



Swedish University of Agricultural Sciences
Department of Soil and Environment

Evaluating solubility, aggregation and sorption of nanosilver particles and silver ions in soils

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Abstract

Engineered nanoparticles (ENPs) are used in so many different products. ENPs are released into different environmental compartments. Silver nanoparticle (AgNP) is one of the most used ENPs. AgNPs may cause damage to the environment due to their toxicity and wide exposure. In this thesis possible exposure ways of AgNPs to the environment was reported. Also sorption-solubility and aggregation of AgNPs and AgNO₃ based on the different concentration of Ag and pH function in clayey and sandy soil was investigated.

Results showed that sorption of both silver nanoparticles and silver ions by the soils were increased with increasing pH. Silver (nano/ion) sorption ratio in clayey treatment was slightly higher than sandy one. It can be due to having higher CEC value and finer texture in clay in comparison with sand. Partitioning between nanosilver and free silver ions was investigated by help of ultrafiltration. It can be concluded that a significant fraction of the silver nanoparticles were oxidized and transformed to free Ag⁺ during the oxic experimental conditions.

The aggregation of AgNPs and silver ions was investigated based on the different concentration of silver in a constant pH. Aggregation of silver nanoparticulate by help of SEM and XRD were identified in 2.5 ppm concentration of AgNPs in sandy soil. No aggregation was found at low concentration of silver nanoparticles. No silver aggregated spot could be recognized at 6.7, 0.65 and 0.05 ppm concentration of silver in silver nitrate polluted soil samples.

Keywords: silver nitrate, silver nanoparticle (AgNP), soil, sorption, solubility, aggregation.

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Introduction

Nanomaterials

Nanotechnology is the study of materials in nanometer scale which is approximately between 1 to 100 nm [1]. It also involves how to control the formation of two and three dimensional building blocks of molecular scale into well-defined nanostructure or nanomaterials (NMs) [2]. Nanoparticles (NPs) exist in the environment from both natural and anthropogenic sources. Natural NPs in air are known as ultrafine particles and in the soil and water systems are also called colloidal particles [3]. The term ‘colloid’ refers to the particle sizes or other suspended material in the 1nm-1µm size range. Figure 1, illustrates the most common components of natural colloids along with their possible methods for separation and analysis. Generally in practical work and laboratory, they can be studied by using cross-flow ultrafiltration with nominal pore sizes between 1 nm and 0.2 to 0.45 µm [3]. In general NMs can be categorized in different groups such as:

- Carbon based material such as Carbon nanotube (CNT) and Fullerenes
- Metal oxides: Zinc oxide (ZnO), Iron Oxide (Fe₂O₃), Titanium Dioxide (TiO₂) NPs, etc
- Metals: Silver (Ag), Gold (Au) and Iron (Fe) NPs, etc

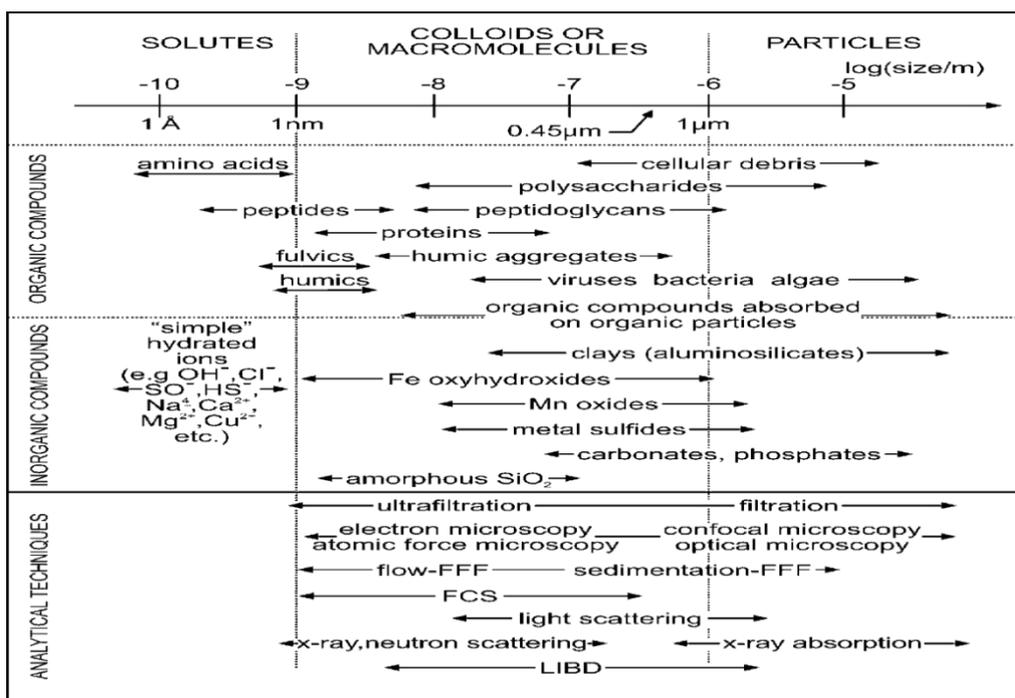


Figure 1. Size distributions of various types of environmental colloids and particles and analytical techniques used for characterization. FFF=field-flow fractionation, FCS=fluorescence correlation spectroscopy, LIBD=laser induced breakdown detection. (Picture is derived from ‘Nanomaterials in the environment: behavior, fate, bioavailability and effects’) [3].

To study the morphology of NPs is interesting due to their unique shapes. Different shapes of material mean different activity potential (surface energy). NMs can be formed in different shapes such as: spheres, tubes, rods and prisms.

Engineered nanoparticles (ENPs) can also be classified according to their chemical compositions and properties. NMs are synthesized by two different ways:

- Top down strategy
- Bottom up strategy

In top down strategy, well-organized assemblies directly originate from the bulk materials via generating isolated atoms by using various distribution techniques. The majority of these methods are physical but in the other type of methods; bottom up strategy, a molecular component is used as a starting material which is linked with chemical reactions to form of more complex clusters [4, 17].

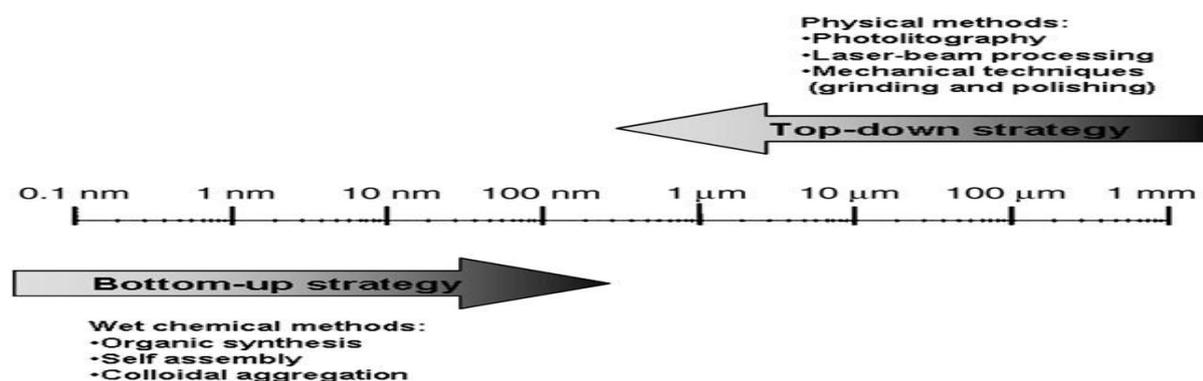


Figure 2. Top down and bottom up strategy. (Picture is taken from the article ‘Manufacture nanoparticles: An overview of their chemistry, interactions and potential environmental implications’) [4].

Having a high surface to volume ratio is a property of ENPs which makes it important for environmental scientists to study the fate and behavior of NPs in the environment [12, 16]. This property can cause different behavior of NPs in chemical reaction in comparison with their bulk materials. Having a high surface area per unit mass gives a specific characteristic to the surface of NPs that makes them have a significant potent energy for reaction with other particles.

ENMs are applied in many commercially available consumer products such as cosmetics, textiles and paints. ENMs can reach the environment in different ways. Recent studies showed release of nano-TiO₂ from the outer layer of exterior facades through water leaching [9]. Releasing of AgNPs from antibacterial socks to the waste water and sewage sludge during washing process is also reported [10]. In some countries treated sewage sludge is used as a soil amendment in order to increase the soil fertility. In case sewage sludges contain toxic nanoparticles, they will cause toxicity to the soil bacteria. Toxic nanomaterials in biosolids and landfills can cause toxicity for the environment. In order to know how to control this negative effect, studying physico-chemical property of NPs like aggregation, solubility-sorption and dispersion of NPs is crucial [8]. In ecotoxicological study, bioavailability, bioaccumulation and aggregation of NPs are key issues to study [18].

Release of silver nanoparticles into the environment

ENMs may reach to environment during production of material or during incorporation of NMs into products [5]. Mueller and Nowack (2008) reported that the current concentration of nano-TiO₂ is toxic to the aquatic organisms in lakes whereas the current concentration of nanosilver and carbon nanotube still seems to be non hazardous but it is approaching the toxic level [6]. They designed a model to assess the exposure of chemicals to the environment in the absence of sufficiently detailed data. The model covers the flows of the NPs from products to environmental compartments e.g. soil, air, water, sediment and groundwater and also to the technical compartments such as; sewage treatment plant (STP), waste incineration plant (WIP), landfills and recycling sites. The unit of the calculated flows is ton/year and the modeled is stimulated based on the available data for Switzerland (Figure 3) [6].

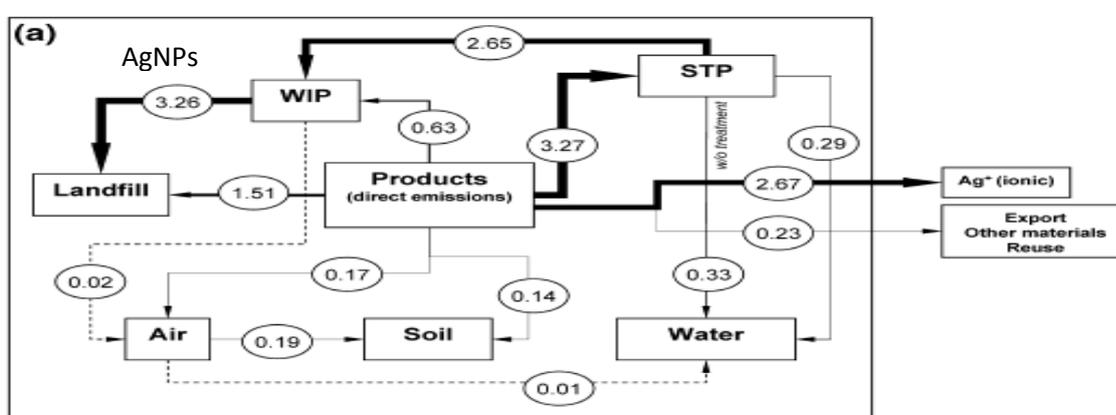


Figure 3. Pathways for nano-Ag from products to the different environmental compartments, Waste Incineration Plant (WIP), Sewage Treatment Plant (STP) and landfill are simulated by the model. Unit of the flows is ton/year and the thickness of the arrows is proportional to the amount of silver flowing between the compartments and dashed arrows represent the very small flows [6].

Based on the existing information and outputs from the model it is concluded that the most dominant flows for silver nanoparticle are from production, manufacturing and consumption to the sewage treatment plant and landfill [6].

Silver can be highly toxic to some aquatic organisms [20]. Silver has antibiotic property which can damage the useful microbial communities in environment [8, 21]. Silver, even in low concentration like 10 ng/l is toxic to zebra fish [22]. In some cases silver is reported to bioaccumulate in phytoplankton and some marine invertebrates [23, 24]. Silver ions have an inhibitory effect on bacterial growth. Ag⁺ tends to have a high sorption to the negatively charged bacterial cell wall. Ag⁺ also leads the bacterial death due to generation of reactive oxygen species and disruption of membrane permeability [25, 26]. Ecotoxicological study in soil media shows that silver nanoparticles are highly toxic to soil nematodes [27]. Silver nanoparticles with less than 5 nm diameter significantly inhibit the activity of nitrification bacteria [12]. Toxicity of silver nanoparticles to nitrification bacteria is highly dependent on the size of the silver nanoparticles [12]. According to [7], concentration of different nanoparticles in sediments and sludge treated soils is increasing (figure 4).

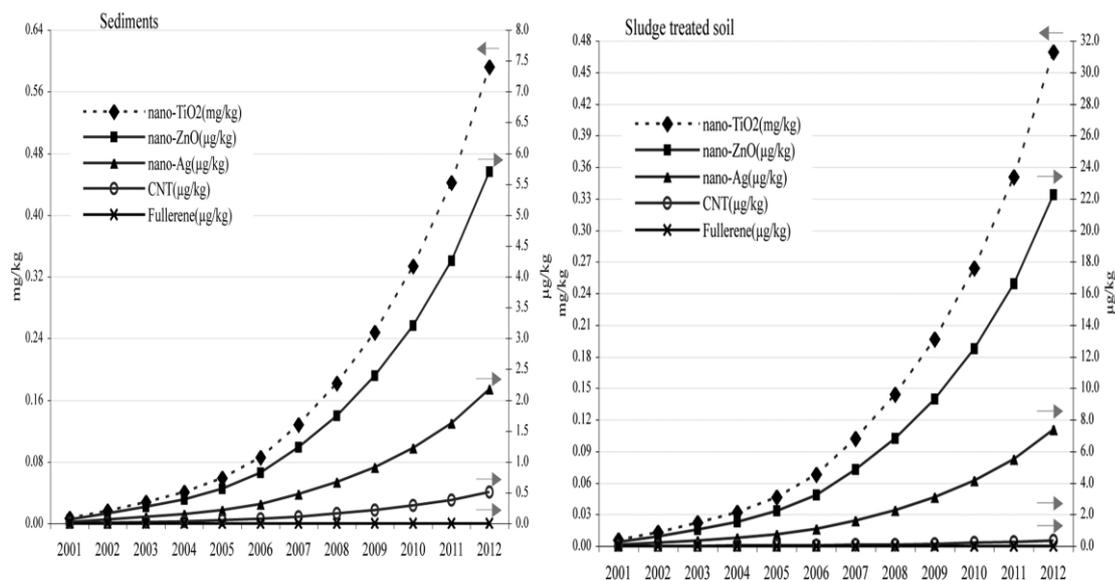


Figure 4. Predicted concentrations of nanomaterials, nano-TiO₂, nano-ZnO, nano-Ag, CNTs and fullerene in sediment and sludge treated soil in U.S during the period 2001-2012 [7].

Factors affecting detachment of nanoparticles from commercial products

There are some factors which affect detachment of NPs from articles. These factors are such as; NPs store in the object, the object's life time, the method with which NPs are built into the fabric and the real usage of the object [5]. Articles with an extended life time, weak incorporation and extreme use will most likely not contain NP anymore at the time of disposal. On the other hand, factors such as short lifetime, low usage and well built fixation increase the likelihood that particles will not be released before disposal [13]. Exposing articles with UV-light increases the chance of releasing NPs from the objective [14]. For example, for silver nanoparticles, one of the most possible ways of releasing Ag⁺ from textile and plastics is detachment of AgNPs in the form of silver ions [15].

Possible fate of silver and silver nanoparticle in soils

Soils are complex systems. Soil solution might contain various concentrations of organic and inorganic ligands. Major compartments involving in metal sorption are soil organic matter (SOM), oxide surfaces (Fe, Al, Mn...) and clay minerals [28, 29]. High pH value and CEC enhance silver sorption to the soil due to higher negatively charged sites and more cation exchange reactions, respectively. Soils with fine texture have higher surface areas which also ease silver sorption [28].

Silver is sorbed more strongly to soils with high organic matter concentration than to mineral soils. Silver can be sorbed to the soil either due to cation exchanges or complexation reactions [28]. Soil organic matters play an important role in silver sorption and mobility [29]. Silver strongly tends to bind with reduced sulfur groups (thiol) on soil organic matter and form S-Ag-S bonds [30]. Regarding the silver nanoparticle in soil systems, there are not many published papers which discuss the fate of AgNPs in soils media. But there are some

investigations which show the effect of different environmental factors like ionic strength, pH, temperature, oxygen availability, time, organic matter on stability, aggregation, mobility and silver ion release kinetics of AgNPs in aquatic medias [19, 31, 32, 33]. Recently effect of fulvic acid on the aggregation of AgNPs in the aquatic systems was investigated and the results surprisingly show that addition of 10 mg/l of fulvic acid had no significant affect on the aggregation kinetic of AgNPs [34].

Objective

The objective of this thesis is to study the solubility of silver nanoparticles and silver ions in two soil types as a function of pH and metal concentration added. Observation and identification of nanosilver aggregated spots in polluted samples were made by help of Scanning Electron Microscopy (SEM) and X-ray Energy Dispersion Spectrometry (XRD).

Materials and Methods

Nanosilver

Commercial silver nanoparticles (<100 nm, 99.5 % metal) were obtained from Sigma-Aldrich Company. X-ray energy dispersion spectrometry and Scanning Electron Microscopy (SEM) were used to characterize the silver nanoparticles. SEM and X-ray energy dispersion spectrometry analysis have been performed in chemistry department of Swedish University of Agricultural Science (SLU) with SEM-Hitachi TEM-1000 and Bruker X-ray diffraction analyzer.

Soil Samples

Two different soil types were used in the study; one clayey and one sandy soil were sampled from Ultuna and Nantuna regions respectively in Uppsala. The texture of the soils was analyzed by pipette and wet sieving using standard methods according to the procedure by Ljung (1987). Water content on mass basis was measured according to international standard ISO-11465. Carbon and Nitrogen content of soil samples based on the mass weight were measured with LECO, CNS-1000 Elemental Analyzer. Exchangeable cations were determined by 0.1 M BaCl₂ extraction.

Batch Experiment

Pilot acid-base titration experiment

In order to investigate the buffering capacities of the soils, batch experiment with different additions of HNO₃ or Ca(OH)₂ were made. 50 ml centrifuge tubes were used. 3 g of air dried soil was added to 12 centrifuge tubes (6 tubes for sand treatment and 6 tubes for clay one), plus various amounts of 0.1 M nitric acid (HNO₃) or 0.1 M calcium hydroxide (Ca(OH)₂) and

0.1 M calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) and deionized water, see Table A1 in Appendix. Prepared samples were shaken for two days in end-over-end shaker in room temperature 20 °C. After shaking, the samples were centrifuged for 15 minutes at 3000 rpm in Sorvall RC 3C plus centrifuge machine. pH was measured in 5 ml of supernatant.

Acid-base titration experiment with Ag^+ and AgNPs

The pilot titration experiment resulted in a pH range in clayey soil between 4 and 7. For the sandy soil pH varied from 3 to 6, see Table A1, Appendix. Sorption experiment with Ag^+ and AgNPs was designed based on the pilot acid-base titration to achieve the desired pH values.

Stock solution with 1.35 ppm concentration of AgNPs/ AgNO_3 in deionized water was prepared in 1 liter glass bottles. Stock solution of silver nanoparticle was ultrasonicated for 10 minutes to get the homogenous suspension and delay the immediate aggregation of nanoparticles. Immediately after ultrasonication, 15 ml of 1.35 ppm concentration of AgNPs and AgNO_3 stock solution were added to centrifuge tubes. See sample preparation schemes in Table A2, Appendix.

After shaking and centrifuging (same instruction as for titration experiment above), pH was measured on 5 ml of unfiltered supernatants. An aliquot of the supernatants were filtered with 0.45 μm membrane filtration. Supernatants were diluted 1000 times with 1% nitric acid in order to make the solution ready to measure silver concentration with ICP-MS (Inductively Coupled Plasma Mass Spectrometry, Leam 6100 ICP-MS Simplifying Ultra trace Analysis machine). In addition dissolved organic carbon (DOC) was measured on a small proportion of filtered (0.45 μm) supernatant with TOC 5000A Total Organic Carbon Analyzer, Shimadzu machine. Batch experiments were designed in two replicates of all treatments.

Aggregation

In order to study the aggregation of AgNPs and Ag^+ , sets of batch experiments based on the titration experiment on sandy soil with fixed pH (4.9) and different concentration of silver (nano/ion) was designed. See Table A1, Appendix, set 2, centrifuge tube number 11. 28.5 ml stock solutions of silver nanoparticle with 2.5, 0.75 and 0.01 ppm concentrations and silver nitrate with 6.7, 0.63 and 0.05 ppm concentrations were added to the centrifuge tubes separately. The samples in centrifuge tubes were shaken for two days in end over end shaker in room temperature 21 °C. The samples were centrifuged for 15 minutes with 3000 rpm in Sorvall RC 3C plus centrifuge machine. Portion of supernatants were separated and sent for silver analysis. Sedimented soils containing silver nanoparticle/silver nitrate were extracted. Thin layers of extracted soil samples were rubbed into impermeable papers. The samples were dried for one day in a fume cupboard. Dried soil samples were prepared for SEM and X-ray energy dispersion investigation to find silver aggregated spots. The design of the aggregation experiment was to study the effect of different concentrations of silver metals (nano/ion) at a constant pH.

Silver size distributions in solution

Batch experiment was set with pH adjusted to 4 and initial constant concentration of 1.35 ppm silver ion and silver nanoparticle separately. See Table A2, Appendix tube No.1 (1CN & 1C⁺) and No.10 (10SN & 10S⁺). The batch experiments was prepared with sand and clay

soils with both silver nanoparticle and silver nitrate in two replicates, exactly with similar preparation scheme to batch experiment of sorption-solubility experiment. After the batch experiment, supernatants were filtered through 0.45 μm membrane, aliquot of supernatants were analyzed with ICP-MS to measure the silver concentration before ultrafiltration. 10000 Dalton ultrafilters was spinned with 1% HNO_3 and then rinsed with deionized water. Ultrafilters were used immediately for filtration before letting their membrane dried. 15ml of 0.45 μm membrane filtered supernatants were added to the ultrafilters in an Amicon Ultra-15 Centrifugal Filter Device. The added supernatants in the ultrafiltration centrifuge tubes were centrifuged for 35 minutes with 2000 rpm until most of the solution had passed the filter cap. Silver concentrations were measured on ultrafiltered solutions in both silver nitrate and silver nanoparticle treatments with ICP-MS.

Results and Discussions

Characterization of nanosilver particles

X-ray diffraction spectrometry shows 100% purity of silver in purchased silver nanoparticles. The result of X-ray diffraction spectrometry is shown in figure 5.

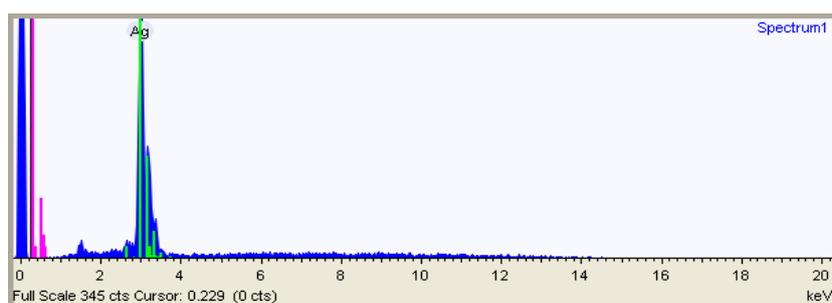


Figure 5. X-Ray energy dispersion spectrometry result of silver nanoparticle.

Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) images of pure silver nanoparticle powder were taken. Figure 6-A and 6-B show that AgNPs have ellipsoidal (sphere) shape.

A)

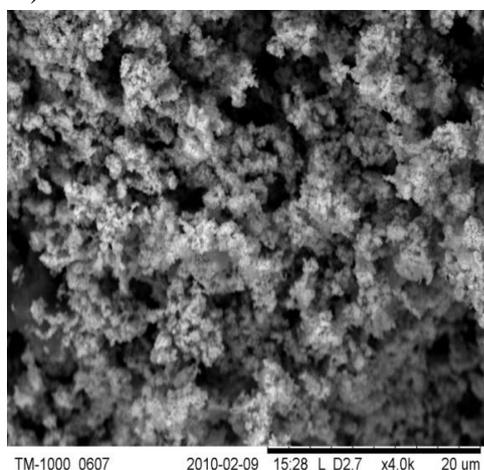
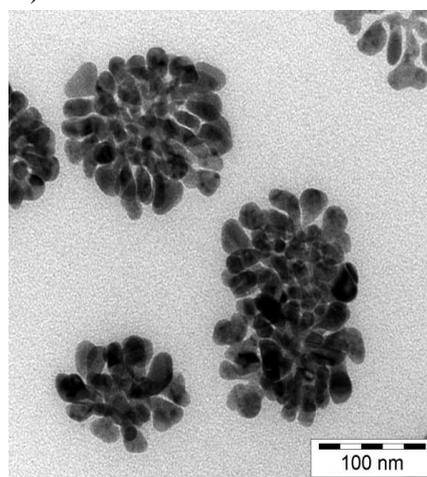


Figure 6. A) SEM image of AgNPs taken at SLU.

B)



B) TEM image of AgNPs (Sigma-Aldrich Co.).

Soil

Results from mechanical analysis of soil samples are shown in Table 1. Based on the mechanical analysis, the soil texture was recognized according to USDA standard method. The clayey Ultuna soil is clay and sandy Nantuna soil is loamy sand. General characteristics of soil samples are shown in Table 2.

Table 1. Mechanical analysis of the experimental soils. Particle size classes are in mm.

	Clay d<0.002	Fine silt 0.002- 0.006	Medium silt 0.006- 0.02	Coarse silt 0.02- 0.06	Fine sand 0.06- 0.2	Medium sand 0.2- 0.6	Coarse sand 0.6- 2	Loss of ignition%
Sand	8	3	1	3	12	57	17	5
Clay	47	12	9	10	17	3	3	5

Table 2. General characteristics of the experimental soils.

	Clay	Sand
pH	6.6	5.3
Water content*, %	1.8	0.9
Carbon content, %	1.5	2.9
Nitrogen content, %	0.16	0.19
Clay, %	47	8
Sand, %	6	74
Silty, %	48	29
Soil texture	Clay	Loamy sand

* Value is based on the mass weight.

The exchangeable cations (Mg, Ca, Al, Na and K) and cations exchange capacity (CEC) in clay and sandy soil samples are shown in (Table 3). The cation exchange capacity is about three times higher in the clay soil compared with the sandy soil sample. This must be due to the higher clay content, since the content of organic matter actually is lower in the clay soil as compared to the sandy soil.

Table3. Exchangeable cations and cations exchange capacity (CEC). CEC calculated as sum of metal cations.

Soil types	Exchangeable Cations (cmolc/kg)					CEC
	Mg	Ca	Al	Na	K	
Sand	0.58	4.43	0.15	0.01	0.08	5.27
Clay	0.85	14.12	0.0	0.02	0.54	15.55

Solubility of AgNPs and Ag⁺ as a function of pH

Solubility of silver nanoparticles and silver ions was highly dependent on the pH. Results showed that at higher pH values, both silver nanoparticles and silver ions tended to be sorbed more strongly by the soil particles in both clay and sandy soils (Tables 4-7, Figure 7).

Table 4. Concentration of AgNPs & DOC in the supernatant at different pH in clay-AgNP sorption.

Acid addition HNO ₃ ml	Base addition Ca(OH) ₂ ml	pH replicate 1	pH replicate 2	DOC conc. ppm replicate 1	DOC conc. ppm replicate 2	Ag conc.ppb replicate 1	Ag conc.ppb replicate 2
3	0	4.2	4.2	12.3	11.3	1.6	1.6
2.4	0	4.7	4.7	8.7	10.6	0.9	0.5
1.8	0	5.2	5.2	7.9	7.1	0.8	0.4
1.2	0	5.8	5.8	5.7	5.9	0.8	0.3
0.6	0	6.4	6.4	4.2	4.7	0.3	0.2
0	0	6.9	6.9	5.5	5.6	0.4	1.6

Table 5. Concentration of AgNO₃ & DOC in the supernatant at different pH in clay-AgNO₃ sorption.

Acid addition HNO ₃ ml	Base addition Ca(OH) ₂ ml	pH replicate 1	pH replicate 2	DOC conc. ppm replicate 1	DOC conc. ppm replicate 2	Ag conc.ppb replicate 1	Ag conc.ppb replicate 2
3	0	4.2	4.2	16.6	13.6	4.6	1.8
2.4	0	4.7	4.7	10.5	10.9	4.6	0.6
1.8	0	5.2	5.2	10.2	10.6	1.9	1.2
1.2	0	5.8	5.8	9.0	9.1	1.0	0.4
0.6	0	6.4	6.4	8.8	**	0.9	0.4
0	0	6.9	6.9	7.3	7.9	0.5	0.6

Table 6. Concentration of AgNPs & DOC in the supernatant at different pH in sand-AgNP sorption.

Acid addition HNO ₃ ml	Base addition Ca(OH) ₂ ml	pH replicate 1	pH replicate 2	DOC conc. ppm replicate 1	DOC conc. ppm replicate 2	Ag conc.ppb replicate 1	Ag conc.ppb replicate 2
1.8	0	3.3	3.2	17.5	17.1	38.2	48.0
1.2	0	3.5	3.4	16.1	14.6	17.7	31.2
0.6	0	4.1	4.0	12.3	12.6	3.5	5.8
0	0	4.9	5.3	9.4	8.5	0.3	0.4
0	0.3	6.9	6.6	10.3	10.4	0.2	0.2
0	0.6	7.4	7.4	15.3	13.9	0.2	0.5

Table 7. Concentration of AgNO₃ & DOC in the supernatant at different pH in sand-AgNO₃ sorption.

Acid addition HNO ₃ ml	Base addition Ca(OH) ₂ ml	pH replicate 1	pH replicate 2	DOC conc. ppm replicate 1	DOC conc. ppm replicate 2	Ag conc.ppb replicate 1	Ag conc.ppb replicate 2
1.8	0	3.2	3.2	18.0	14.8	16.4	17.9
1.2	0	3.5	3.4	16.1	14.4	9.4	12.9
0.6	0	4.0	4.0	13.2	12.3	5.5	6.4
0	0	5.1	5.3	11.3	12.0	0.9	0.5
0	0.3	6.6	6.8	13.6	12.5	0.4	0.5
0	0.6	7.3	7.3	18.5	17.1	0.7	0.9

Furthermore, silver nanoparticles and silver ions behave similarly, showing a similar pH dependency. The solubility of silver ions is slightly higher than silver nanoparticles, but this difference is surprisingly small (Figure 7).

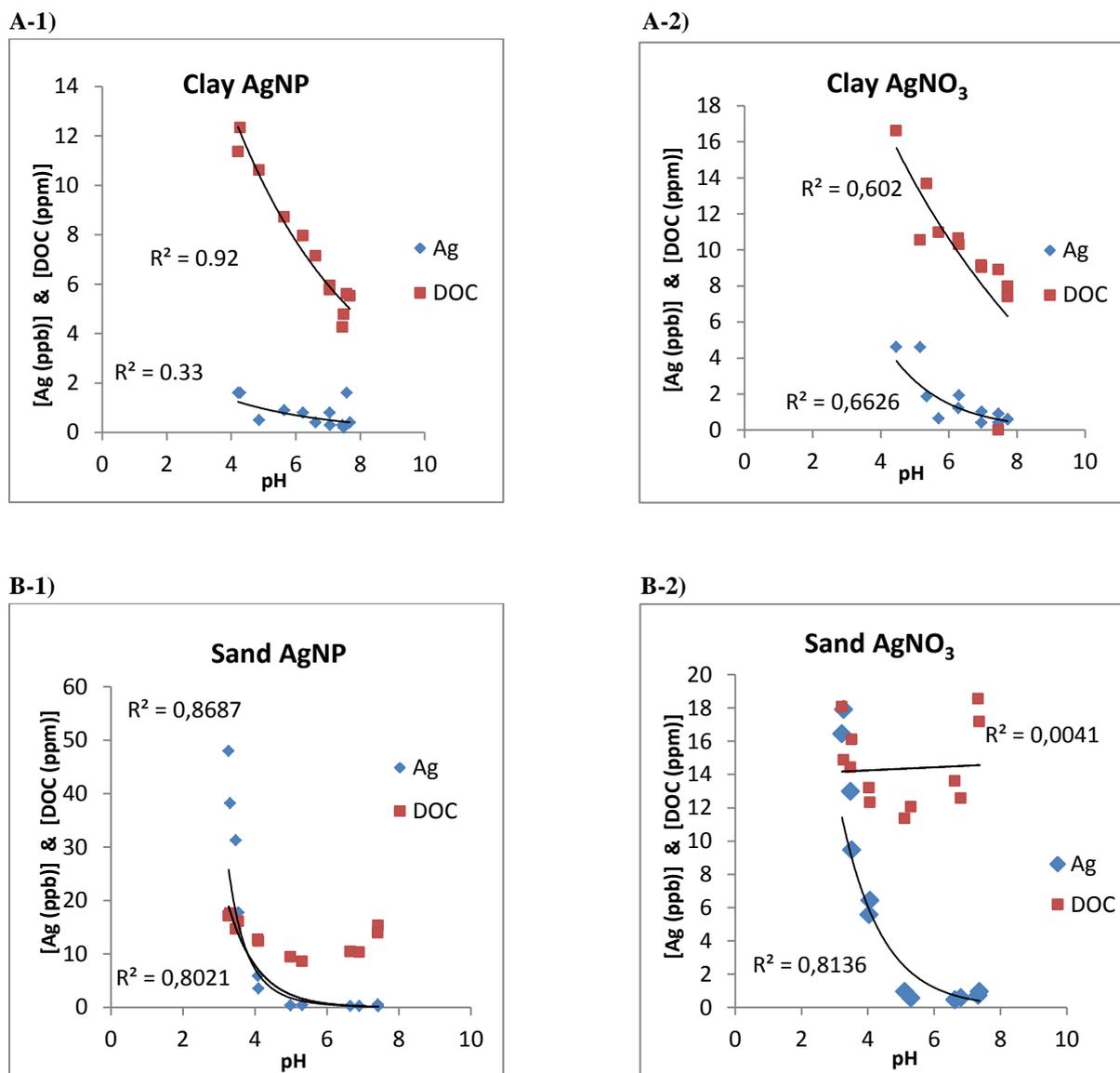


Figure 7. A-1) Solubility of AgNP and DOC vs. pH in clayey soil treatment. A-2) Solubility of AgNO₃ and DOC vs. pH in clayey soil treatment. B-1) Solubility of AgNP and DOC vs. pH in sandy soil treatment. B-2) Solubility of AgNO₃ and DOC vs. pH in sandy soil treatment.

The concentration of Ag in solutions varied from 0 to 5 ppb and from 0 to 60 ppb in clay and sand treatment respectively. The high concentration of silver in the supernatant of sandy treatment could be due to less free surfaces available for metal binding in sandy soil in comparison with clayey soil. This is in accordance with the higher CEC of the clay sample (Table 3). However, a factor also contributing to the higher concentrations of Ag (both Ag⁺ and AgNPs) is the fact that lower pH values were achieved in the sandy soil. Since solubility increases with decreasing pH, this will explain, at least partly, the higher Ag concentrations obtained in the sandy soil.

One possible explanation for the similar behavior of silver nanoparticles and silver ions could be that they both have a net positive charge. Silver nanoparticles have zero charge [Ag(0)] in their metallic form. However, part of the Ag(0) atoms at nanoparticle surfaces might be ionized and oxidized when particles are exposed to aerobic environmental compartments.

This will give a net positive charge of the silver nanoparticles. From Figure 7, it can be assumed that AgNPs have net positive charges in their diffuse layer since they act like silver cations in sorption.

Silver ions might also be strongly bound by soil organic matter [28]. Silver strongly tends to bind with reduced sulfur groups (thiol) on soil organic matter and form S-Ag-S bonds [30]. As shown in Figure 7, Ag concentrations follow DOC concentrations in suspensions of the clay soil but not in the sandy soil. Thus, dissolution of organic matter does not seem to be the major driver for controlling the solubility of Ag ions. Instead it is likely a pH dependent partitioning of Ag ions between the solid and solution phases, which is governing the solubility.

Silver size distribution in the solution

According to the manufacturer Malvern Co, it is assumed that only silver ions (Ag^+) can pass the 10000 Dalton ultrafiltration membranes [11]. Therefore by using ultrafiltration separation, nanosilver particles and silver ions in the solution can be separated according to their size.

According to [19], silver nanoparticles can be oxidized and transformed to free silver ions in the presence of oxygen molecules. If this occurs to a large extent with the particles introduced into the sand and clay soil suspensions, this would be an alternative explanation for the similar behavior of silver nanoparticles and silver ions. One way to investigate if this was the case in my experiment was to apply ultrafiltration on equilibrium solutions.

The size distribution of silver in the solutions of silver ion and silver nanoparticle suspensions, before and after ultrafiltration (10000 D) is shown in Figure 8.

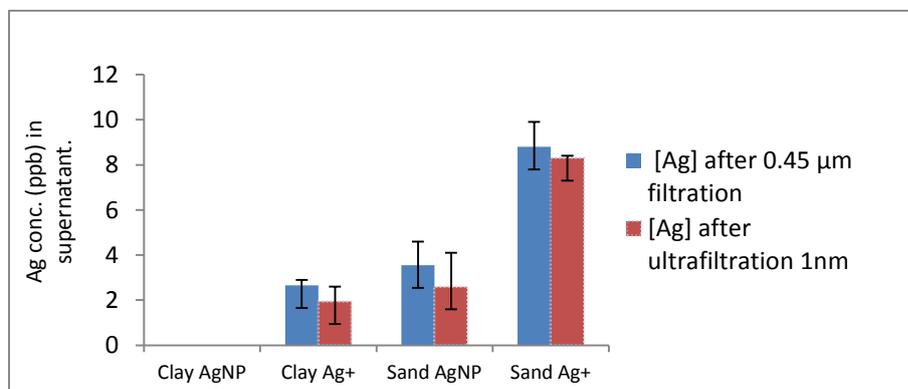
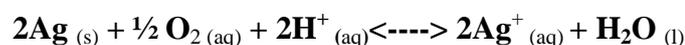


Figure 8. Ag (ion/nano) concentration after and before ultrafiltration. Ag conc. in clay AgNP treatment was below the detection limit. Error bars show the standard error values (n=2).

The concentrations of silver in the ultrafiltered solutions in clay and sand were slightly lower than in the unfiltered (unultrafiltered) solutions (red bars are smaller than the blue bars, see figure 8). It can therefore be concluded that a significant fraction of the added silver nanoparticles were transformed and oxidized to the free silver ions, which could pass the ultrafiltration membrane. In the clay AgNP treatment the silver concentrations before and after the ultrafiltration were below the detection limit and results for this treatment was not plotted.

Silver ion release from silver nanoparticles is an oxidation process which needs both dissolved oxygen and protons [19] (Equation 1). The oxidation of silver nanoparticles is followed by peroxide production. Peroxide is a more powerful oxidant than oxygen and reacts faster than oxygen with AgNPs under ambient conditions [19].

Equation 1:



Silver ions release from silver nanoparticles may vary based on the different abiotic environmental factors. According to [19], Silver ion release from silver nanoparticle will increase with increasing temperature in the range of 0 – 37 °C. Silver ion release is decreasing with increasing pH and addition of humic or fulvic acid will decrease the ion release rate [19]. But these factors were not studied in this thesis. In this thesis kinetics of silver ion release was investigated at constant room temperature 21 °C.

Aggregation of silver nanoparticles in soil

With help of SEM and XRD, polluted sandy soil samples with different concentration of silver ions and silver nanoparticles were inspected carefully. An aggregated spot in treatment with 2.5 ppm concentration of silver nanoparticles treatment was found in sandy soil (Figure 9).

A)

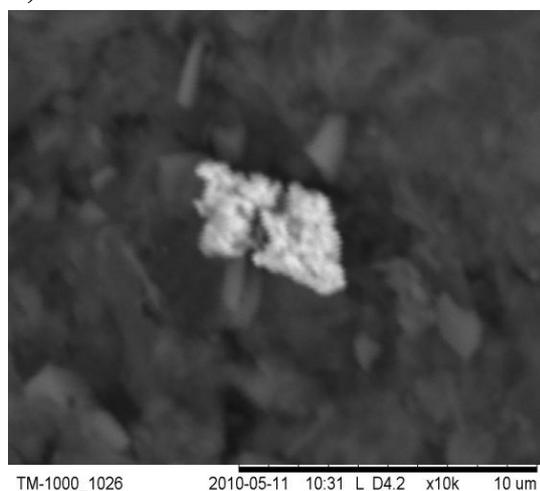
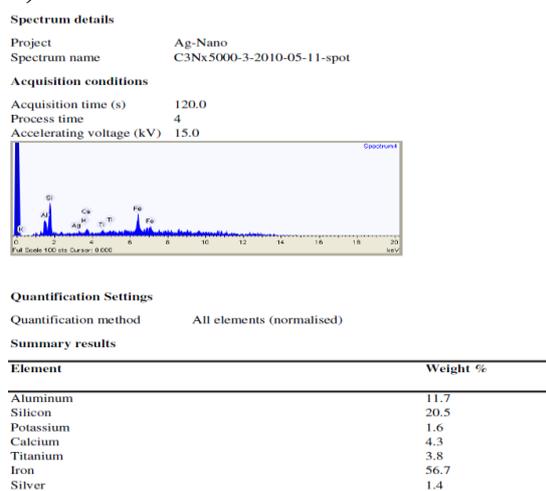


Figure 9. A) Aggregated spot of AgNP found in sand treatment.

B)



B) XRD spectrum showing the existence of Ag in aggregated spot.

No aggregation was found in 0.01 and 0.75 ppm concentrations of silver nanoparticles. In the treatments polluted with silver nitrate no aggregation of silver was found at any concentration. Possible reason for having no aggregation of silver in silver nitrate treatment could be no reduction of Ag⁺ to metallic silver.

Some studies in aquatic mediums show that abiotic factors such as ionic strength, pH, concentration and salinity affect the aggregation of nanoparticles in aquatic systems [18]. NPs tend to highly interact with other molecules to reduce their surface energy. NPs bounded

with capping agents tend to remain stabilized [17]. In aquatic mediums, aggregation of metal nanoparticles can be described by DLVO theory (Derjaguin, Landau, Verwey, Overbeek theory). DLVO theory explains the forces between charge surfaces interaction in liquid mediums. DLVO theory describes the vanderwaals attraction forces and electrostatics repulsion forces in electrical diffuse layer between two particles [18]. Soils are more complex systems than the aquatic mediums; therefore aggregation of metal nanoparticles in soil cannot directly be interpreted by DLVO theory. But since aggregation of silver nanoparticle could only found in the treatment with the highest concentration of metal, it can be concluded that concentration is a driving factor in aggregation of silver nanoparticle in soil media which also can be interpreted by DLVO theory. The aggregation experiment in this thesis was based on the different concentrations of silver metals (nano/ion) and did not investigate the other abiotic factors.

Conclusion

The experiments in this work showed that the solubility-sorption of Ag^+ and AgNP is a function of pH. Ag^+ and AgNP behave similarly in pH dependency. A possible explanation for the similar behavior of Ag^+ and AgNP could be that, they both have the net positive charges. In both silver ion and silver nanoparticle treatment it is shown that the solubility of silver is higher at lower pH. Increasing the pH value, will increase the sorption of Ag. The solubility of Ag^+ is slightly higher than the AgNP but this difference is surprisingly small. By comparing the silver sorption between the sand and clay treatments it can be understood that clayey soil can retain more silver (nano/ion) concentration rather than sandy one. Higher sorption of silver in clay soil can be due to its higher CEC value. DOC doesn't seem to be major factor for controlling the solubility of the Ag ions. Size speciation with ultrafiltration shows that parts of the AgNPs are oxidized to Ag^+ in oxic conditions. This is an alternative explanation of similar behavior of Ag^+ and AgNP. AgNPs appear to have higher aggregation tendency than Ag^+ since the aggregation spot could just be found in the treatments with silver nanoparticles and no aggregation spot could be found in the silver ion treatments.

Future Study

Studies of the current concentration of nanoparticles in different environmental compartments show that in close future the concentration of metal nanoparticles may reach to the toxic level for soil microorganisms in sewage sludge treated soils, landfills and sediments. In order to control the toxicity of NPs to the soil microorganisms, further toxicological studies of NPs is needed. In environmental chemistry, studies of the aggregation, sorption-solubility (dispersion) of NPs in different abiotic conditions is needed. Toxicity of NPs can be ascribed to different shapes, charge, surface area and surface structure, wettability of NPs and also availability of different surfactants in the solution. Also partitioning between nanoparticles and free ions is fundamental in order to examine if the toxicity affect is due to free ions derived from nanoparticles or intact nanoparticles or both. In literature most of the papers

have discussed the fate of NPs in aquatic conditions. There is not that much studies regarding the fate of metal nanoparticles in soil.

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Appendix

Table A1.

Design of pilot acid-base titration experiment on clay and sand.

Clay soil:

Tube no.	0.10 M HNO ₃ ml	H ₂ O (DW) ml	0.10 M Ca(NO ₃) ₂ ml	0.10 M Ca(OH) ₂ ml	pH
1	3	27	0	0	4.2
2	2.4	27.3	0.3	0	4.7
3	1.8	27.6	0.6	0	5.2
4	1.2	27.9	0.9	0	5.8
5	0.6	28.2	1.2	0	6.4
6	0	28.5	1.5	0	6.9

Sand soil:

Tube no.	0.10 M HNO ₃ ml	H ₂ O (DW) ml	0.10 M Ca(NO ₃) ₂ ml	0.10 M Ca(OH) ₂ ml	pH
7	2.4	27.3	0.3	0	3.1
8	1.8	27.6	0.6	0	3.2
9	1.2	27.9	0.9	0	3.5
10	0.6	28.2	1.2	0	4.0
11	0	28.5	1.5	0	4.9
12	0	28.5	1.2	0.3	5.9

Table A2.

Design of sorption experiment of AgNPs and AgNO₃ as a function of pH in clay and sand.

Set 1)

CN: Clay AgNPs (replicate 1).

Tube no.	0.10 M HNO ₃ ml	H ₂ O (DW) ml	0.10 M Ca(NO ₃) ₂ ml	0.10 M Ca(OH) ₂ ml	pH ₁	pH ₂	Add AgNPs 1.35 ppm ml
1 CN	3	12	0	0	4.2	4.2	15
2 CN	2.4	12.3	0.3	0	4.7	5.6	15
3 CN	1.8	12.6	0.6	0	5.2	6.2	15
4 CN	1.2	12.9	0.9	0	5.8	7.0	15
5 CN	0.6	13.2	1.2	0	6.4	7.4	15
6 CN	0	13.5	1.5	0	6.9	7.6	15

CN: Clay AgNPs (replicate 2).

Tube no.	0.10 M HNO ₃ ml	H ₂ O (DW) ml	0.10 M Ca(NO ₃) ₂ ml	0.10 M Ca(OH) ₂ ml	pH ₁	pH ₂	Add AgNPs 1.35 ppm ml
1 CNr	3	12	0	0	4.2	4.2	15
2 CNr	2.4	12.3	0.3	0	4.7	4.8	15
3 CNr	1.8	12.6	0.6	0	5.2	6.6	15
4 CNr	1.2	12.9	0.9	0	5.8	7.0	15
5 CNr	0.6	13.2	1.2	0	6.4	7.4	15
6 CNr	0	13.5	1.5	0	6.9	7.5	15

C+: Clay AgNO₃ (replicate 1).

Tube no.	0.10 M HNO ₃ ml	H ₂ O (DW) ml	0.10 M Ca(NO ₃) ₂ ml	0.10 M Ca(OH) ₂ ml	pH ₁	pH ₂	Add Ag ⁺ 1.35 ppm ml
1 C+	3	12	0	0	4.2	4.4	15
2 C+	2.4	12.3	0.3	0	4.7	5.1	15
3 C+	1.8	12.6	0.6	0	5.2	6.3	15
4 C+	1.2	12.9	0.9	0	5.8	6.9	15
5 C+	0.6	13.2	1.2	0	6.4	7.4	15
6 C+	0	13.5	1.5	0	6.9	7.7	15

C+: ClayAgNO₃ (replicate 2).

Tube no.	0.10 M HNO ₃ ml	H ₂ O (DW) ml	0.10 M Ca(NO ₃) ₂ ml	0.10 M Ca(OH) ₂ ml	pH ₁	pH ₂	Add Ag ⁺ 1.35 ppm ml
1 C+r	3	12	0	0	4.2	5.3	15
2 C+r	2.4	12.3	0.3	0	4.7	5.7	15
3 C+r	1.8	12.6	0.6	0	5.2	6.2	15
4 C+r	1.2	12.9	0.9	0	5.8	6.9	15
5 C+r	0.6	13.2	1.2	0	6.4	7.4	15
6 C+r	0	13.5	1.5	0	6.9	7.7	15

Set 2)

SN: Sand AgNPs (replicate 1).

Tube no.	0.10 M HNO ₃ ml	H ₂ O (DW) ml	0.10 M Ca(NO ₃) ₂ ml	0.10 M Ca(OH) ₂ ml	pH ₁	pH ₂	Add AgNPs 1.35 ppm ml
8SN	1.8	12.6	0.6	0	3.2	3.3	15
9SN	1.2	12.9	0.9	0	3.5	3.5	15
10SN	0.6	13.2	1.2	0	4.0	4.1	15
11SN	0	13.5	1.5	0	4.9	4.9	15
12SN	0	13.5	1.2	0.3	5.9	6.9	15
13SN	0	13.2	1.2	0.6	***	7.4	15

SN: Sand AgNPs (replicate2).

Tube no.	0.10 M HNO ₃ ml	H ₂ O (DW) ml	0.10 M Ca(NO ₃) ₂ ml	0.10 M Ca(OH) ₂ ml	pH ₁	pH ₂	Add AgNPs 1.35 ppm ml
8SNr	1.8	12.6	0.6	0	3.2	3.2	15
9SNr	1.2	12.9	0.9	0	3.5	3.4	15
10SNr	0.6	13.2	1.2	0	4.0	4.0	15
11SNr	0	13.5	1.5	0	4.9	5.3	15
12SNr	0	13.5	1.2	0.3	5.9	6.6	15
13SNr	0	13.2	1.2	0.6	***	7.4	15

S+: Sand AgNO₃ (replicate 1).

Tube no.	0.10 M HNO ₃ ml	H ₂ O (DW) ml	0.10 M Ca(NO ₃) ₂ ml	0.10 M Ca(OH) ₂ ml	pH ₁	pH ₂	Add Ag ⁺ 1.35 ppm ml
8S+	1.8	12.6	0.6	0	3.2	3.2	15
9S+	1.2	12.9	0.9	0	3.5	3.5	15
10S+	0.6	13.2	1.2	0	4.0	4.0	15
11S+	0	13.5	1.5	0	4.9	5.1	15
12S+	0	13.5	1.2	0.3	5.9	6.6	15
13S+	0	13.2	1.2	0.6	***	7.3	15

S+: Sand AgNO₃ (replicate 2).

Tube no.	0.10 M HNO₃ ml	H₂O (DW) ml	0.10 M Ca(NO₃)₂ ml	0.10 M Ca(OH)₂ ml	pH₁	pH₂	Add Ag⁺ 1.35 ppm ml
8S+r	1.8	12.6	0.6	0	3.2	3.2	15
9S+r	1.2	12.9	0.9	0	3.5	3.4	15
10S+r	0.6	13.2	1.2	0	4.0	4.0	15
11S+r	0	13.5	1.5	0	4.9	5.3	15
12S+r	0	13.5	1.2	0.3	5.9	6.8	15
13S+r	0	13.2	1.2	0.6	***	7.3	15

Note: In the appendix section, (C) stands for clay;(S) stands for sand, (N) stands for nanoparticle, (+) stands for ion and (r) stands for replicate.