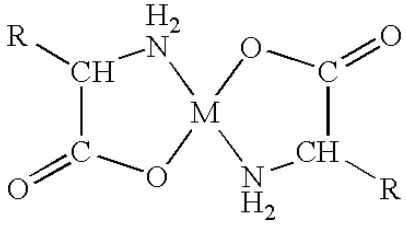
- The retention of FeNP in growth media was substantiated in a second large scale trial. Here the proportion of the iron was retained in the upper level of the media (*ca.* 5 cm).

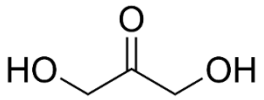
Results: Higher amounts of iron were retained in the soil from the application of 59FeNP.

Conclusion: There is less potential of leaching into the surrounding environment and waterways from the NP formulations (as it is retained in the substrate) compared to the habitual EDTA source of iron.

**** Publication in press.***







Fe-EDTA (Ethylenediaminetetraacetic acid ferric sodium salt)	Iron oxide (II,III), magnetic nanoparticles solution **CAS 1317-61-9**	Silicon dioxide nanoparticles (10-20 nm) **CAS 7631-86-9**	Dihydroxyacetone (sunless tanning) **CAS 96-26-4**
General advice Consult a physician. Show this safety data sheet to the doctor in attendance. **If inhaled** If breathed in, move person into fresh air. If not breathing, give artificial respiration. Consult a physician. **In case of skin contact** Wash off with soap and plenty of water. **Consult a physician**. **In case of eye contact** Flush eyes with water as a precaution. **If swallowed** Never give anything by mouth to an unconscious person. Rinse mouth with water. Consult a physician.	**General advice** Consult a physician. Show this safety data sheet to the doctor in attendance. **If inhaled** If breathed in, move person into fresh air. If not breathing, give artificial respiration. **In case of skin contact** Wash off with soap and plenty of water. **In case of eye contact** Flush eyes with water as a precaution. **If swallowed** Never give anything by mouth to an unconscious person. Rinse mouth with water.	**General advice** Consult a physician. Show this safety data sheet to the doctor in attendance. **If inhaled** If breathed in, move person into fresh air. If not breathing, give artificial respiration. Consult a physician. **In case of skin contact** Wash off with soap and plenty of water. Consult a physician. **In case of eye contact** Rinse thoroughly with plenty of water for at least 15 minutes and consult a physician. **If swallowed** Never give anything by mouth to an unconscious person. Rinse mouth with water. Consult a physician	**If inhaled** If breathed in, move person into fresh air. If not breathing, give artificial respiration. **In case of skin contact** Wash off with soap and plenty of water. **In case of eye contact** Flush eyes with water as a precaution. **If swallowed** Never give anything by mouth to an unconscious person. Rinse mouth with water.

Iron Oxide and Silicon Dioxide Nanoparticles

- Iron oxide (Fe_3O_4) and silicon dioxide (SiO_2) are naturally occurring materials.
- Within the European Union and Switzerland, iron oxides and hydroxides (E172) and silicon dioxides (E551) are permitted to be used as food additives. Toxic effects begin to occur at doses above 10–20 mg/kg (10-20 ppm).
- Fe-EDTA is observed to precipitate out of solution, a process that is accelerated when exposed to UV light. The nano formulations remain suspended in aqueous solution indefinably.
- Iron oxide (Fe_3O_4) nanoparticles can be up taken far more efficiently by plants without the need for protonic energy and at a wide range of pH.
- Silicon dioxide (SiO_2) nanoparticles can be added at higher concentrations than other silicon products (*e.g.* potassium silicate) without affecting the pH of the nutrient solution.

https://www.food.gov.uk/science/additives/enumberlist

Silicon Dioxide Study on Genovese Basil (*Ocimum basilicum)*

Nanoparticle uptake

Extensive trials using various NP's as a nutrient supplement have been conducted as a part of a PhD sponsored by the Agriculture and Horticulture Development Board (AHDB) and the UK's Biotechnology and Biological Sciences Research Council (BBSRC). The metal oxide NP formulations have shown a consistent increase mineral uptake (figure 2) compared the traditional Fe-EDTA (figures 3a and 3b).

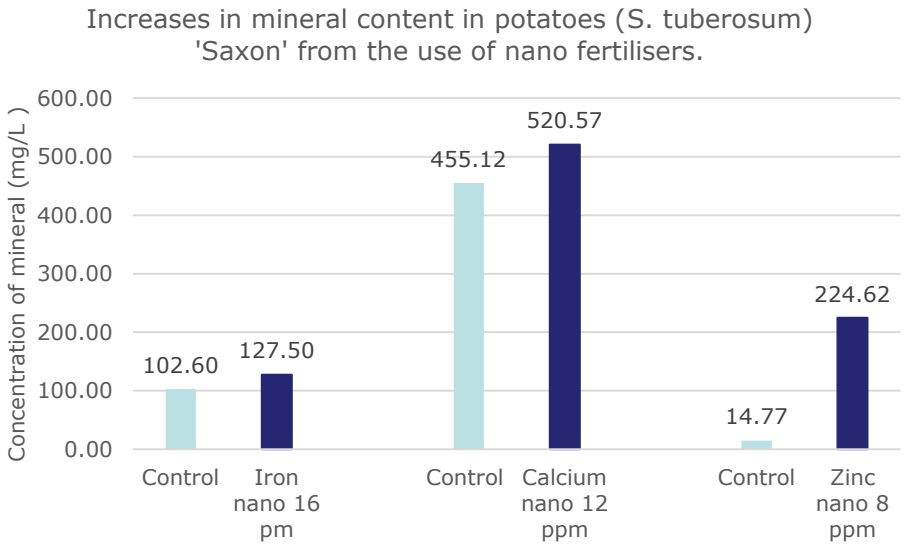


Fig. 3: Mineral content of Saxon cultivar tubers at harvest (n=20)

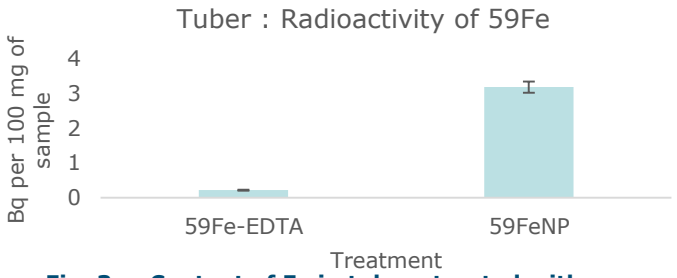


Fig. 3a: Content of Fe in tubers treated with 59Fe-EDTA and 59FeNP

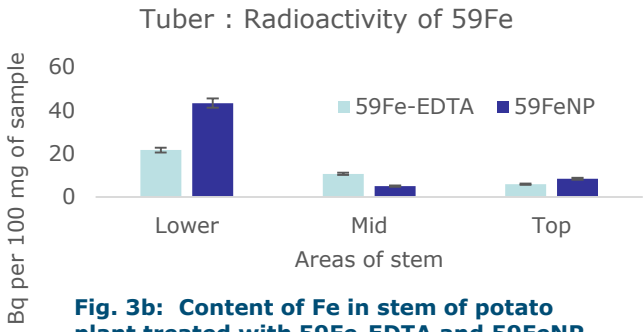


Fig. 3b: Content of Fe in stem of potato plant treated with 59Fe-EDTA and 59FeNP

The Future

Based on our field trials and research, we believe that nanotechnology could help to make fertilizers more efficient and could also play a role in reducing phosphate and nitrate groundwater contamination.

Nanotechnology also has the potential to increase the viability time of hydroponic nutrient solutions helping to conserve fresh water.

Crops can be bio-fortified using nanoparticle-based fertilizers or supplements helping to increase the nutritional value of animal fodder and staple food crops.

Other synthesised NP's within the research group	
Calcium	Selenium
Copper	Silica
Gadolinium	Silver
Gold	Titanium
Iron	Zinc
Magnesium	
Manganese	

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Any Questions?