Effect of Coating Agents of Silver Nanoparticles on Their Accumulation in and Growth of Radish (*Raphanus sativus* L.)

A. Bazoobandi¹, A. Fotovat^{1*}, A. Halajnia¹, and A. Philippe²

ABSTRACT

The widespread use of silver Nanoparticles (AgNPs) in various industries has raised concerns about the fate of these materials. Therefore, the present study aimed to assess the effects of coating agents of Ag particles in soil and how they interact with plants as the first step in the human food chain. Radish (Raphanus sativus) was exposed to silver Nitrate (AgNO₃) as well as AgNPs with different coatings: Citrate (AgNPs-Cit), Polyethyleneimine (AgNPs-PEI), and Polyvinylpyrrolidone (AgNPs-PVP) at different concentrations. The effect of concentration (5, 25, 125 mg kg^{-1} soil) and the type of coatings on the dry weight of radish were compared with the control. The results revealed that the type of treatments affected dry weight of radish and, among all treatments, AgNO₃ had the highest weight loss, in which shoot dry weight decreased by 51%. Total silver measurement in radish root, tuber, and shoot indicated that the accumulation of AgNPs was influenced by the type and concentration of the coating. The AgNPs with positive charge coating (PEI) had a higher transfer ratio than other treatments. The findings indicated that radish had the ability to store silver in its root, tuber, and shoots in large amounts, thus having the potential to act as a source of silver contamination for humans.

Keywords: AgNPs, Citrate coating, Polyethyleneimine, Polyvinylpyrrolidone.

INTRODUCTION

Release of metallic nanoparticles into the environment has attracted international attention (Rajput et al., 2018). The important issues in this case are the unknown effects of large amounts of these particles entering the soil and various parts of the environment (Belal and El-ramady, 2017). One of the most important nanoparticles that can be considered potentially toxic and dangerous for the environment is AgNPs. The unique of element properties this and its form have led to its nanoparticulate widespread use in various industries (Noori et al., 2019). In this regard, it is important study behavior of AgNPs in the to

environment (Tkalec et al., 2019). There are many sources of entry for AgNPs into soil, for example, the use of wastewater sludge as a soil amendment, the use of nano fertilizers, aerosols, or waste disposal in landfills (El Hadri et al., 2018). Release of AgNPs into the soil can lead to their leaching into groundwater, or they may enter the human body directly by breathing or swallowing (Inshakova and Inshakov, 2017). After accumulating in the soil, they can be absorbed by edible plants and vegetables and enter the human food chain and potentially induce adverse effects (Inshakova and Inshakov, 2017).

Aggregation behavior, size, and surface properties of Engineered Nanomaterials

¹ Faculty of Agriculture, Department of Soil Science, Ferdowsi University of Mashhad, Mashhad, Islamic Republic of Iran.

² iES Landau, Institute for Environmental Sciences, Group of Environmental and Soil Chemistry, Koblenz-Landau University, Fortstraße 7, 76829 Landau, Germany.

^{*}Corresponding author; e-mail: afotovat@um.ac.ir

(ENMs) are the most important factors in controlling their mobility and transport in aquatic and terrestrial systems (Badawy et al., 2010). Those factors determine the dependence and interaction with sorptive surfaces, such as biofilms, algae, plants, fungi, humic substances, and soil sediments (Navarro et al., 2008). One of the most important issues in this case is the surface coatings of the nanomaterials. ENMs are usually coated in order to tune their surface properties (Reinhart et al., 2010). These coatings are usually small ligands (e.g., citrate). polymers (e.g., polyvinylpyrrolidone) or fibers (He et al., 2019), which can render the surface charge of nanoparticles neutral, positive, or negative . These kinds of charges can create widespread changes in behavior of these nanoparticles (Abbaszadegan et al., 2015), which has caused concerns in the environmental field.

Therefore, many studies have been done to determine the behavior of nanoparticles and especially AgNPs in the environment. Most of the studies deal with biological and chemical effects on specific plants, such as Arabidopsis thaliana. Some studies have reported that AgNPs accumulated in the plant when grown in various environments such as soil (Geisler-Lee et al., 2013), agar (Kaveh et al., 2013) and Hoagland (Nair and Chung, 2014). The various effects of accumulation in this specie have been reported, including mortality (Kaveh et al., 2013), reduction in root/shoot weight (Qian et al., 2013) and reduction of chlorophyll content (Sosan et al., 2016). Due to the negative effects observed for plants. numerous studies have been conducted on aquatic media (Jiang et al., 2017) and edible plants (Torrent et al., 2020). Recently Torrent et al. (2020) reported accumulation of silver in various tissues of lettuce and indicated the effect of toxicity on this plant. Meanwhile, Tripathi et al. (2017) reported that AgNPs reduced growth parameters, photosynthesis, and ascorbic and glutathione pigments content in pea (Pisium sativum). In another study, Quah et al. (2015)

investigated the toxicity, accumulation, and transport of AgNPs with different properties in two different agricultural products Glycine max and Triticum aestivum. They reported that the toxicity and fate of AgNPs were different, depending on their size and type. In a study to investigate the effect of AgNPs, TiO₂, fluorine and carbon nanotubes on the suppression of mosaic virus, concentrations of 100, 200 and 500 mg L⁻ of these nanomaterials were used (Adeel et al., 2021). The results showed that fluorine and carbon nanotubes had the most suppressive effect. Cvjetko et al (2017a) considered the toxicity of silver nitrate and three types of AgNPs in onion (Allium cepa) and reported that the toxicity of these particles was directly dependent on their shape, surface properties, and type of surface coating agents.

Edible plants such as radish, cabbage, lettuce, play an essential role in the nutritional transmission of pollutants from soil to human bodies. They are considered very important in human health assessment. Radish (Raphanus sativus L.) is a popular vegetable with high global consumption and can mature in three to four weeks under favorable growth conditions. Radish is also an underground vegetable, with its edible tissues directly exposed to AgNPs in soil. Therefore, radish may accumulate high concentrations of nanoparticle in their edible tissues (Zhang et al., 2017). A previous study demonstrated that the radish tubers grown in a loamy sand soil with 250 and 500 mg kg⁻¹ of CeO₂ NPs accumulated high concentrations of Ce, posing potential risks for human exposure (Corral-Diaz et al., 2014). However, detailed distribution of Ce in the tubes and the role of soil properties were not reported in that study. On the other hand, in previous studies less attention was paid to radish, which is capable of storing pollutants in its tubers and even its leaves(Zhang et al., 2017). Gui et al. (2017) studied the phytotoxicity of cerium oxide nanoparticles on radish plant and reported that nanoparticles can enter the human food chain through soil and consumption of edible parts.

Indeed, detailed information on the behavior of AgNPs with different coatings in soil and plant, in particular for radish, is still missing. Therefore, the aims of this study were: (1) Investigating the effect of AgNPs with different coatings and concentrations on its uptake and distribution in different parts of radish, and (2) Evaluation of toxic effects of silver nanoparticle on shoot, root, and tuber dry weight of radish.

MATERIALS AND METHODS

Reagents and Apparatus

AgNPs with citrate, polyethyleneimine and polyvinylpyrrolidone coating agents as well as silver nitrate were purchased from ASEPE Nano Tech (Tabriz, Iran). For the digestion procedures of radish tissues, nitric acid (HNO₃ 69%) hydrochloric acid (conc. HCl, 37% w/w), concentrated perchloric acid, and hydrogen peroxide (H₂O₂ 30%) purchased from Sigma Aldrich were (Tehran, Iran). Distilled de-ionized water was used in all the experiments. Ag were determined using concentrations AA990 Atomic Absorption (Petrović et al., 2001).

Table	1.	The	main	characteristics	of	the	test
soils.							

Parameter	Amount	
pН	7.97	
EC ($dS m^{-1}$)	0.45	
CEC (cmolc kg ⁻¹)	8.5	
OM	0.58	
$CaCO_3(\%)$	17	
Sand (%)	63	
Silt (%)	13.3	
Clay (%)	23.7	
Texture class	Sandy clay loam	

Soil Treatment and Plant Culture

Soil samples used in this study were obtained from 0-15 cm field in Khorasan Razavi Agricultural Research Education and Extension Organization (AREEO). The main characteristics of the test soils were measured, and are listed in Table 1. This experiment was conducted using а completely randomized design with factorial arrangement including 12 treatments with three replications (Figure 1). AgNO₃ and AgNPs with three types of coating agents, namely, Citrate (Cit), Polyethyleneimine (PEI), and Polyvinylpyrrolidone (PVP), were weighed. Then, AgNPs and silver nitrate were mixed with 2 kg soil, using an electrical mixer, in three concentration levels of 5, 25,



Figure 1. General schematic of the experimental design.

and 125 mg kg⁻¹ and were transferred to plastic pots, as a simulation of adding sludge amendment or fertilizers directly to the soil. Previous studies reported that up to 5 mg kg⁻¹, no serious toxicity symptoms were seen in different plants (Tripathi et al., 2017). In order to investigate the effect of increasing concentration in this study, treatments were selected from 5 mg kg⁻¹ to 125. For better drainage, a 4 cm layer of uncontaminated sand was added at the bottom of the pots following previously reported methods (Vittori Antisari et al., 2015). Thirty-six pots treated with AgNPs and silver nitrate were randomly placed in the greenhouse of Ferdowsi University of Mashhad, where temperature and light were controlled. The 35-day length of the growth period to the reproductive stage was set to 16 hours of light and 8 hours of darkness at 20±5°C. Before planting, radish seeds were placed in tap water overnight, then, they were planted in the pots. After 24 hours, the first sprouts were observed in the pot. After five days, three plants per pot (and 3 pots for each treatment) were maintained and the rest were removed (Figure 2). Irrigation was done daily and, in order to avoid the release of AgNPs and AgNO₃ from the pots, it was done in such a way that no water drained out of the pots.

Sampling and Analyses

At the end of the growth period (35 days), each radish plant was removed from the pots and leaves, tubers, and fine roots were separated, washed with deionized water and weighed (wet-weight). They were then dried at 60°C until constant weight and weighted again (dry weight) prior to grinding using an electrical mill (Naniwa 100w/N95/"F" class). After that, the samples were stored in the freezer in vacuum plastic containers until digestion.

Digestion on a heating plate was used to determine the amount of silver in different parts of plant. Half a g of the milled samples were transferred to a beaker, then 8 mL of nitric acid (69%) and 2 mL of H_2O_2 (30%) were added to each sample (v/v= 4:1). After covering the dishes with watch glass, the samples were heated at 250°C for 1 hour. After cooling, the samples were transferred to a 25 mL volumetric flask, which was filled up to the mark with deionized water. The samples were finally filtered using Whatman filter paper and stored in a



Figure 2. The plants situation in the greenhouse.

polypropylene centrifuge tube at 4°C prior to AAS analysis.

Statistical Analyses

The statistical design was completely randomized with the factorial arrangement and data were considered as three replicates. The data were analyzed using JUMP software and Tukey's test.

RESULTS AND DIS CUSSION

Fine Root Dry Weight

As shown in Figure 3, the dry weight of the decreased fine roots with increasing concentration of silver. with significant differences (P< 0.05)between most treatments, including the lowest concentration, compared to the control. This reduction in the dry weight of the fine root can reduce growth of the plant and other organs of the plant and thus decrease the dry weight of the tubers and shoots. The most significant reduction in fine root dry weight was seen in the AgNO₃ treatments. According to the results in the AgNO₃ treatment at concentrations of 25 and 125 mg kg⁻¹, fine roots dry weight decreased 32 and 76%, respectively. This sharp decrease in dry weight could be attributed to the release of silver ions causing toxic effects on the plant, decreasing growth, and/or due to Reactive Oxygen Species (ROS) mediating damages to the biomolecules linked with the photosynthetic apparatus (Tripathi et al., 2017b). In contrast, roots dry weight in $AgNO_3$ 5 mg kg⁻¹ treatment increased significantly about 4%. Such an increase in dry weight of fine roots, tubers, and shoots at 5 mg silver nitrate per kg soil was, probably, because the concentration of silver was still not high enough to cause toxicity to the plant and, on the other hand, the nitrate fraction of this treatment could act as a growth stimulant to improve growth conditions.

Tuber Dry Weight

In the case of the tubers, there was also a decreasing trend, except for AgNO₃-5 that that increased (Figure 3). The decrease can be due to the negative or, perhaps, toxic effects of silver on the roots, which prevented root development and reduced the growth of the plants. The problem with tubers is that they are in direct contact with soil and silver can also have negative effects of the tubers. on the shape Also Vishwakarma et al. (2017) reported that AgNPs and AgNO₃ treatments induced morphological modifications not only on the



Figure 3. Effect of AgNO₃ and AgNPs with 3 different coating types on dry weight of radish seedlings. [Data are means \pm standard error of three independent experiments with three replicates (n= 9). Bars followed by different letter(s) show significant differences (P< 0.05) according to the Tukey's test.

contact parts of the roots but also in the tubers, stem, and leaves. There was a significant difference between AgNPs-Cit-125, AgNPs-PEI-25, AgNO₃-5 and AgNPs-Cit-5 (P< 0.05). Other treatments at different concentrations and with different coatings reduced dry weight compared to the control.

Shoot Dry Weight

As shown in Figure 3, the amount of shootdry-weight decreased with increasing concentration of all treatments, except silver nitrate treatment at a concentration of 5 mg kg ¹. Meanwhile, the highest weight loss was related to the Ag-NO₃-125, in which shoot dry weight decreased by 51%. This effect might be due to the toxic effects of silver ions on the plant reducing its yield (Vishwakarma et al. 2017). However, this also could be attributed to the increased uptake of silver by plants (Harris and Bali, 2008). In the AgNO₃-5 treatment, dry weight increased by about 19% compared to the control. Changes in the shoot dry weight indicate a negative effect of experimental treatments on the growth rate and the consequent dry weight of radish. As can be seen in the Figure 3, there is a statistical difference at some of treatments (AgNPs-Cit-AgNPs-PVP-125, AgNPs-PEI-125, 125. AgNPs-PEI-25, AgNO₃-125 AgNPs-Cit-125, AgNPs-PEI-125) (P< 0.05). Accordingly, the difference in shoot-dry-weight at high concentrations of treatments is significant. AgNPs-PEI treatment, after silver nitrate, had the highest dry weight reduction, possibly due to the positive charge on the surface of these nanoparticles, which may affect its behavior and transformations in the soil as well as toxicity of this particle to plants (Tkalec et al., 2019). Also it can increase amount of uptake of these particles by negative charges on the root surface of the plant (Yang et al., 2013). Cvjetko et al. (2017) reported that the highest impact of AgNPs with different coating charges was recorded for positively charged AgNP-CTAB, induced which changes significantly different from the control and other AgNPs in the majority of tested

parameters in Allium cepa roots. Among the treatments, the lowest weight loss was observed in citrate-coated nanoparticles. This could be due to their surface's negative charge which causes the adsorption of these nano particles by ligands and multivalent cations such as Ca2+ and Mg2 + in the soil, preventing their uptake and impact on the plant. (Beer et al., 2012). Moreover, due to the aggregation as well as the negative charge, uptake of AgNP-citrate by root was probably difficult. Another reason could be the decrease in the AgNPs available surface for interaction with organic molecules and the AgNP-citrate toxic effects (Šinko et al., 2014).

Overall, the results show that dry weights were more affected by the concentration of treatments than the type of coatings or speciation. In other words, the effective factor in reducing the dry weight of radish plant was silver element, and increasing its the concentration caused toxicity to the plant and, as a result, reduced plant growth. Nonetheless, the AgNO₃ treatments had slightly higher impacts on the dry weight, suggesting that most of the toxic effect results from the silver ions and that nanoparticles dissolved fast in the producing system, hence, an effect independent from their initial state. This is in agreement with previous results from Yasur and Rani (2013) who described that AgNPs expressed lower toxicity than AgNO₃, as a result of their coating that can stabilize AgNPs towards dissolution and reduce their toxicity. Likewise, the toxicity of treatments was more pronounced in roots compared to the shoots, because roots are the main sites of interaction while the plant's self-defense mechanism involve translocation of the AgNPs from roots to shoots and thus restrict its accumulation in tubers completely or partially (Vannini et al., 2014). Previous studies have investigated the effect of AgNPs on different plants such as wheat (Jiang et al., 2012; Dimkpa et al., 2013) , cucumber (Shams et al., 2013), B. juncea (Vishwakarma et al., 2017), and watermelon and corn (Almutairi and Alharbi, 2015). All these researchers reported that the AgNPs decreased the root and shoot dry weight. Galazzi and Arruda (2018) also investigated



 $mg_{Ag}/kg_{dry matter}$

Figure 4. The effect of different treatments (AgNO₃ and AgNP-Citrate, AgNPs-PVP and AgNPs-PEI) on silver concentration in radish plant. Bars followed by different letter(s) show significant differences (P < 0.05) according to the Tukey's test. Control samples were < limit of detection (LOD).

the effects of 50 mg kg⁻¹ AgNPs and AgNO₃ on soybean and they reported 19 to 25% total weight reduction compared to the control.

Plant Uptake and Accumulation of Silver

Figure 4 shows the amount of silver uptake by radish plants' parts in a soil polluted with different treatments of silver over 35 days. Accordingly, silver was not only absorbed by the plant but also transferred to the tubers and leaves after

absorption. As can be seen in all treatments, concentration of silver in the roots was higher than tubers and shoots, suggesting that the main pathway for the Ag-NPs is through the root, e.g. through water uptake. There is a significant difference between all treatments in terms of accumulation of silver in shoots (P < 0.05). This might be due to the surface characteristics of the treatments or the ability of radish. As Torrent et al. (2020) indicated, the uptake and accumulation of AgNPs in different plants as well as their subsequent toxicological effects depend on various factors such as nanoparticle

JAST

[Downloaded from jast.modares.ac.ir on 2024-05-19]

1479

physicochemical properties, metal concentration, and type of plants. Also, the AgNPs-PEI treatment (positively charged) had the highest accumulation rate in both tuber and the shoot with even higher concentration than in the roots, contrasting with the other coatings. This result is in agreement with Wang et al. (2014) who reported the uptake and accumulation of nanoparticles with positive charge coatings such as PEI were higher than those with negative charge in poplar trees (Populus deltoides nigra). Meanwhile, Zhu et al (2012) reported that positively charged AuNPs accumulated in radish to a greater extent than those with neutral and negative charge.

Based on the results, the lowest absorption and accumulation in tubers and shoots were observed in AgNPs-PVP and AgNPs-Citrat treatments. The low accumulation rate of AgNPs-Citrate in the tuber and shoots may be attributed to the fact that the electrostatic repulsion between the root surface and the nanoparticles with negative surface charge reduces the rate of absorption (Anjum et al., 2013). These results are in agreement with Cvjetko et al. (2017) who reported that the amount of uptake and accumulation of PVP and citrate treatments in the root of Allium cepa was similar and the lowest among the treatments. Seemingly, AgNPs (PEI-AgNPs) and AgNO₃ with positively charged surface were more easily transported from tuber to shoots compared to negatively charged AgNPs (citrate-AgNPs).

Based on the results of this study, it was found that accumulation of AgNPs by the plant was also affected by the type of coating of nanoparticles, while Torrent et al. (2019) reported that accumulation of was influenced by size AgNPs and concentration, but not by nanoparticle coating. Also, silver nitrate treatment had less absorption and accumulation than AgNPs-PEI treatment. This result is incompatible with published studies with other edible plants (Cvjetko et al., 2017b; Soria et al., 2017; Torrent et al., 2020; Vinković et al., 2017; Vishwakarma et al.,

2017), as they indicated that the absorption and accumulation of silver nitrate treatment in plants were higher than AgNPs. Figure 3 clearly reveals that the amount of Ag accumulated at the fine-roots differs from the tuber and shoots. Accordingly, the highest accumulation was with AgNO₃ application, which was significantly different from the other treatments (P< 0.05). The amount of silver present in radish's fine root in AgNO₃-125 treatment was almost similar to the soil, indicating a high accumulation in the fine-roots. The high accumulation of AgNPs-citrate in the roots, which is the highest accumulation after AgNO₃, is also notable. However, due to the negative charge of these particles and root surface, the absorption rate of this type of nanoparticles is expected to be lower than Meanwhile, the others. the lowest accumulation was observed in AgNPs-PEI treatment, which was significantly different from other treatments (P < 0.05). Therefore, due to the high concentration in the tubers and shoots, it is clear that Ag was rapidly translocated from the roots, and this could be a serious threat to human health. Overall, as indicated by Gupta et al. (2019), it seems that the source and form of metals as well as the concentration of available metal in soil the factors affecting AgNPs are accumulation. As previously noted, plant properties also contribute to the uptake and accumulation of nanoparticles, and this may be related to the radish uptake properties. To the best of our knowledge, the mechanism of nanoparticle interaction with plants is not entirely understood, however, it is accepted that, depending on their properties, some nanoparticles may form complexes with membrane transporter proteins or root exudates resulting in their translocation into the plant system (Yadav et al., 2014). It is conceivable that such mechanisms are selective towards nanoparticles having a certain surface composition. One the other hand, one cannot exclude the possibility that nanoparticles completely dissolve during the exposure duration. The observed selectivity would then be related to the formation of Ag-complexes with the free ligands from the coating and with soil organic matter.

CONCLUSIONS

In this study, it became clear that different forms of silver, including bulk silver nitrate and silver nanoparticles with different coatings, had negative effects on dry weight of root, tuber, and shoot of radish. These effects increased significantly with increasing concentration of treatments, due to the increase in silver content in root media. These different coatings of silver nanoparticle also had different levels of accumulation in the root, tuber, and shoot. The silver nitrate form probably accumulated more in the roots due to its higher solubility and lower interaction with the soil components. Positively charged particles behave differently in terms of uptake than negatively charged particles or ions. Due to the positive charges on the surface of the nanoparticles, PEI treatment was rapidly absorbed by the negative charges of the root surfaces and was highly transmitted to the tuber and shoots, which can be a threat to human health. Based on the results, oral consumption of radish plant cultivated in contaminated soil, which is capable of storing large amounts of nanoparticles and silver nitrate, may have detrimental effects on human health. These findings should be completed by looking at the speciation of Ag in the different part of the plant and in the soil. In addition, we could also look for other application scenarios. For example, from aerial deposition on the leaf or from sludge amendment using contaminated sludge.

REFERENCES

 Abbaszadegan, A., Ghahramani, Y., Gholami, A., Hemmateenejad, B., Dorostkar, S., Nabavizadeh, M. and Sharghi, H. 2015. The Effect of Charge at the Surface of Silver Nanoparticles on Antimicrobial Activity against Gram-Positive and Gram-Negative Bacteria: A Preliminary Study. *J. Nanomater.*, **16(1)**: 53.

- Adeel, M., Farooq, T., White, J.C., Hao, Y., He, Z. and Rui, Y. 2021. Carbon-Based Nanomaterials Suppress Tobacco Mosaic Virus (TMV) Infection and Induce Resistance in *Nicotiana benthamiana*. J. Hazard. Mater., 404: 124167.
- Almutairi, Z. M. and Alharbi, A. 2015. Effect of Silver Nanoparticles on Seed Germination of Crop Plants. J. Adv. Agric., 4: 283–288.
- Anjum, N.A., Gill, S.S., Duarte, A.C., Pereira, E. and Ahmad, I. 2013. Silver Nanoparticles in Soil-Plant Systems. J. Nanoparticle Res., 15.
- Badawy, A. M. El, Luxton, T. P., Silva, R. G., Scheckel, K. G., Suidan, M. T. and Tolaymat, T. M. 2010. Impact of Environmental Conditions (pH, Ionic Strength, and Electrolyte Type) on the Surface Charge and Aggregation of Silver Nanoparticles Suspensions. *Environ. Sci. Technol.*, 44: 1260–1266.
- Beer, C., Foldbjerg, R., Hayashi, Y., Sutherland, D. S. and Autrup, H. 2012. Toxicity of Silver Nanoparticles— Nanoparticle or Silver Ion? *Toxicol. Lett.*, 208: 286–292.
- Belal, E. and El-Ramady, H. 2017 OR 2016?? Also corret its into body of text. Nanoparticles in Water, Soils and Agriculture. Chapter 10. In: "Sustainable Agriculture Reviews: Nanoscience in Food and Agriculture 2", (Eds): Ranjan, S., Dasgupta, N. and Lichtfouse, E. Springer International Publishing, Cham, Switzerland, Volume 21.
- Corral-Diaz, B., Peralta-Videa, J. R., Alvarez-Parrilla, E., Rodrigo-García, J., Morales, M. I., Osuna-Avila, P., Niu, G., Hernandez-Viezcas, J. A. and Gardea-Torresdey, J.L. 2014. Cerium Oxide Nanoparticles Alter the Antioxidant Capacity but Do Not Impact Tuber Ionome in *Raphanus sativus* (L). *Plant Physiol. Biochem.*, 84: 277–285.
- 9. Cvjetko, P., Milošić, A., Domijan, A. M., Vinković Vrček, I., Tolić, S., Peharec

Štefanić, P., Letofsky-Papst, I., Tkalec, M. and Balen, B. 2017a. Toxicity of Silver Ions and Differently Coated Silver Nanoparticles in *Allium cepa* Roots. *Ecotoxicol. Environ. Saf.*, **137:** 18–28.

- Dimkpa, C. O., and Anderson, A. J. 2013. Supporting Information Silver Nanoparticles Disrupt Wheat (*Triticum aestivum* L.) Growth in a Sand Matrix. 4.
- El Hadri, H., Louie, S. M., Hackley, V. A. 2018. Assessing the Interactions of Metal Nanoparticles in Soil and Sediment Matrices: A Quantitative Analytical Multi-Technique Approach. *Environ. Sci. Nano*, 5: 203–214.
- Galazzi, R. M. and Arruda, M. A. Z. 2018. Evaluation of Changes in the Macro and Micronutrients Homeostasis of Transgenic and Non-Transgenic Soybean Plants after Cultivation with Silver Nanoparticles through Ionomic Approaches. J. Trace Elem. Med. Biol., 48: 181–187.
- Geisler-Lee, J., Wang, Q., Yao, Y., Zhang, W., Geisler, M., Li, K., Huang, Y., Chen, Y., Kolmakov, A. and Ma, X. 2013. Phytotoxicity, Accumulation and Transport of Silver Nanoparticles by *Arabidopsis thaliana*. *Nanotoxicology*, **7**: 323–337.
- Gui, X., Rui, M., Song, Y., Yuhui, M., Rui, Y., Zhang, P., He, X., Li, Y., Zhang, Z. and Liu, L. 2017. Phytotoxicity of CeO2 Nanoparticles on Radish Plant (*Raphanus* sativus). Environ. Sci. Pollut. Res., 24: 13775–13781.
- Gupta, N., Yadav, K. K., Kumar, V., Kumar, S., Chadd, R. P., and Kumar, A. 2019. Trace Elements in Soil-vegetables Interface: Translocation, Bioaccumulation, Toxicity and Amelioration - A Review. *Sci. Total Environ.*, 651: 2927–2942.
- Harris, A. T. and Bali, R. 2008. On the Formation and Extent of Uptake of Silver Nanoparticles by Live Plants. J. Nanoparticle Res., 10: 691–695.
- He, J., Wang, D. and Zhou, D. 2019. Transport and Retention of Silver Nanoparticles in Soil: Effects of Input Concentration, Particle Size and Surface Coating. Sci. Total Environ., 648: 102–108.
- Inshakova, E. and Inshakov, O. 2017. World Market for Nanomaterials: Structure

and Trends. *MATEC Web Conf.*, **129:** 02013.

- Jiang, H., Li, M., Chang, F., Li, W. and Yin, L. 2012. Physiological Analysis of Silver Nanoparticles and AgNO3 Toxicity to *Spirodela polyrhiza*. *Environ. Toxicol. Chem.*, **31**: 1880–1886.
- Jiang, H. S., Yin, L., Ren, N. N., Xian, L., Zhao, S., Li, W. and Gontero, B. 2017. The Effect of Chronic Silver Nanoparticles on Aquatic System in Microcosms. *Environ. Pollut.*, **223**: 395–402.
- Kaveh, R., Li, Y. -S., Ranjbar, S., Tehrani, R., Brueck, C. L. and Van Aken, B. 2013. Changes in *Arabidopsis thaliana* Gene Expression in Response to Silver Nanoparticles and Silver Ions. *Environ. Sci. Technol.*, 47: 10637–10644.
- 22. Nair, P. M. G. and Chung, I. M. 2014. Cell Cycle and Mismatch Repair Genes as Potential Biomarkers in *Arabidopsis thaliana* Seedlings Exposed to Silver Nanoparticles. *Bull. Environ. Contam. Toxicol.*, **92:** 719–725.
- Navarro, E., Piccapietra, F., Wagner, B., Marconi, F., Kaegi, R., Odzak, N., Sigg, L. and Behra, R. 2008. Toxicity of Silver Nanoparticles to *Chlamydomonas reinhardtii. Environ. Sci. Technol.*, **42**: 8959–8964.
- Noori, A., Donnelly, T., Colbert, J., Cai, W., Newman, L. A. and White, J. C. 2019. Exposure of Tomato (*Lycopersicon esculentum*) to Silver Nanoparticles and Silver Nitrate : Physiological and Molecular Response. Int. J. Phytoremediation, 22(1): 40-51.
- Petrović, N., Buđelan, D., Cokić, S. and Nešić, B., 2001. The Determination of the Content of Gold and Silver in Geological Samples. J. Serbian Chem. Soc., 66: 45–52.
- Qian, H., Peng, X., Han, X., Ren, J., Sun, L. and Fu, Z. 2013. Comparison of the Toxicity of Silver Nanoparticles and Silver Ions on the Growth of Terrestrial Plant Model Arabidopsis thaliana. J. Environ. Sci. (China), 25: 1947–1956.
- 27. Quah, B., Musante, C., White, J. C. and Ma, X. 2015. Phytotoxicity, Uptake, and Accumulation of Silver with Different

Particle Sizes and Chemical Forms. J. *Nanoparticle Res.*, **17.**

- Rajput, V. D., Minkina, T., Fedorenko, A., Tsitsuashvili, V., Mandzhieva, S., Sushkova, S. and Azarov, A. 2018. Metal Oxide Nanoparticles: Applications and Effects on Soil Ecosystem. In: "Soil Contamination: Sources, assessment and Remediation". Nova Science Publishers, Hauppauge, PP. 81-106.
- 29. Reinhart, D. R., Berge, N. D., Santra, S. and Bolyard, S. C. 2010. Emerging Contaminants: Nanomaterial Fate in Landfills. *J. Waste Manag.*, **30(11):** 2020-2021.
- Saha, N., and Dutta Gupta, S. 2017. Low-Dose Toxicity of Biogenic Silver Nanoparticles Fabricated by *Swertia chirata* on Root Tips and Flower Buds of *Allium cepa. J. Hazard. Mater.*, 330: 18– 28.
- Shams, G., Ranjbar, M. and Amiri, A. 2013. Effect of Silver Nanoparticles on Concentration of Silver Heavy Element and Growth Indexes in Cucumber (*Cucumis sativus* L. Negeen). J. Nanoparticle Res., 15: 1630.
- Šinko, G., Vrček, I.V., Goessler, W., Leitinger, G., Dijanošić, A. and Miljanić, S. 2014. Alteration of Cholinesterase Activity as Possible Mechanism of Silver Nanoparticle Toxicity. *Environ. Sci. Pollut. Res.*, 21: 1391–1400.
- Soria, N.G.C., Montes, A., Bisson, M. A., Atilla-Gokcumen, G. E. and Aga, D. S. 2017. Mass Spectrometry-Based Metabolomics to Assess Uptake of Silver Nanoparticles by Arabidopsis thaliana. Environ. Sci. Nano, 4: 1944–1953.
- Sosan, A., Svistunenko, D., Straltsova, D., Tsiurkina, K., Smolich, I., Lawson, T., Subramaniam, S., Golovko, V., Anderson, D., Sokolik, A., Colbeck, I. and Demidchik, V. 2016. Engineered Silver Nanoparticles Are Sensed at the Plasma Membrane and Dramatically Modify the Physiology of *Arabidopsis thaliana* Plants. *Plant J.*, 85: 245–257.
- Tkalec, M., Peharec Štefanić, P. and Balen,
 B. 2019. Phytotoxicity of Silver

Nanoparticles and Defence Mechanisms. *Compr. Anal. Chem.*, **84:** 145-198.

- 36. Torrent, L., Iglesias, M., Marguí, E., Hidalgo, M., Verdaguer, D., Llorens, L., Kodre, A., Kavčič, A. and Vogel-Mikuš, K. 2020. Uptake, Translocation and Ligand of Silver in *Lactuca sativa* Exposed to Silver Nanoparticles of Different Size, Coatings and Concentration. *J. Hazard. Mater.*, 384: 121201.
- Torrent, L., Marguí, E., Queralt, I., Hidalgo, M. and Iglesias, M. 2019. Interaction of Silver Nanoparticles with Mediterranean Agricultural Soils: Lab-Controlled Adsorption and Desorption Studies. J. Environ. Sci. (China), 83: 205– 216.
- Tripathi, A., Liu, S., Singh, P. K., Kumar, N., Pandey, A.C., Tripathi, D. K., Chauhan, D. K. and Sahi, S. 2017. Differential Phytotoxic Responses of Silver Nitrate (AgNO3) and Silver Nanoparticle (AgNps) in *Cucumis sativus* L. *Plant Gene*, **11**: 255– 264.
- Tripathi, D. K., Singh, S., Singh, Sh., Srivastava, P. K., Singh, V. P., Singh, S., Prasad, S. M., Singh, P. K., Dubey, N. K., Pandey, A. C. and Chauhan, D. K. 2017. Nitric Oxide Alleviates Silver Nanoparticles (AgNps)-Induced Phytotoxicity in *Pisum sativum* Seedlings. *Plant Physiol. Biochem.*, **110**: 167–177.
- 40. Tripathi, D. K., Tripathi, A., Singh, Sh, Singh, Y., Vishwakarma, K., Yadav, G., Sharma, S., Singh, V. K., Mishra, R. K., Upadhyay, R. G., Dubey, N. K., Lee, Y. and Chauhan, D. K., 2017. Uptake, Accumulation and Toxicity of Silver Nanoparticle in Autotrophic Plants, and Heterotrophic Microbes: A Concentric Review. Front. Microbiol., 8(7): 1-16.
- Vannini, C., Domingo, G., Onelli, E., De Mattia, F., Bruni, I., Marsoni, M. and Bracale, M., 2014. Phytotoxic and Genotoxic Effects of Silver Nanoparticles Exposure on Germinating Wheat Seedlings. *J. Plant Physiol.*, **171**: 1142–1148.
- Vinković, T., Novák, O., Strnad, M., Goessler, W., Jurašin, D. D., Parađiković, N. and Vrček, I. V. 2017. Cytokinin Response in Pepper Plants (*Capsicum*)

annuum L.) Exposed to Silver Nanoparticles. *Environ. Res.*, **156**: 10–18. https://doi.org/10.1016/j.envres.2017.03.01

- 43. Vishwakarma, K., Shweta, Upadhyay, N., Singh, J., Liu, S., Singh, V. P., Prasad, S. M., Chauhan, D. K., Tripathi, D. K. and Sharma, S., 2017. Differential Phytotoxic Impact of Plant Mediated Silver Nanoparticles (AgNPs) and Silver Nitrate (AgNO3) on *Brassica* sp. *Front. Plant Sci.*, 8: 1–12.
- 44. Vittori Antisari, L., Carbone, S., Gatti, A., Vianello, G. and Nannipieri, P. 2015. Uptake and Translocation of Metals and Nutrients in Tomato Grown in Soil Polluted with Metal Oxide (CeO 2, Fe 3 O 4, SnO 2, TiO 2) or Metallic (Ag, Co, Ni) Engineered Nanoparticles. *Environ. Sci. Pollut. Res.*, 22: 1841–1853.
- 45. Wang, J., Yang, Y., Zhu, H., Braam, J., Schnoor, J. L. and Alvarez, P. J. J. 2014. Uptake, Translocation, and Transformation of Quantum Dots with Cationic versus Anionic Coatings by *Populus deltoides*×Nigra Cuttings. *Environ. Sci. Technol.*, 48: 6754–6762.
- Wang, P., Lombi, E., Sun, S., Scheckel, K. G., Malysheva, A., McKenna, B. A., Menzies, N. W., Zhao, F. J. and Kopittke, P. M. 2017. Characterizing the Uptake, Accumulation and Toxicity of Silver Sulfide Nanoparticles in Plants. *Environ. Sci. Nano*, 4: 448–460.

- Yadav, H. M., Otari, S. V, Koli, V. B., Mali, S. S., Hong, C. K., Pawar, S. H. and Delekar, S. D. 2014. Preparation and Characterization of Copper-Doped Anatase TiO2 Nanoparticles with Visible Light Photocatalytic Antibacterial Activity. J. Photochem. Photobiol. A Chem., 280: 32– 38.
- Yang, Y., Wang, J., Xiu, Z. and Alvarez, P. J. J. 2013. Impacts of Silver Nanoparticles on Cellular and Transcriptional Activity of Nitrogen-Cycling Bacteria. *Environ. Toxicol. Chem.*, **32**: 1488–1494. https://doi.org/10.1002/etc.2230
- Yasur, J. and Rani, P. U. 2013. Environmental Effects of Nanosilver: Impact on Castor Seed Germination, Seedling Growth, and Plant Physiology. *Environ. Sci. Pollut. Res.*, 20: 8636–8648.
- Zhang, W., Musante, C., White, J. C., Schwab, P., Wang, Q., Ebbs, S. D. and Ma, X. 2017. Bioavailability of Cerium Oxide Nanoparticles to *Raphanus sativus* L. in Two Soils. *Plant Physiol. Biochem.*, **110**: 185–193.
- 51. Zhu, Z. -J., Wang, H., Yan, B., Zheng, H., Jiang, Y., Miranda, O. R., Rotello, V. M., Xing, B. and Vachet, R. W. 2012. Effect of Surface Charge on the Uptake and Distribution of Gold Nanoparticles in Four Plant Species. *Environ. Sci. Technol.*, 46: 12391–12398.

اثرات عوامل پوشش سطح نانوذرات نقره بر تجمع آنها و رشد گیاه تربچه

۱. بازوبندی، ۱. فتوت، ۱. حلاج نیا، و ۱. فلیپ

چکیدہ

استفاده گسترده از نانوذرات نقره در صنایع مختلف باعث بروز نگرانی های بسیاری در مورد سرنوشت این مواد شده است. از این رو مطالعه حاضر با هدف بررسی اثرات پوشش های سطح نانوذرات نقره در خاک و چگونگی برهمکنش آنها با گیاهان به عنوان اولین مرحله از زنجیره غذایی انسان انجام شد. گیاه تربچه(Raphanus sativus) در معرض نیترات نقره و نانوذرات نقره با سه نوع پوشش سیترات، پلی اتیلن ایمین و پلی وینیل پیرولیدون در غلظت های مختلف قرار گرفت. اثر غلظت (۵، ۲۵ و ۱۲۵ میلی گرم بر کیلوگرم خاک) و نوع پوشش سطح بر وزن خشک با مقدار کنترل مقایسه شد. نتایج نشان داد که نوع تیمار بر وزن خشک اثر معنی داری نشان داده و در بین تیمار ها نیترات نقره با ۵۱ درصد کاهش بیشترین کاهش وزن خشک برگ را نشان داد. مقدار کل نقره در ریشه، غده و برگ تربچه نشان داد که تجمع نانوذرات نقره تحت تاثیر پوشش و غلظت است. نانوذرات با بار مثبت (پلی اتیلن ایمین) بیشترین میزان انتقال را نسبت به تیمارهای دیگر نشان داد. در نهایت یافته های مطالعه حاضر نشان داد که تربچه توانایی ذخیره نقره در ریشه، غده و برگ ها در مقدار بالا را دارد بنابراین این گیاه پتانسیل دارد تا به عنوان یک منبع آلودگی نقره برای انسان تلقی شود.

JAST