Abstract

Nanoparticles are becoming popular from their use in medicine for therapy, diagnostics and imaging, in pharmacy for drug delivery, to its use in electronics, engineering and manufacturing industries. This wide application has increased their presence in the environment especially in wastewater from municipal and industrial sources. They end up in the final product; biosolids which are treated sewage sludge from wastewater treatment plants. Due to limited space in landfills and cost effectiveness, biosolids are predominantly disposed in land applications as organic fertilizer for crop production or land reclamation. Nanoparticles have been detected in wastewater and biosolids raising concerns about their effect on soil health and crop growth.

While a large number of studies have been conducted on effect of nanoparticles on seed germination and plant growth, few studies have been carried out using biosolids. The sole effect of nanoparticles may be different from when it’s present in biosolids due to reaction with some components in biosolids. Hence more work is needed in this area to provide direction for regulation of biosolids. Studies have reported both positive and negative effects of nanoparticles on plant growth showing that it depends on plant species, type of nanoparticle, and dose of nanoparticle and method of application. There is also very little work on effect of nanoparticles on soil health. Most of the work done has shown the antimicrobial effect of some nanoparticles which could affect nutrient release from the organic matter fraction in the soil and disrupt some plant-microbe relationships that promote soil fertility. Although nanoparticles have proved beneficial in many aspects of life, they need to be monitored due to their increasing use in the environment.

Introduction

Nanoparticles are used in a wide range of consumer products with applications in the fields of medicine, pharmacy, electrical appliances and manufacturing industries. It has been estimated that greater than 15% of consumer products have some kind of nanotechnology incorporated into their manufacturing process [1]. The increase in production of nanoparticles will ultimately increase their release into the environment especially via municipal and industrial wastewater [2]. Several studies have confirmed the presence of nanoparticles in municipal and industrial wastewater which ends up at wastewater treatment plants (WWTPs) [3–5].

Sewage sludge from wastewater treatment plants (WWTPs) is converted to biosolids after treatment to remove pathogens and volatile solids [6]. Biosolids contain both essential nutrients for plant growth and other contaminants of emerging concern such as nanoparticles, heavy metals, pharmaceuticals and personal care products. The land application of biosolids may be a potential release of these substances into the environment. While a lot of studies have been conducted on heavy metals and pharmaceuticals in biosolids, there is limited information on nanoparticles.

Although there is a lot of information on effect of nanoparticles on plant growth especially on seed germination, not much work has been done to characterize biosolids with respect to the presence of nanoparticles and their effects on plant growth and soil health [7–9]. The effect of nanoparticles determined solely on plants may be different from their effect when present in biosolids due to reactions with other components of biosolids. Hence more work is needed to determine the effect of nanoparticles in biosolids on plant growth and soil health when applied on agricultural soils.

Even though most researchers agree that the effects of organic compounds, metals, and microorganisms in biosolids are not harmful to humans or the environment if managed carefully, information of their potential impact on soil health and plant growth is still needed at this time [10]. Hence this paper provides information on nanotechnology, types of nanoparticles, nanoparticles in biosolids and their effect on soil health and plant growth.
Nanotechnology

Background

Nanotechnology has been defined as the understanding, control or manipulation of particles at scales as small as the nanometer (nm), specifically between 1 and 100 nm to create new materials with new properties and functions [11]. One nanometer (nm) is the one thousand millionth of a meter (1 nm = 10⁻⁹ m) and this size may be its strength in many applications. Nanotechnology explores electrical, optical, and magnetic activity as well as structural behavior at the molecular and submolecular level [12]. There are two approaches of nanotechnology; first, molecular nanotechnology which involves the building of organic and inorganic structures while the second involves the breaking down of bulk materials into nanoparticles [13].

Nanotechnology has been used in energy, pharmacy, electronics, biotechnology, medicine and engineering to improve material performance [14,15]. Nanotechnology manufactures drugs in sizes as small as the nanometer scale which enhances the performance in a variety of dosage forms [14]. Advantages of nanotechnology in pharmacy includes increased surface area, increased dissolution, enhanced solubility, and increased oral bioavailability, lower dosages required and faster therapeutic action in patients [14].

In orthopedics, nanotechnology has been used in bone tissue engineering, implantable materials, diagnosis and therapeutics, and surface adhesives [16]. In dentistry, nanomaterials are being used in caries inhibitors, antimicrobial resins, hard tissue remineralizing agents, scaffolds, bio-membranes, restorative cements, adhesion promoters and boosters, reinforced methacrylate resins, root canal disinfectants, and friction free orthodontic arch wires [17]. Nanoparticles have also been used in the diagnosis, imaging, screening, and treatment of primary and metastatic tumors of lung cancer [18]. In general medicine, nanoparticles have been used in imaging probes in the treatment of cardiovascular disorders, ocular, neurodegenerative, respiratory diseases, AIDS and enhancement of wound healing [19].

In agriculture, nanotechnology has been used for the controlled release of agrochemicals (e.g., fertilizers, pesticides, and herbicides) and target-specific delivery of biomolecules (e.g., nucleotides, proteins, and activators) [20]. Nanotechnology has been used in the production of fertilizers with better release and pesticides with better broad–spectrum pest protection efficiency [21]. Nanotechnology has been used to deliver DNA to plant cells, enhance nutrient absorption, detect plant pathogens, regulate plant hormones, and in animal husbandry, nanocapsules have been devised to deliver vaccines [22]. Nanotechnology has several applications in all stages of production, processing, storing, packaging and transport of agricultural products [23]. However, most of the work on nanotechnology in agriculture are at the developmental stage and not yet commercialized [22].

Types of nanoparticles

Nanoparticles are particles ranging in size from 1 to 100 nm [24]. They are different from the bulk material and can be synthesized chemically or biologically [24]. Metallic nanoparticles such as Ag or Au have been synthesized by plants such as Azadirachta indica, Capsicum annuum and Carica papaya or microorganisms such as Verticillium sp., and Aspergillus fumigates [24, 25]. Properties of nanoparticles that contribute to their usefulness include increased surface area, surface reactivity and solubility, ability to agglomerate or change size in different media and enhanced endurance over conventional-scale substance [19].

Nanoparticles are characterized by the material, shape and magnetic property. Based on material, they can be classified Table 1 into metallic nanoparticles, carbon based nanoparticles, silica based nanoparticles, polymeric (organic) nanoparticles. Based on shape, they can be classified into quantum dots, nanotubes, nanofibres, nanorods, nanosheets, aerogel and nanoballs [19]. They can also be classified as either magnetic or non–magnetic nanoparticles.

Metallic nanoparticles can be silver (Ag), gold (Au), titanium oxide (TiO₂), iron oxide (Fe₂O₃), zinc oxide (ZnO), or copper (Cu). Silver nanoparticles are the most commonly used as antimicrobial agents for water treatment and in textile industries; in electronics, drug delivery, and agriculture [26–29]. Gold nanoparticles are used in diagnosis of cancer,

### Table 1: Types of nanoparticles based on material.

<table>
<thead>
<tr>
<th>Class</th>
<th>Types</th>
<th>Uses</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metallic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silver (Ag)</td>
<td>Drug delivery, water treatment, electronics</td>
<td>Nair et al., 2010</td>
<td></td>
</tr>
<tr>
<td>Gold (Au)</td>
<td>Cancer diagnosis, DNA fingerprinting, stem cell detection</td>
<td>Tomar and Garg, 2013</td>
<td></td>
</tr>
<tr>
<td>Titanium dioxide (TiO₂)</td>
<td>Food additive, water purification, medical applications</td>
<td>Weir et al., 2012</td>
<td></td>
</tr>
<tr>
<td>Zinc oxide (ZnO)</td>
<td>Cosmetics, drug delivery, biosensors</td>
<td>Sabir et al., 2014</td>
<td></td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>Electronics, catalyst, medicine, bioanalysis</td>
<td>Chandra et al., 2014</td>
<td></td>
</tr>
<tr>
<td>Carbon based</td>
<td>Fullerenes</td>
<td>Drug carrier, medical imaging</td>
<td>Partha et al., 2009</td>
</tr>
<tr>
<td>Graphene</td>
<td>Cancer therapy, tissue engineering, bioimaging, drug delivery</td>
<td>Wu et al., 2015</td>
<td></td>
</tr>
<tr>
<td>Silica based</td>
<td>SiO₂</td>
<td>Biosensors, drug additives</td>
<td>Piperigkou et al., 2016</td>
</tr>
<tr>
<td>Polymeric/organic</td>
<td>Chitosan, poly(lactide-co-glycolide), polyacrylates</td>
<td>Drug delivery</td>
<td>Zhang et al., 2013</td>
</tr>
</tbody>
</table>
detection of cancer stem cells, in DNA fingerprinting, to detect antibiotics such streptomycin, gentamycin and neomycin, and for identification of different classes of bacteria [30]. Nanoparticles of metalloids such as Se are also commonly used in diagnostics and therapy, electronic devices, catalysis, fuel cells and bio and environmental remediations [31].

Examples of carbon nanoparticles include fullerene and graphene. Carbon nanotubes are cylindrical layers of graphene which could be single or multi walled with open and closed ends [32,33]. Individual carbon nanotube walls can be metallic or semiconducting depending on the orientation of the graphene lattice [33].

Fullerene has been used as targeted therapeutic agent in osteoporosis and cancer; proposed as drug carrier and used in diagnostic and medical imaging [34-36]. On one hand, synthesized carbon nanoparticles have been proved to be effective in removal of metal ions (Zn, Ni, Cu, Sb, Co, Cd, Cr, etc.) from contaminated water samples [37]. On the other hand, engineered carbon nanoparticles have been considered emerging environmental contaminants [38].

Silica nanoparticles are used as additive to drugs, cosmetics, food, biomedical applications and biosensors [19]. Polymeric nanoparticles are used as drug carriers for cancer therapy due to their biodegradability, biocompatibility and non-toxicity [39]. Polymeric nanoparticles are used for drug delivery techniques such as conjugation and entrapment of drugs, prodrugs, stimuli-responsive systems, imaging modalities, and theranostics [40].

Quantum dots (QDs) are a class of engineered nanoparticles with nanometer diameter size (2–10 nm) [41]. They are heterostructures with quantum confinement to zero dimensions containing nanocrystals with quantized energy levels directly related to size [42]. Nanocrystal quantum dots are semi-conducting materials with bright fluorescence, narrow emission, broad UV excitation and high photostability [43]. Ninety percent of QDs produced are used for light-emitting diode or organic light-emitting diode while 10% are used for imaging purposes [44].

Toxicity of nanoparticles

A recent study in Poland has shown that short term exposure to graphene oxide induces oxidative stress and DNA damage in some insects. They also found numerous degenerative changes in the cells of the gut and testis of Acheta domestica ten days after applying graphene oxide [45]. Although, fullerene has exceptional antioxidant capacity which has made it a promising core ingredient in many dermatological and skin care products, it may be toxic to skin cells at high doses and with longer exposure time [46].The cytotoxicity of carbon nanotubes is affected by its surface chemistry and size with shorter carbon nanotubes being less toxic than longer ones. Cells exposed to carbon nanotubes undergo oxidative stress which leads to inflammation and cytotoxicity at higher levels. Even when they don’t cause lung inflammation or tissue damage, they may alter immune function [19]. TiO₂ nanoparticles have been reported to be genotoxic, carcinogenic and phototoxic [47]. TiO₂ nanoparticles may induce oxidative DNA damage, lipid peroxidation, and increased hydrogen peroxide [48].

Nanoparticles In Biosolids

Background

About 7 million tonnes of biosolids are produced by WWTPs in the United States alone with about 60% applied on agricultural lands as organic fertilizer [49]. Biosolids contain nutrients and organic matter which may be used to enhance soil fertility and crop yield [50, 51]. Land application of biosolids is also a means of disposal of sewage sludge produced at WWTPs [52].

Biosolids are useful as a low-grade fertilizer and soil amendment to improve soil chemical and physical properties [53]. Biosolids are especially rich in phosphorus, have potentials for sustainable nutrient management and can be used to reduce exploitation of nonrenewable phosphorus resources such as phosphate rock [54,55]. Biosolids also provides a slow release source of nitrogen from the mineralization of organic matter [56]. Biosolids application produced greater NO₃–N concentrations than N fertilizer in the 30–60 and 60–90 cm depths for the dryland no–till wheat (Triticum aestivum, L.)–fallow rotation [57].

Fate and Transport of Nanoparticles in Biosolids

Despite the beneficial effects of biosolids, excessive application rates may be harmful to the environment leading to regulation of biosolids by governing agencies [58]. Biosolids are regulated based on their biological content into class A if pathogens are completely undetectable or class B for higher detectable pathogens [58]. Class A is regulated and restricted to use in lawns, home gardens, or other types of land, or bagged for sale, or land application while class B is used for other applications [59]. However, there are other contaminants of emerging concern that should be considered during regulation which includes nanoparticles and pharmaceuticals.

Land application of biosolids is one way nanoparticles are released into the environment especially in agriculture where biosolids are used as organic fertilizers. Silver nanoparticles have been detected in the final stage sewage sludge Figure 1 of a municipal WWTP [60]. Even though a fraction of nanoparticles may be removed by the treatment, a significant amount is retained in the biosolids produced from sludge [61,62]. Titanium–containing nanoparticles between 50 nm and 250 nm in diameter were identified in soils with long term biosolids application in the United States [63].

Effect of nanoparticles on soil health

Soil health has been defined as “the capacity of soil to function as a living system, with ecosystem and land use boundaries, to sustain plant and animal productivity, maintain or enhance water and air quality, and promote plant and

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animal health. Healthy soils maintain a diverse community of soil organisms that help to control plant disease, insect and weed pests, form beneficial symbiotic associations with plant roots; recycle essential plant nutrients; improve soil structure with positive repercussions for soil water and nutrient holding capacity, and ultimately improve crop production” [64].

[65]. proposed that soil health is dependent on the maintenance of four major functions: carbon transformations; nutrient cycles; soil structure maintenance; and the regulation of pests and diseases. They explained that each of these functions is manifested as an aggregate of a variety of biological processes provided by a diversity of interacting soil organisms under the influence of the abiotic soil environment.

**Indicators of soil health**

A combination of soil physical, chemical and biological properties Figure 2 can be used as indicators of soil health. For example, soil physical properties such as soil texture, aggregation, moisture, porosity, and bulk density; chemical properties such as total C and N, mineral nutrients, organic matter, cation exchange capacity (CEC); and soil biological properties such as microbial biomass C and N, biodiversity, soil enzymes, soil respiration, in addition to macro and mesofauna can be used [66]. Biological indicators are central to soil health because they can influence both chemical and physical properties of the soil.
Soil organisms are involved in nutrient mineralization and availability. Macro and mesofauna may also influence physical properties such as porosity, aeration and water infiltration. For example, earthworms can modify soil structure and enhance nutrient availability. Estimation of microbial biomass and activity may provide information of potential nutrient status of the soil. Soil organic matter is an important component of the soil which determines soil productivity but mineralization of soil organic matter may be greatly reduced in the absence of soil microorganisms. Hence, microbial activity is an important soil health indicator.

A previous study tested the effect of nanoparticles in biosolids on soil microbial community and results showed that Ag nanoparticles also caused a reduction in microbial biomass and changes in microbial activity probably due to Ag⁺ released from partially sulfidized silver nanoparticles. The magnitude of the AgNO₃ treatment effect on microbial abundance, community composition, and function was consistently equal to or less than the effects of silver nanoparticle treatment [69]. Unlike the first day, differences in microbial community structure were not detected after 50 days, suggesting that a period of aging of nanoparticles in either sewage sludge and/or soils may cause transformations that render the potential toxic effects minimal. A recent study showed that there were no differences in total transformations that render the potential toxic effects minimal. Unlike the AgNO₃ treatment effect on microbial abundance, community composition, and function was consistently equal to or less than the effects of silver nanoparticle treatment [69].

Many studies have used earthworms as indicators of soil health [71]. In their review on the effect of nanoparticles on earthworms in the soil, [72] explained that several studies have shown that the effect of nanomaterials on growth and survival of adult earthworms is negligible while some other studies reported that the reproductive activity of earthworms may be reduced by nanomaterials. However, it’s not clear if these tests are conducted with nanoparticles in biosolids. A past study has reported 100% mortality of earthworms in mine tailing soil amended with biosolids but could not identify the component that was toxic to the earthworms [73]. In the study, the addition of biosolids to mine tailing soil almost doubled plant biomass production and increased carbon substrate utilisation compared to untreated stockpiled or unmodified soils.

On the contrary, in another study, all of the adult earthworms survived in the biosolids amended soils at all concentrations that were aged for 2 weeks; while only 20% of the adults survived in the soil amended with the highest concentration of biosolids and aged for 8 weeks [74]. This suggests there may be chemical transformations within biosolids with longer aging time [75]. Reported that 97.5% of earthworms in a low organic matter soil survived, and the survival of the earthworms was not significantly affected by the addition of biosolids although biosolids reduced the gain in mass of earthworms. This is different from the results of yet another study that reported that biosolids enhanced the biomass of earthworms though the earthworms accumulated copper [76].

### Effect of nanoparticles on crop growth

Several studies have shown that nanoparticles can be taken up directly by plants [77, 78], and translocated to the edible parts of the mustard plant (Brassica juncea) [79]. This indicates potential contamination of the food chain for both animals and humans. However, studies have reported positive and negative effects of nanoparticles Table 2 on plant growth and development [80].

### Effect of nanoparticles on plant growth

The effect of nanoparticles on plant growth depends on the plant spp, type of nanoparticle, its mode and dose of application [80, 81]. Reported that the majority of the work on nanoparticles suggests low to moderate overall phytotoxicity in terrestrial plant species. [82]. explained that nanoparticles can cause phytotoxicity through dissolution and release of toxic ions, production of excess reactive oxygen species (ROS) through redox cycling, binding interactions and oxidation of biomolecules.

### Table 2. Effect of nanoparticles on plant growth

<table>
<thead>
<tr>
<th>Plant species</th>
<th>Type of nanoparticle</th>
<th>Dose of nanoparticle</th>
<th>Effect on plant growth</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brassica rapa (Canola)</td>
<td>CuO</td>
<td>10mg/L</td>
<td>Promoted growth</td>
<td>Rahmani et al., 2016</td>
</tr>
<tr>
<td>Arabidopsis thaliana</td>
<td>Fe₂O₃</td>
<td>25 mg/L</td>
<td>Reduced seedling and root length</td>
<td>Sergey et al., 2015</td>
</tr>
<tr>
<td>Lycopersicum esculentum (Tomato)</td>
<td>SiO₂</td>
<td>8 g/L</td>
<td>Improved seed germination</td>
<td>Siddiqui and Al-Whaibi, 2013</td>
</tr>
<tr>
<td>Oryza sativa (Rice)</td>
<td>Ag</td>
<td>10-100 mg/L</td>
<td>Inhibited plant growth</td>
<td>Thuesombat et al., 2014</td>
</tr>
<tr>
<td>Vigna radiate (Mung bean)</td>
<td>TiO₂</td>
<td>10 mg/L</td>
<td>Improved plant growth</td>
<td>Raliya et al., 2015</td>
</tr>
<tr>
<td>Cucumis sativus (Cucumber)</td>
<td>ZnO</td>
<td>200-800 mg/L</td>
<td>Improved seed germination</td>
<td>Calabrese and Baldwin, 2001</td>
</tr>
<tr>
<td>Arabidopsis</td>
<td>ZnO</td>
<td>200-300 mg/L</td>
<td>Reduced plant growth</td>
<td>Wang et al., 2016b</td>
</tr>
</tbody>
</table>

It has been reported that silver nanoparticles had a toxic effect on rice seedlings and the effect was dependent on size and dose of silver nanoparticles. Increasing the silver nanoparticle concentration over the range of 0.1 to 1000mgL⁻¹ and increasing the size of the silver nanoparticles over the 20–150nm diameter range increased the inhibition effect upon seed germination and seedling growth [8]. The size and dose of nanoparticles play an important role in their behavior, reactivity and toxicity [83].

Though the addition of ZnO nanoparticles to the soil at a concentration of 500 mg kg⁻¹ did not significantly affect the growth of maize, it inhibited root AM infection and plant phosphorus uptake [84]. At a concentration of 3000 mg kg⁻¹, ZnO nanoparticle significantly inhibited the growth of soybean plants and also inhibited arbuscular mycorrhizal (AM) colonization in soybean roots at concentrations from 2000 mg kg⁻¹ and higher [85]. The AM inhibitory effect of ZnO nanoparticles raised suggestions about its potential to be used in plant fungal control strategies. A study revealed that ZnO nanoparticles inhibited growth of fungal plant pathogens such as Fusarium graminearum in a mung bean broth agar and in sand [86].

However, the addition of phosphorus and inoculation of AM fungi reduced the bioavailability of Zn from ZnO nanoparticles which led to a reduction in the translocation and accumulation of Zn in maize shoots [84]. This suggests that P and AM fungi can be used to reduce plant uptake and ameliorate the effects of ZnO nanoparticles. A previous study evaluated the bioavailability of Zn in ZnO nanoparticles and effect on plant growth of maize plants [87]. Results show that the effect of ZnO nanoparticles on maize growth and nutrition, photosynthetic pigments, and root activity (dehydrogenase) was dependent on dose. At concentrations between 100 and 200 mg kg⁻¹, the effect of nanoparticles was stimulatory; neutral at 400 mg/kg, and toxic between 800 and 3200 mg kg⁻¹. Toxicity of ZnO nanoparticles may be higher than bulk or soluble Zn because the dissolved Zn²⁺ from ZnO nanoparticles may make a dominant contribution to their phytotoxicity [87].

Nanoparticles have also had some beneficial impacts on plant growth. Graphene quantum dots enhanced the growth rate in coriander and garlic plants when the seeds were treated with graphene quantum dots [9]. Tomato seeds exposed to carbon nanotubes had faster germination rates and higher plant biomass production. Faster germination rate of seeds was attributed to the ability of carbon nanotubes to penetrate thick seed coat and support water uptake inside seeds [88].

Nano-SiO₂ enhanced seed germination and stimulated the antioxidant system of squash under NaCl stress [7]. Nano–SiO₂ enhances plant growth and development by increasing gas exchange and chlorophyll fluorescence parameters, such as net photosynthetic rate, transpiration rate, stomatal conductance, effective photochemical efficiency, actual photochemical efficiency and electron transport rate [7]. It has also been reported that silica coated with quantum dots promoted root growth of rice plants [89].

Titanium dioxide (TiO₂) nanoparticles stimulate carbohydrate production and increases rate of photosynthesis in plants [90]. It has been shown to increase plant growth of wheat and enhance radicle and plumule growth of canola seedlings [90, 92]. The effect of TiO₂ nanoparticles may be due to its role in controlling enzymes involved in the metabolism of nitrogen. These enzymes help plants to absorb nitrate and also aids in the conversion of inorganic nitrogen to organic nitrogen [93].

**Conclusion**

Although, the application of nanotechnology in fields like medicine, pharmacy could be lifesaving, elevated levels of nanoparticles in the environment may not be good for public health. The detection of nanoparticles in biosolids indicates that increasing production of nanoparticles has released them beyond the boundaries where they are needed. This does not however mean we should stop land application of biosolids which provides cheap source of nutrients and organic matter for good soil health and crop growth. There may be the need to develop more efficient treatment processes at WWTPs to increase removal of these contaminants of emerging concern before land application. Regulations also need to be modified to include allowable levels of nanoparticles in biosolids before land application. However, studies have shown that effect of nanoparticles on crop growth depend on plant species, type of nanoparticles and dose applied. More studies are needed to determine threshold levels for land application of these nanomaterials for different crops in biosolids amended soils. The antimicrobial effect of some nanoparticles may also affect plant–microbe relationships that promote soil fertility and crop growth. Hence, these nanoparticles need to be properly identified and regulated before land application of biosolids.

**References**


