Geochemical Effect and Fate of Gold Nanoparticles (AuNPs) in Saturated Soil Matrices

Theodore D. Williams
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Abstract

Gold nanoparticles (AuNPs) are extensively used in a number of applications including molecular detection through surface-enhanced Raman scattering, multifunctional nanocarriers for drug delivery, cancer diagnosis and treatment, catalysis and photonic/plasmonic devices. However, environmental fate and toxicity of AuNPs are not well understood or characterized. In this work, AuNPs of different concentrations were introduced and allowed to filter through various soil matrices in an effort to determine the physico-chemical interactions between the AuNPs and the aqueous porous soil medium. AuNPs deposition onto the soil particles and the mechanisms of their transport and release into the soil matrix are key factors that influence the leaching of nutrients, i.e., ionic species of various elements such as sodium (Na), magnesium (Mg), aluminum (Al), phosphorous (P), potassium (K), calcium (Ca), manganese (Mn), iron (Fe), copper (Cu) and gold (Au). Simultaneously, soil matrix composition and properties also greatly influence the transport, reactivity and fate of AuNPs in a porous environment. The surface electrical charge of a soil matrix can affect the transport of gold nanoparticles by electrostatic repulsion or attraction, thus increasing mobility or hindering movement.

In this study I utilize a saturated filtering column to explore the soil-AuNPs interaction and to illustrate its effect of ten environmentally important elemental species using ICP-MS analysis of the effluent of each soil matrix. Natural soil-AuNPs matrix retained 99.9% of the total AuNPs introduced. Sandy soil, though very porous and negatively charged, retained 85% of the gold nanoparticles added. A mixture of clay and clean sand ranging from 10%-40% of clay retained gold particles between 99.43%, and 99.52% respectively. However, results show that aggregation, grain size distribution and
electrostatic forces are contributors to such high retention rates. Further experiment was conducted to exam the outcome of precipitation as a mean to evaluate the fate gold nanoparticles after deposition.

Keywords: Gold nanoparticles, soil matrix, geochemistry, nanotoxicity, environmental fate
GEOCHEMICAL EFFECT AND FATE OF GOLD NANOPARTICLES (AuNPs) IN SATURATED SOIL MATRICES

by

Theodore D’Williams

B.S., Syracuse University, 2012

Thesis
Submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering.

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Chapter 1

Overview

1.1 Introduction

Environmental fate, potential uptake by organisms and cytotoxicity of nanoparticles are becoming a major concern as the use of imaging, therapeutics, diagnostics, catalysis, sensing and energy harvesting continues to grows (Nangia & Surehkumar, 2012). Recent experimental and computational modeling studies suggest that the nanoparticle shape, size and surface charge could greatly influence their transport through lipid membranes (Nangia & Surehkumar, 2012). Hence, considerations of the environmental and biological impact of the nanoparticles are of paramount importance in the design of nanoparticle-based technologies. As nanoparticles applications expand, these materials are likely to enter the environment during their lifecycle at different locations, concentrations, and sizes. Metal nanoparticles are highly reactive, unstable and are easily oxidized in the presence of water (Kralchevsky, et al., 2013). Gold nanoparticles (AuNPs) can be easily prepared from its salt, gold tetrachloride by a method of reduction and stabilized by various coatings.

Chemical pollution is a serious environmental problem that threatens the health of animals and humans. The presence of unwanted chemicals in the environment also has consequences for society and the economy. Understanding the factors controlling nanoparticle response in the environment would lead to safer fabrication and decrease environmental impacts. Many substances are released into the environment in various
methods and forms, their route of release and deposition is important in determining the appropriate approach and monitoring. The high surface to volume ratio, surface modification, properties and modest synthesis methods has thrust gold nanoparticles as the material of choice in many projects, experiments and applications (Lin & Tseng, 2012). The internalization mechanics of nanoparticles are not well understood though it is widely recognized that shape, size, surface charge and coating changes the functionality of the particles and their toxicity in an environmental system.

The purpose of this study is to evaluate the geochemical impact of gold nanoparticles as they are transported through a porous soil environment. It is believed that through bond formation, electrostatic interactions, hydrophobic adsorption and molecular recognition that gold nanoparticles can influence the chemistry of the soil (Lin & Tseng, 2012). The evaluation of AuNPs transport is important to further understand the properties of gold nanoparticles in the environment, interaction, and biogeochemical changes. Gold nanoparticles were evaluated with changing concentrations, mobility and the electrostatic surface charge of the each soil matrices.
Materials and Methods of Analysis

2.1 Soil Formation

The formation of soil is a direct result of biological, climatic, topographic and weathering phenomena of parental rocks and other materials over time. Soil is mostly composed of aluminum and silicate ions combined with various positively charged ions.

2.2 Grain size and porosity

The grain size of soil particles and the aggregate structures they form affect the ability of a soil to transport and retain water, air and nutrients. Table 1 illustrates the different soil matrices that were used for this study. Grain sizes are used to differentiate a soil type from another; clay particles are smaller than 0.002 mm in diameter, silt particles are between 0.002 mm and 0.075 mm, and sand particles are between 0.075 mm and 4.75 mm.

Porosity is the space or lack thereof between soil particles. The porosity of soil reflects its ability to hold air and water. The porosity of soil is also related to the permeability of the soil as it dictates the ease of fluid transport. As porosity of the soil increases, its texture becomes larger, whereas the permeability decreases as the pore size becomes smaller (Encyclopaedia Britannica, 2014). Clay affects the porosity and permeability of the soil by binding soil grains together into aggregates, thus making it difficult for the movement...
of water and other fluids (Price, 2008). The porosity of a soil depends on several factors, including packing density, particle size distribution, shape of particles, quantity of soil organic matter and cementation (Nimmo, 2004).

2.2.1 Soil Types

Clay is made up of very fine sized particles, less than two micrometer in diameter. This soil type is mostly composed of silica, aluminum and magnesium. Iron can substitute for aluminum and magnesium in various ways. Substantial quantities of potassium, sodium and calcium are frequently present. Clay minerals are able to adsorb cations and anions and retain them around their structure for ion exchange. Heavy metals are strongly attracted to the negatively charged sites on the surfaces of the mineral (Clay Mineral, 2014). The clay type used for this study is a mixture of both kaolinite $\text{Al}_2\text{Si}_2\text{O}_5$(OH)$_4$ and illite $(\text{Al},\text{Mg},\text{Fe})_2(\text{Si},\text{Al})_4\text{O}_{10}[(\text{OH})_2,(\text{H}_2\text{O})]$ with a porosity of 3 – 100 nm in diameter (Kuila & Prasad, 2013).

Silt may occur both as soil and as suspended particles in water ranging from 0.002 mm to 0.075 mm in diameter. It can be transported in solutions and can be fine enough to be transported by the wind. Deposit by the wind is called loess. Sediments are rarely composed of pure silt, but rather a mixture of clay and sand. The porosity of this sediment ranges from 250 nm to 280 nm (Delage, et al., 1996).

Sand is mostly composed of quartz and feldspars, sand particles range from 0.075 mm to 4.75 mm in diameter. There are three categories used to classify the different kinds of
sand: fine sand (ranging from 0.075 mm to 0.425 mm), medium sand (ranging from 0.425 mm to 2.0 mm) and coarse sand (ranging from 2.0 mm to 4.75 mm). The pore size distribution of sand ranges from 3.6 nm to 206 µm (Minagawa, et al., 2008). The type of clean sand used in this study was pure silica (silicon dioxide, SiO$_2$) with a diameter between 0.210 mm and 0.297 mm.

Natural soil is a result of biological, climatic, geologic and topographic processes; this porous media is a reservoir of water and nutrients. Natural soil is a mixture of different soil types including humus and microorganisms and is great for filtration. As a result of such assortment, natural soil has a range of pore size distribution.

Table 1: The properties of each soil type.

<table>
<thead>
<tr>
<th>Soil Component</th>
<th>Water Infiltration Capacity</th>
<th>Water Holding Capacity</th>
<th>Nutrient Holding Capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay</td>
<td>Poor</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>Silt</td>
<td>Medium</td>
<td>Medium</td>
<td>Medium</td>
</tr>
<tr>
<td>Sand</td>
<td>Excellent</td>
<td>Poor</td>
<td>Poor</td>
</tr>
<tr>
<td>Natural Soil</td>
<td>Good</td>
<td>Excellent</td>
<td>Excellent</td>
</tr>
<tr>
<td>Clean Sand</td>
<td>Excellent</td>
<td>Poor</td>
<td>Poor</td>
</tr>
</tbody>
</table>

Soil samples as illustrated in Table 1 were collected except for clay and clean sand that was purchased from Clayscapes Pottery Inc. and Sigma-Aldrich® respectively. Silt, sand and natural soil was from a bore site in Tully, New York.
2.3 Sieve Analysis of soils

Sieve analysis is a method used to determine various soil types and particle size distribution. Soil samples were passed through a set of sieves: #4 (4.75 mm), #10 (2.0 mm), #30 (0.599 mm), #60 (0.251 mm), #80 (0.178 mm), #140 (0.104 mm) and #200 (0.075 mm). Particles larger than 75 µm are categorized as variation of sand, while particles smaller than 75 µm were called fines. Fines are a composition of silt and clay and can only be separated through a sedimentation procedure. This sedimentation technique is called a hydrometer analysis, where the particle size can be determined using Stokes’ law.

Sieve analyzes were conducted on two soil matrices, natural soil and sandy soil that are illustrated by Table 2 and Table 3 respectively. The result of natural soil shows a composition of mainly sand particles with various size distributions as compared to sandy soil that is mainly comprised of fine sand. A significant difference between both soil types is the percentage of fines composition, 11% and 32% respectively.

Table 2: Soil composition of natural soil.

<table>
<thead>
<tr>
<th>Natural Soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sieve #</td>
</tr>
<tr>
<td>&lt; #200</td>
</tr>
<tr>
<td>#200</td>
</tr>
<tr>
<td>#140</td>
</tr>
<tr>
<td>#80</td>
</tr>
<tr>
<td>#60</td>
</tr>
<tr>
<td>#30</td>
</tr>
<tr>
<td>#10</td>
</tr>
<tr>
<td>#4</td>
</tr>
</tbody>
</table>
Table 3: Soil composition of sandy soil.

<table>
<thead>
<tr>
<th>Sieve #</th>
<th>Sieve (mm)</th>
<th>Weight (g)</th>
<th>Soil Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; #200</td>
<td>Fines</td>
<td>100.1</td>
<td>32%</td>
</tr>
<tr>
<td>#200</td>
<td>0.075</td>
<td>119.8</td>
<td>38%</td>
</tr>
<tr>
<td>#140</td>
<td>0.106</td>
<td>83</td>
<td>27%</td>
</tr>
<tr>
<td>#80</td>
<td>0.18</td>
<td>4.4</td>
<td>1.4%</td>
</tr>
<tr>
<td>#60</td>
<td>0.25</td>
<td>2.3</td>
<td>0.7%</td>
</tr>
<tr>
<td>#30</td>
<td>0.6</td>
<td>1.3</td>
<td>0.4%</td>
</tr>
<tr>
<td>#10</td>
<td>2</td>
<td>0.8</td>
<td>0.3%</td>
</tr>
<tr>
<td>#4</td>
<td>4.75</td>
<td>0.5</td>
<td>0.2%</td>
</tr>
</tbody>
</table>
2.4 Hydrometer Analysis

Hydrometer analysis is based on the relationship of soil types to soil particles of various shapes and sizes. This relationship relates the terminal velocity of a free-falling sphere in a fluid to its diameter (Department of the Army, 2000). The grain-size distribution and soil particle size of silt and clay are calculated from the hydrometer analysis that is an application of Stokes’ law, \( v = \frac{\gamma_s - \gamma_w}{18\eta} \cdot D^2 \)

where \( v = \) velocity (cm/s)

\( \gamma_s = \) specific weight of soil solids (g/cm\(^3\))

\( \gamma_w = \) unit weight of water (g/cm\(^3\))

\( \eta = \) viscosity of water (g*s/cm\(^2\))

\( D = \) diameter of soil particle (mm)

A total weight of 50 g of soil that had passed through the #200 sieve (<0.075 mm) was mixed into a slurry using 125 mL of dispersing agent solution for one (1) minute using a mechanical mixer. The slurry was transferred to a graduate cylinder and filled to 1000 mL using distilled water. Using a polymer to seal the opening, the cylinder was rotated upside down multiple times. After setting the graduated cylinder right side up for the final time, a stopwatch was started immediately along with the insertion of the hydrometer (Figure 1). Readings from the hydrometer were taken at 15, 30 and 60 second intervals. Additional readings were taken at 2, 5, 15, 30, 60, 120 and 1140 minutes.
The density of a soil-water suspension depends on the concentration and specific gravity of the soil’s particles. If the suspension is allowed to stand, the particles gradually settle out of the suspension at a known depth below the surface. The percentage of dispersed soil in suspension can be determined at a specific time and depth once the specific gravity and the density measurement of the soil is known (Department of the Army, 2000).
The depth at which the measurement is made is found by calibrating the hydrometer. Stokes’ law is used to calculate the maximum equivalent particle diameter for the material in suspension at the depth and for the elapsed time of settling (Department of the Army, 2000). The particles diameter (D) is calculated from Stokes’ equation using the hydrometer reading. The data for natural and sandy soils are shown in Table 4 and Table 5 respectively. Equation 1 and Equation 2 were used to calculate the size of the particles and the percent of silt and clay from the hydrometer analysis correspondingly.

Table 4: Hydrometer result of natural soil

<table>
<thead>
<tr>
<th>Time (hrs.)</th>
<th>Hydrometer Δ</th>
<th>Effective Depth, L (cm)</th>
<th>D (mm)</th>
<th>% finer</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.004</td>
<td>48</td>
<td>8.4</td>
<td>0.077</td>
<td>96</td>
</tr>
<tr>
<td>0.008</td>
<td>38</td>
<td>10.1</td>
<td>0.060</td>
<td>76</td>
</tr>
<tr>
<td>0.017</td>
<td>31</td>
<td>11.2</td>
<td>0.045</td>
<td>62</td>
</tr>
<tr>
<td>0.033</td>
<td>25</td>
<td>12.2</td>
<td>0.033</td>
<td>50</td>
</tr>
<tr>
<td>0.083</td>
<td>22</td>
<td>12.7</td>
<td>0.021</td>
<td>44</td>
</tr>
<tr>
<td>0.25</td>
<td>18</td>
<td>13.3</td>
<td>0.013</td>
<td>36</td>
</tr>
<tr>
<td>0.5</td>
<td>18</td>
<td>13.3</td>
<td>0.009</td>
<td>36</td>
</tr>
<tr>
<td>1</td>
<td>16</td>
<td>13.7</td>
<td>0.006</td>
<td>32</td>
</tr>
<tr>
<td>2</td>
<td>16</td>
<td>13.7</td>
<td>0.004</td>
<td>32</td>
</tr>
<tr>
<td>17.75</td>
<td>14</td>
<td>14</td>
<td>0.002</td>
<td>28</td>
</tr>
</tbody>
</table>
Table 5: Hydrometer result of sandy soil.

<table>
<thead>
<tr>
<th>Time (hrs.)</th>
<th>Hydrometer Δ</th>
<th>Effective Depth, L (cm)</th>
<th>D (mm)</th>
<th>% finer</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.004</td>
<td>45</td>
<td>8.9</td>
<td>0.079</td>
<td>90</td>
</tr>
<tr>
<td>0.008</td>
<td>35</td>
<td>10.6</td>
<td>0.061</td>
<td>70</td>
</tr>
<tr>
<td>0.017</td>
<td>25</td>
<td>12.2</td>
<td>0.046</td>
<td>50</td>
</tr>
<tr>
<td>0.033</td>
<td>17</td>
<td>13.5</td>
<td>0.035</td>
<td>34</td>
</tr>
<tr>
<td>0.083</td>
<td>10</td>
<td>14.7</td>
<td>0.023</td>
<td>20</td>
</tr>
<tr>
<td>0.25</td>
<td>8</td>
<td>15</td>
<td>0.013</td>
<td>16</td>
</tr>
<tr>
<td>0.5</td>
<td>7</td>
<td>15.2</td>
<td>0.009</td>
<td>14</td>
</tr>
<tr>
<td>1</td>
<td>7</td>
<td>15.2</td>
<td>0.007</td>
<td>14</td>
</tr>
<tr>
<td>2</td>
<td>7</td>
<td>15.2</td>
<td>0.005</td>
<td>14</td>
</tr>
<tr>
<td>17.42</td>
<td>6.5</td>
<td>15.25</td>
<td>0.002</td>
<td>13</td>
</tr>
</tbody>
</table>

\[ D (mm) = K \sqrt{L/T} \]

Equation 1. Soil particle size calculated with respect to time and particle’s density.

D: diameter (mm)

K: constant that depends upon specific gravity of the solid particles

L: depth at which the density of the suspension is being measured (cm)

T: time elapsed (min)

Percent finer = \( \frac{aR_{cp}}{W_s} \times 100\% \)

Equation 2. Percentage of clay/silt soil composition.

a: correction for specific gravity (a=1 for hydrometer 152H)

R_{cp}: hydrometer reading

W_s: total sample weight (g)
2.5 Soil Structure

The soil structure is composed of a mixture of clay, silt, sand and organic matter. The percentage of each soil type varies along with their particles sizes. Clay particles are negatively charged with a large surface area. This characteristic is important for plants, because they rely on positively charged ions: calcium, magnesium potassium and sodium. The ability of soil to adsorb positive ions is known as cation exchange capacity (CEC). Soil that exhibits high CEC tends to hold larger quantities nutrients and exhibits limited leaching losses. The more clay a soil has, the greater its cation exchange capacity and organic matter (Troxler, 1999).

Soil matrices will vary in many ways, but one notable condition is the clay content. Clay is effective at creating linkages within the soil that allows moisture to be held against the force of gravity by binding soil particles (Troxler, 1999). Clay contributes to the biological, chemical and physical attributes of the soil. As clay content increase, the cation exchange capacity of the soil also increases, thus reducing nutrient losses. Clay also produces a buffering effect of the soil, thus resisting the change of pH. Fundamentally, clay has a vital role in the productivity of any soil mixture by holding moisture and nutrients.

ASTM D 2974 standard was used to determine the percentage of organic matter of the clay used in this study. This standard reference is the laboratory testing method for moisture, ash and organic matter based on the engineering properties of soil. Results showed that the clay soil contained 5% organic matter.
Grain distribution of natural soil, sandy soil, clean sand and silt are shown in Table 6.

Table 7 shows the four (4) mixtures of clay and clean sand matrices used in this study: 10% clay with 90% clean sand, 20% clay with 80% clean sand, 30% clay with 70% clean sand and 40% clay with 60% clean sand. These mixtures were composed to evaluate the clay-AuNPs interaction as the porosity of the soil gradually decreases as cation exchange capacity and organic matter gradually increases.

Table 6: Composition of soil samples used in this experiment.

<table>
<thead>
<tr>
<th>Soil Composition</th>
<th>Natural Soil</th>
<th>Sandy Soil</th>
<th>Clean Sand</th>
<th>Silt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay</td>
<td>3.2%</td>
<td>4.2%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Silt</td>
<td>7.3%</td>
<td>24.4%</td>
<td>-</td>
<td>100%</td>
</tr>
<tr>
<td>Sand</td>
<td>89%</td>
<td>68%</td>
<td>100%</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 7: Composition of additional soil models - mixture of clay and clean sand soil matrices.

<table>
<thead>
<tr>
<th>Soil Composition</th>
<th>Clay Mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample 5</td>
</tr>
<tr>
<td>Clay</td>
<td>10%</td>
</tr>
<tr>
<td>Clean Sand</td>
<td>90%</td>
</tr>
</tbody>
</table>
2.5.1 Soil Column

Soil columns were used in conjunction with GE Whatman Glass Microfiber Filters, Grade 934-AH, 47 mm–diameter as shown in Figure 2. The NALGENE® Reusable Filter Holder and Receiver is of polysulfone material and is also convenient for vacuum filtration (tubing adapter can be stuffed with cotton for sterile venting: 6 to 8 mm). This filter holds 250 mL in both upper and lower cavities and provides a filtering surface area of 1734 mm². The Whitman Glass Microfiber Filter offers a surface small enough that soil particles cannot pass but large enough to allow the gold nanoparticles to pass through. The AuNPs were introduced to the soil column as a slurry mixture and allowed to be filter. The effluent was captured and acidified with 1% nitric acid to prevent elements from precipitating and later analyzed using inductively coupled plasma mass spectrometry.

Figure 2: Soil column used in this experiment for soil-AuNPs filtration.
2.6 Gold Nanoparticles

Gold nanoparticles are nano-sized gold particles suspended in a fluid; usually water. Depending on the sizes of the particles, the fluid color will vary. At the sub micrometer size, gold nanoparticles tend to have unique optical, electronic and molecular properties.

2.6.1 Gold Nanoparticle Synthesis

A volume of 690 µL of gold chloride (AuCl₃) was added to 100 mL of deionized water to form 0.69 mM of chloroauric acid (H[AuCl₄]). 100 mM of (H[AuCl₄]) was mixed with 500 mL of deionized water. 500 mg of 1% sodium citrate (Na₃C₆H₅O₇) was mixed in 50 mL of distilled water. The synthesis of gold nanoparticle is produced by chloroauric acid being reduced by sodium citrate. Sodium citrate also acts as a shielding agent to preserve the gold as nanoparticles in the concentrated solution (Tabrizi, et al., 2009).

Figure 3 illustrate the products of gold chloride and sodium citrate prior mixing. 1.14 g of sodium citrate was added to 100 mL of deionized water that was subsequently heated to boil. The citrate solution reacts with the gold solution to form gold nanoparticles. The color of the solution during this process changed from pale yellow with the addition of gold chloride to the boiling sodium citrate solution to clear and then to deep purple, Figure 4. The color changing phenomena is directly correlated to atoms aggregation and different sized nanoparticle formation. Upon attaining the desired color of solution associated with the desired size of nanoparticles, the reaction was stopped immediately by eliminating the heat source and reducing the solution’s core temperature below the threshold of 80 °C.
Figure 3: Gold chloride (left) and sodium citrate (right).

Figure 4: Synthesized gold nanoparticles.
Following further overnight cooling, a spectrophotometer was used to determine the concentration of the gold nanoparticle solution from its absorbance and wavelength measurements. With an absorbance and wavelength measurement of 1.5 and 512-516 nm respectively and using the Beer-Lambert law, the concentration of the gold nanoparticle solution was calculated to be 2.95 µg/L or 2.95 parts per billion (ppb). After being labeled “Au0”, the solution was then diluted with deionized water by a factor of 0.5 and 0.25 and then subsequently labeled as “2x” and “4x” respectively. Spectrophotometer analysis was conducted on each dilution to confirm the following concentrations as 1.48 µg/L and 0.74 µg/L respectively. In calculation the concentration of the gold nanoparticle solution, the molar extinction coefficient of gold nanoparticles is important and also correlated to its wavelength. By exploiting the Beer-Lambert’s law with knowledge of their atomic size, the final concentration can be computed. To determine the physical size of the synthesized gold nanoparticles, a transmission electron microscope was used to image and measure the tangible particle sizes illustrated by Figure 5 and Figure 6.
Figure 6: Transmission electron microscope image of spherical gold nanoparticles.

Figure 5: Measurements of gold nanoparticles imaged by transmission electron microscope.
2.6.2 Beer-Lambert Law

The Beer Lambert Law is a linear relationship between absorbance and concentration of an electromagnetic radiation absorber.

The Beer-Lambert law is written as: \( A = \varepsilon * b * c \)

where: A: Measured absorbance (unit less)
\( \varepsilon \): Wavelength-dependent absorption coefficient (L/mol-cm)

b: Path length (cm)

c: Analysis concentration (mol/L)

To find the gold nanoparticle concentration, the trailing equation was rearranged as follows (Maye, et al., 2006):

\[
c = \frac{A}{\varepsilon * b} = \frac{1.5}{1.0 \times 10^8 \frac{L}{mol - cm} * 1 \text{ cm}} = 1.5 \times 10^{-8} \text{ mol/L}
\]

To properly account for the gold nanoparticles, its molecule weight must be accounted.

\[
c = 1.5 \times 10^{-8} \text{ mol/L} * \frac{196.97 \text{ g Au}}{\text{mol}} * \frac{1000 \text{ mg}}{\text{g}} = 0.00295 \text{ mg/L}
\]

Note: 1 mg/L = 1 ppm
1000 ppm = 1 ppb
2.7 Instrumentation

Spectrophotometer (Ocean Optics: USB4000-U-VIS) was used to authenticate the presence of gold nanoparticle after synthesis based on absorbance and wavelength correlation. Dynamic light scattering (Malvern Zetasizer Nano ZS) was used to validate the size of the suspended gold nanoparticles. Transmission electron microscopy (FEI T12 Spirit TEM STEM) was used to further evaluate the physical size of the gold particles. The effluents collected from each soil matrix along with the gold nanoparticle solution were analyzed before and after the soil-AuNPs transport using the inductively coupled plasma mass spectrometry (PE SCIEX ELAN 6100).

2.7.1 Spectrophotometry

A spectrophotometer measures the properties of light over an electromagnetic spectrum by using a light source to analyze reflection and absorbance. The synthesized gold nanoparticles were measured by a spectrometer that reveals the particles’ wavelength to be between 515-520 nm, Figure 7.
2.7.2 Transmission Electron Microscope

Transmission electron microscope (TEM) was used to characterize the microscopic structure of materials. This apparatus uses high-energy electron beam transmitted through a thin layer of sample to image and analyze the structure of the material on an atomic scale in order to reveal high levels of detail and complexity inaccessible by light microscopy as illustrated by Figure 5 and Figure 6 as compared to Figure 7-8. Gold nanoparticles sample was prepared for TEM analysis by being deposited onto a glass substrate and allowed to dry at ambient temperature. The dried sample was transferred to a Cu-grid (copper grid) that was furthered dried by vacuum before being analyzed by the TEM. SiO$_2$ coated grid was used over carbon for the AuNPs preparation because of their robustness.

Figure 7: Absorbance of sample 2x gold nanoparticles over different wavelength.
2.7.3 Dynamic Light Scattering

Dynamic light scattering or DLS is a technique used to determine the size distribution profile of particles suspended in solution from a light source as shown by Figure 8. DLS uses scattered light intensity to measure the fluctuations due to diffusing particles. These intensity fluctuations produce the Brownian motion velocity and by using the Stokes-Einstein relationship, the particle sizes can be determined.

![Size Distribution by Number](image)

*Figure 8: AuNPs size distribution by dynamic light scattering (average 10.75 nm).*

2.7.4 Inductively Coupled Plasma Mass Spectrometry

Inductively coupled plasma mass spectrometry (ICP-MS), Figure 9 is an analytical instrument that can detect elemental metals and several non-metals at concentrations as low as part per trillion, typically introduced as an aerosol. Atoms of elements are converted into ions from samples by the high temperature inductively coupled plasma (ICP); ions are then separated and detected by the mass spectrometer (MS).
Figure 9: Inductively coupled plasma mass spectrometry used in this research.
2.8 Design

Gold nanoparticles of 10 nm suspended in water was mixed by hand with each soil type in a 3:1 ratio of AuNPs to soil, 15 mL to 5 g respectively into a slurry and then transferred to each soil column, Figure 10. The filter used for this experiment was GE Whatman Glass Microfiber Filters, Grade 934-AH, Figure 11. Having a pore size opening of 1.5 µm, it was large enough to allow the nanoparticles to pass, while being small enough to avoid the transport of the soil particles. The filter is graded for high retention efficiency of fine particles, high loading capacity and a smooth surface that is typically recommended for water pollution monitoring. After infiltration was completed, the effluent of the soil slurry was collected and again filtered using the same graded filter and acidified with 1% nitric acid for ICP-MS analysis.

Figure 10: Soil-AuNPs slurry and filtration column.
Using the greater concentration of gold nanoparticles, Au0 or 2.95 μg/L, a separate analysis was conducted. This supplementary analysis added 15 mL of deionized water to the soil after filtration was completed to stimulate precipitation and to evaluate the fate of gold nanoparticles after deposition. This stimulated precipitation was administered on top of the soil and allowed to filtered through the already saturated and contaminated soil. The effluent was collected and labeled “pH2O” for each corresponding soil types and acidified with 1% nitric acid for ICP-MS analysis.

To evaluate the natural chemical composition of the soil, an acid extraction was prepared using an aqua regia mixture. Aqua regia or nitro-hydrochloric acid is a 3:1 ratio mixture by volume of hydrochloric acid and nitric acid respectively. Such an acidic solution was used to extract the nutrients of the soil into solution for analysis by the ICP-MS.
Each soil matrix was be analyzed for sodium (Na), magnesium (Mg), aluminum (Al), phosphorus (P), potassium (K), calcium (Ca), manganese (Mn), iron (Fe), copper (Cu) and gold (Au). These elements are important nutrients to a productive soil biota not only for plants but also for soil microbes.

2.9 Filtration Experiments: Challenges

Initial introduction of gold nanoparticles was dispensed into the soil column onto the soil’s surface. Allowing gravity to drive the transport process, a cement-like structure was formed causing this methodology to be unsuccessful as the flow of solution was restricted, Figure 12. After difficulties trying to resolve this issue, it was finally decided to abandon the use of this filter type (Figure 13) for another model (Figure 2). This column had a larger surface area for filtration and a higher flow rate. Thirdly, in assessing the proper filter for the experiment, a sand stone filter was used, but was constantly being clogged. A geosynthetic membrane (Figure 14) was used and was also unsuccessful as it allowed soil particles to pass into the effluent.

The Nalgene® soil column illustrated by Figure 2 helped to overcome these difficulties by having a larger surface area that allowed the dispensing of the AuNP-soil slurry. The use of GE Whatman microfiber filter also made this experiment possible as the pore size of the filter was large enough to permit nanoparticle size particles to flow, but small enough to restrict soil particles from mixing with the effluent thereafter. The soil column also had additional features that were not used such as vacuum to increase effluent flow.
Figure 12: Cementation of soil within the column.

Figure 13: Original column for soil filtration
Figure 14: Geosynthetic filter fiber.
Chapter 3

Results and Discussion

The result of this experiment focuses on the evaluation of chemical changes of soil and how different matrices may impact the transport of gold nanoparticles through soil. Properties of gold nanoparticles and soils are important to understand the nature of the reactions occurring. Important characteristics of this type of interaction include surface charge and electrostatic forces between both AuNPs and soil matrices. Soil particles usually have a negative surface charge. Organics are mostly acidic and negatively charged, but depending on concentration and other conditions, AuNPs may aggregate as it travels through the porous soil matrix and interacts with elements of the soil (Diegoli, et al., 2008). Electrostatic interactions of soil materials alter the transport of nanoparticles transport in a soil environment; organic matter will adsorb positively charged nanoparticles by electrostatic attraction (Darlington, et al., 2009).

The analysis was conducted around the principal of mass balance and analyzing the influent and effluent of gold nanoparticles transport and the chemistry each soil matrix. Changes within soil matrices and environmental conditions affect the mobility and reactivity of the AuNPs. Different soil types will result various aggregation kinetics influencing the reactivity with the porous media. Clay has electrostatic surface charges that attract the solution ions and hold them. In the presence of divalent cations, AuNPs will aggregate regardless of pH (El Badawy, 2011).
Figure 15: Nutrient leachate of clean sand after gold nanoparticles deposition.

Figure 16: Nutrient leachate of natural soil after gold nanoparticles deposition.
Figure 17: Nutrient leachate of sandy soil after gold nanoparticles deposition

Figure 18: Nutrient leachate of silt after gold nanoparticles deposition
Figure 19: Nutrient leachate of 10% clay 90% clean sand after gold nanoparticles deposition.

Figure 20: Nutrient leachate of 20% clay 80% clean sand after gold nanoparticles deposition.
Figure 21: Nutrient leachate of 30% clay 70% clean sand after gold nanoparticles deposition.

Figure 22: Nutrient leachate of 40% clay 60% clean sand after gold nanoparticles deposition.
Comprised of pure quartz, clean sand, as expected had very limited and low amount of elements detected (Figure 15). The retention of gold nanoparticles was calculated to be 13.8%. There was not much reaction of the clean sand-AuNPs matrix. Nevertheless, there was an 8.5% additional gold nanoparticles removal from the matrix with the stimulated precipitation condition, making the final AuNPs retention 5.3%. An increase of iron and aluminum was also visible in the effluent from the added precipitation.

Natural soil (Figure 16) is negatively charged and reacted well with its natural soil-AuNPs matrix. The AuNPs influent was purple in color upon entering the filtering column but exited clear as its effluent. It is hypothesized that there were numerous reactions and interactions occurring within this matrix. By having a mixture of clay, silt and sand, this matrix was a great filtration system. It is believed that some AuNPs aggregated and was effectively fixed within the soil. Supported by (Darlington et al., 2009) the organics of the soil adsorb the reactive AuNPs by electric static forces. Calculation the retention of AuNPs in the natural soil matrix, it was revealed to be 99.9%. Notable nutrients from this matrix leachate were sodium (Na) and calcium (Ca). These nutrients are important for plants and does show an increase in leachate as AuNPs concentration increases. The simulated precipitation reduced the total retention of AuNPs by 0.1% to 99.8%. Such resilience indicates that these nanoparticles are held strongly within this matrix. The precipitation also increased the leachate of additional sodium and calcium that could be a result of further reaction of the already deposited AuNPs.
Sandy soil (Figure 17) shows significantly more leachate of elements in correspond to AuNPs – Au0 solution. The largest leaching of nutrients are sodium, magnesium and aluminum. Aluminum is usually insoluble and becomes soluble as the pH decreases and is known to be toxic to plants. The retention of AuNPs was calculated to be 85%. Stimulated precipitation released 6.4% of the deposited AuNPs making the total retention of AuNPs 78.45%.

Silt matrix (Figure 18) shows little effect with the diluted AuNPs solutions: 2x and 4x. However, the higher concentration reaction caused the leaching of sodium and calcium, while retaining 99.7% of the gold nanoparticles introduced. Surprisingly, very little aluminum was leached from the AuNPs-soil matrix, but from the stimulated precipitation, there was a 35 µg/g increase in aluminum concentration. This is assumed to occur as a result of decreasing pH because aluminum becomes soluble as pH decreases. The precipitation also decreases the retention of AuNPs deposit by 3.7% making the total deposit 96%.

Clay mixtures presented in Figure 19, Figure 20, Figure 21 and Figure 22 are 10% clay 90% clean sand, 20% clay 80% clean sand, 30% clay 70% sand and 40% clay 60% clean sand mixtures respectively. The clay models show inconsistency in regards to elemental leaching. Figure 19-22 does shows significant leaching of aluminum in comparison to other elements. It is hypothesized that a decreasing pH may be the result of such event. The filtration of the clay models did take significant time to filter when compared to other models that would take 30 minutes to a few hours. The clay models as the
percentage of clay increases took upwards of 3 days to filter. Such elapsed time, it is assumed that carbonic acid was also a factor in lower the pH of the filtrating solution. The gold retention among the clay matrices was between 99.43% and 99.52%. Other noted leaching elements was iron and small quantities of potassium and magnesium. As believed by (Troxler, 1999), the absence of other elements from the clay matrix could be associated with an increasing cation exchanging capacity. As the percentage of clay increased that would reduced the likelihood of nutrient loss.

The results of the soil-AuNPs matrices have supported the notion of grain size distribution that corresponds to the porosity of each soil matrix. The size of soil grains is much greater than that of AuNPs. Essentially, AuNPs can deposit on these surfaces due to favorable coloumbic or van der waals interactions. The AuNPs are suspended in water and once in contact with the soil, the environment changes as demonstrated by the leaching of elements. If such changes reduce the magnitude of the zeta potential, the AuNPs could aggregate rather than remaining in suspension as isolated particles. Aggregates typically are less reactive compared to individual nanoparticles and might pass through or might clog the pores depending on the ratio of the aggregate size to the pore size. Knowing the pore size (Figure 23) of clay (3-10 nm), silt (250-280 nm) and sand (36-206 nm), one can correlated the retention of gold nanoparticles to the pore size of each matrix. Pure clay was not used for this study because it is considered impermeable from an engineering standpoint. Having a maximum mixture of 40% and 60% clean sand, it was able to retain upwards of 99.5% of AuNPs, while silt retained 99.7% and sandy soil 86%.
The charge of soil particles profoundly impacts the mobility of gold nanoparticles in the environment. Mobility through negatively charged soil, repulsion forces, would likely result in an increase of nanoparticles movement within a porous media. Likewise, attraction forces would hinder the transport of gold nanoparticles. Furthermore, soils with

Figure 23: Porosity of different soil matrices (Evans, et al., 2014).
high clay content may be a stronger sink for the electrostatically stabilized AuNPs as compared to porous media containing other minerals (El Badawy, 2011).

Organic matter is known to adsorb colloidal particles. The process would facilitate the change of surface properties and thus affect the transport through electrostatic stabilization (Jerez, et al., 2006). The attraction of AuNPs onto particles of opposite charge (Figure 24) as illustrated with the sand matrix is expected. However, the attraction onto a same charged matrix is unlikely unless there are positively charged edges or organic matter presented that would facilitate the adsorption of AuNPs onto a negatively charged matrix (Jerez, et al., 2006).

3.1  Environmental Effects and Concerns

The synergies between the soil-AuNPs matrices may have greater interaction than is likely to exist in more natural systems. Furthermore, additional work would need to address how particles interaction may change over time in different porous media. It is recognized that nanoparticles can enter the environment directly through manufacturing processes, leachate from industrial and consumer products. “Engineered nanoparticles that remain soluble or in high concentrations in the environment are more likely to affect organisms by altering the chemical environment, regardless of whether any organism experiences lethal or sub-lethal effects. If the nanoparticles is incorporated into tissues or into detritus, it is susceptible to trophic transfer and bioaccumulation” (Bernhardt, et al., 2010).

The introduction of nanoparticles into the environment is of concern because of the impact to ecosystems. However, this study showed that in terms of soil infiltration and transport, gold nanoparticles would not be transported very far beneath the soil surface. Though larger concentration of gold nanoparticles will cause increased nutrient leachate, other factors need more consideration and evaluation in the areas of bio-concentration, bio-magnification and trophic transfer. Nanoparticle waste will need to be addressed before appearance in the environment in large quantities especially as the nano-product market increases. Traditional waste removal systems may help, but will need modification based on the smaller material sizes and the effect nanoparticles have on wastewater microbes. Though aggregation of nanoparticles will occur and particle size will increase, treatment plants rely heavily on microbial activity and nanoparticles are not
only smaller but are also known to affect and mutate microorganisms. While there is an
increase growth of nanoparticle application and market, the constituent materials are
themselves expensive, the fabrication conditions require extreme precision and highly
specialized facilities. Although making nanoparticles are very expensive to produce,
others believe it is unlikely for nanoparticles and materials to enter the environment in
large quantities (e.g., gold or platinum nanoparticles and quantum dots) (Bernhardt, et al.,
2010).
Chapter 4

Conclusions and Future Work

The fundamental understanding of this study was to identify the factors governing the mobility of gold nanoparticles in the environment and its geochemical effects in different soil matrices. The physiochemical interaction between the soil matrix and nanoparticles was the source responsible for the retardation of the AuNPs transport within the matrices investigated. Major factors that limit the transport of AuNPs include electrostatic forces, organic matter and porosity of the porous media. While other methods rely on chemical interaction, porosity of the soil is truly mechanical and has shown to be especially successful as the soil particle sizes decrease. In a natural multi-layer environment, little risk of transport is presumed. This study illustrated that a mixture of different soil type, natural soil, was effective retaining 99.9% deposited gold nanoparticles and after precipitation, 99.8%. Stimulated precipitation did increase the leachate of nutrients and AuNPs after deposition, and this is believe to be a result of AuNPs aggregation and lack of transport within the porous media and further electrostatic contact between the AuNPs and the constituents of the soil. However, since the soil can hold and temporarily sequester gold nanoparticle within its media, a key factor to weigh is the long-term fate of the deposited nanomaterial in the environment.

Firstly, future work would investigate relevant toxicity studies and risk assessment. Evaluations would need to be undertaken to answer various questions including the concerns of the biota of the soil, bio-concentration, bio-magnification and trophic transfer. Secondly, the long-term effects of gold nanoparticles deposition under various conditions
would also need evaluation. Prospect work would need to elucidate the holding capacity of the soil in regards to different nanoparticles and its adhesiveness of holding the gold nanoparticles and preventing further transport and leaching. Thirdly, the stimulated precipitation was conducted on wet soils; it would be interesting to see if there is any difference when the soil is dry and then re-saturated. Porosity and organic matter would also need further evaluation to properly identify the effects of both properties. Finally, future studies should quantify the analysis of the surface charge densities and zeta potentials of gold nanoparticles, monitoring pH change within the column, manipulation of the chemical environment and exploring other nanoparticle shapes and architectures, such as cylinder, cone, and cube.
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Vita

THEODORE D. WILLIAMS

EDUCATION

Master of Science
Major: Chemical Engineering
May 2014

Bachelor of Science
Major: Environmental Engineering
Minor: Policy Studies
May 2012

Syracuse University, Syracuse, NY

PROFESSIONAL EXPERIENCE

Graduate Researcher
Syracuse University Dept. of Biomedical & Chemical Engineering
Sept. 2011 – May 2014
Syracuse, NY
• Demonstrate the geochemical Effects and Fate of Gold Nanoparticles (AuNPs) in Saturated Soil Matrices.

Energy Analyst Intern
Energy Systems and Sustainability Management – Syracuse University
Syracuse, NY
• Created an analyzing tool to evaluate energy efficiency and performance of the University’s energy systems, particularly newly implemented solar panels.

Energy Engineering Intern
ANTARES Group Incorporated
May 2013 – Aug. 2013
Fayetteville, NY
• Consulted on a multitude of projects within the areas of energy system, commercial and Industrial energy efficiency analysis.
  ○ Assisted in proposal preparation
  ○ Performed energy efficiency measure cost/benefit analyses
  ○ Prepared written reports for energy analyses (renewable & energy efficiency projects)

Anaerobic Digestion Consultant
Jan. 2012 – May 2013
Converting Organic Waste (COW) – Syracuse University
Syracuse, NY
• Designed an anaerobic digester for Syracuse University, converting organic waste into viable energy to be utilized on campus and its aqueous waste for a hydroponic greenhouse to growing plants.
Lead Counselor (Aquatic Chemist)  
**Milton J. Rubenstein Museum of Science and Technology**  
Syracuse, NY  
May 2012 – July 2012  
- Conduct aquatic experiments and chemistry analysis with students accepted into the MOST’s summer program.

Analytical Chemist  
**Syracuse University Center for Environmental Systems Engineering**  
Syracuse, NY  
Jan. 2010 – May 2012  
- Analyze mercury sequestration of zebra mussels in Seneca River and Onondaga Lake.  
- Examine total and methyl mercury in solids and solutions by thermal decomposition and digestion.  
- Measure levels of mercury in solution by oxidation, purge, trap, and cold vapor capture.  
- Analyze mercury samples for Cornell University and Queen’s University.  
- Titrate, analyze, and report data samples for the Hubbard Brook Research Forest watersheds.

Wastewater Analyst Microbiology  
**Dept. of Environmental Protection - (µbio, chem & metal lab)**  
Wards Island, NY  
- Exam samples from the onsite wastewater treatment plant for the sludge’s volatile organic acid content. Test levels of orthophosphate and ammonia from plant’s effluent for proper and legal operations.

Legal Intern  
**Law Offices of Leslie Jones-Thomas & Earl Antonio Wilson**  
New York, NY  
June 2009 – Aug. 2011  
- Assisted attorneys with general litigation and paralegal services, such as document review, filing court documents, case preparation and maintaining client and business files.

**LEADERSHIP & INVOLVEMENT**

Research Officer, **Syracuse University Investment Club**  
- Analyst, report and stock pitch for the energy sector.  
- Helped support a portfolio of over $100,000

*Senator, National Society of Black Engineers (NSBE), SU*  
Aug. 2008 – Aug 2013  
- Represented the Syracuse University Chapter at the national level dealing with the society’s operations, funding and voting for candidate members of the national board.

*Co-Founder & Pres., Society of Environmental Engr. (SEE)*  
Jan. 2010 – May 2012  
- Created an aquatic program for middle school students interested in STEM.  
- Created laboratory opportunities for students interested in research.
OTHER INVOLVEMENT

Syracuse University Fencing Club 2012 - Present
Syracuse University Cricket Club 2009-2011, Present
American Institute of Chemical Engineers 2008-2011
Syracuse University Track and Field 2008-2009

RESEARCH

Graduate Thesis (2014)
* Department of Biomedical and chemical engineering, Syracuse University, Syracuse, NY
  * Geochemical Effects and Fate of Gold Nanoparticles (AuNPs) in Saturated Soil Matrices.

Undergraduate Thesis (2012)
* Department of Civil and Environmental Engineering, Syracuse University, Syracuse, NY
  * Converting organic waste (COW) into viable energy.

Other Research
* Center for Environmental systems (SU), and Upstate Freshwater Institute Syracuse NY
  * Mercury Sequestration by Zebra Mussels in the Seneca River

AWARDS AND HONORS

* McNair Fellow, 2013-2014
* Samuel P. Clemence Award for Outstanding Senior Design – Winner, 2012
* Our Time Has Come – Corning Scholarship, 2009-2012
* National Society of Black Engineers (NSBE) Technical Research Exhibition – Finalist, 2011
* Syracuse University Summer symposium for Undergraduate Research – Winner, 2011
* 1st Annual Life Science Symposium – Winner, 2011
* 1st Annual Invention and Creativity Competition – Winner, 2011
* Emerging Researchers national (ERN) Conference; Engineering and Technology – Winner, 2011

TECHNICAL SKILLS

* Advance Microsoft Excel computation and modeling.
* Energy assessment and energy efficiency analyses.
* Wet chemistry, quality controls, and heavy metal analysis.
* Nanomaterial, water chemistry, methylmercury, and total mercury.
VOLUNTARY INVOLVEMENT

Society of Environmental Engineering Fund Raising 2012
- Created a “Fish for Fish” fund raising event to buy fishes for a local middle school that had an indoor pond. Chemistry kits were also purchased to test the water quality. A discuss was held to talk about water quality followed by testing demonstration by the students.

Office of multicultura l Affair 2012
- Mentor underclassmen that need guidance and feel disconnect from the Syracuse University community.

L.C. Smith Ambassador 2011
- Conducted experiments and help to encourage students in middle schools interested in science, technology, engineering, and mathematics.

Wilson Park Tutoring Program 2010
- Tutored middle school students for mathematics, science, and Spanish.

CERTIFICATIONS
- Scuba Diving – Stress and Safety Rescue
- Chemical Hygiene – OSHA’s Laboratory Standard (29 CFR 1910.1450)

CONFERENCE AND PRESENTATIONS


- Syracuse Center of Excellence 2011. Poster Presentation, Syracuse, NY.
- Life Science Symposium 2011. Poster Presentation, Syracuse University, Syracuse NY.


Theodore D. Williams (2011) “tCam – Security software that protects your information and your computer.” 1st Annual Invention and Creativity Competition. 2011. Poster Presentation, Syracuse University, Syracuse NY.

## Appendix

### Clean sand

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Na (µg/g)</th>
<th>Mg (µg/g)</th>
<th>Al (µg/g)</th>
<th>P (µg/g)</th>
<th>K (µg/g)</th>
<th>Ca (µg/g)</th>
<th>Mn (µg/g)</th>
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<th>Cu (µg/g)</th>
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<tr>
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<td>0</td>
<td>65.05</td>
<td>37.80</td>
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<td>0.00</td>
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<td>0.19</td>
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Figure 25: Nutrient release of clean sand from AuNPs interaction.

### Natural soil

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<tr>
<th>Sample Name</th>
<th>Na (µg/g)</th>
<th>Mg (µg/g)</th>
<th>Al (µg/g)</th>
<th>P (µg/g)</th>
<th>K (µg/g)</th>
<th>Ca (µg/g)</th>
<th>Mn (µg/g)</th>
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<td>255.05</td>
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<td>64.46</td>
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<td>2.63</td>
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<td>0.00</td>
<td>71.30</td>
<td>0.03</td>
<td>5.72</td>
<td>0.02</td>
</tr>
<tr>
<td>Effluent NS 2x</td>
<td>0.00</td>
<td>4.46</td>
<td>0.69</td>
<td>0.00</td>
<td>0.04</td>
<td>43.23</td>
<td>0.04</td>
<td>1.47</td>
<td>0.00</td>
</tr>
<tr>
<td>Effluent NS 4x</td>
<td>8.38</td>
<td>3.98</td>
<td>0.25</td>
<td>0.00</td>
<td>0.00</td>
<td>40.35</td>
<td>0.00</td>
<td>0.91</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Figure 26: Nutrient release of natural soil from AuNPs interaction.
### Sandy soil

<table>
<thead>
<tr>
<th></th>
<th>Sample Name</th>
<th>Na (µg/g)</th>
<th>Mg (µg/g)</th>
<th>Al (µg/g)</th>
<th>P (µg/g)</th>
<th>K (µg/g)</th>
<th>Ca (µg/g)</th>
<th>Mn (µg/g)</th>
<th>Fe (µg/g)</th>
<th>Cu (µg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil</td>
<td>Sand</td>
<td>419.05</td>
<td>34044.18</td>
<td>5912.86</td>
<td>403.98</td>
<td>1814.55</td>
<td>19730.9</td>
<td>584.97</td>
<td>15010.9</td>
<td>30.26</td>
</tr>
<tr>
<td>Effluent</td>
<td>Sand Au0</td>
<td>103.79</td>
<td>14.94</td>
<td>13.49</td>
<td>0.01</td>
<td>0.23</td>
<td>76.09</td>
<td>0.45</td>
<td>2.81</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>Sand pH20</td>
<td>9.08</td>
<td>5.91</td>
<td>3.24</td>
<td>0.00</td>
<td>0.21</td>
<td>32.67</td>
<td>0.31</td>
<td>2.11</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>Sand 2x</td>
<td>2.90</td>
<td>5.84</td>
<td>5.98</td>
<td>0.01</td>
<td>0.40</td>
<td>23.13</td>
<td>0.24</td>
<td>5.65</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>Sand 4x</td>
<td>6.64</td>
<td>4.79</td>
<td>8.44</td>
<td>0.01</td>
<td>0.30</td>
<td>13.03</td>
<td>0.18</td>
<td>2.54</td>
<td>0.19</td>
</tr>
</tbody>
</table>

Figure 27: Nutrient release of sandy soil from AuNPs interaction.

### Silt

<table>
<thead>
<tr>
<th></th>
<th>Sample Name</th>
<th>Na (µg/g)</th>
<th>Mg (µg/g)</th>
<th>Al (µg/g)</th>
<th>P (µg/g)</th>
<th>K (µg/g)</th>
<th>Ca (µg/g)</th>
<th>Mn (µg/g)</th>
<th>Fe (µg/g)</th>
<th>Cu (µg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil</td>
<td>Silt</td>
<td>540.21</td>
<td>46369.40</td>
<td>12273.9</td>
<td>531.94</td>
<td>3599.24</td>
<td>23084.8</td>
<td>1001.63</td>
<td>26871.7</td>
<td>83.76</td>
</tr>
<tr>
<td>Effluent</td>
<td>Silt Au0</td>
<td>58.09</td>
<td>1.59</td>
<td>4.26</td>
<td>0.01</td>
<td>0.00</td>
<td>54.03</td>
<td>0.51</td>
<td>1.25</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>Silt Au1</td>
<td>18.26</td>
<td>3.05</td>
<td>41.26</td>
<td>0.03</td>
<td>0.48</td>
<td>5.34</td>
<td>0.92</td>
<td>5.52</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>Silt Au2</td>
<td>0.00</td>
<td>0.00</td>
<td>0.57</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.05</td>
<td>0.06</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>Silt Au3</td>
<td>0.00</td>
<td>0.00</td>
<td>0.07</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.01</td>
<td>0.00</td>
<td>0.06</td>
</tr>
</tbody>
</table>

Figure 28: Nutrient release of silt from AuNPs interaction.
### 10% clay and 90% clean sand

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Na (µg/g)</th>
<th>Mg (µg/g)</th>
<th>Al (µg/g)</th>
<th>P (µg/g)</th>
<th>K (µg/g)</th>
<th>Ca (µg/g)</th>
<th>Mn (µg/g)</th>
<th>Fe (µg/g)</th>
<th>Cu (µg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Soil</strong></td>
<td><strong>Sand + clay</strong></td>
<td>0.00</td>
<td>0.56</td>
<td>61.71</td>
<td>34.05</td>
<td>57.27</td>
<td>4601.27</td>
<td>0.02</td>
<td>450.28</td>
</tr>
<tr>
<td><strong>Effluent</strong></td>
<td>10 Au0</td>
<td>0.00</td>
<td>0.00</td>
<td>2.51</td>
<td>0.03</td>
<td>0.00</td>
<td>38.64</td>
<td>0.00</td>
<td>1.15</td>
</tr>
<tr>
<td></td>
<td>10 pH20</td>
<td>0.00</td>
<td>0.46</td>
<td>2.95</td>
<td>0.03</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>1.23</td>
</tr>
<tr>
<td></td>
<td>10 2x</td>
<td>0.00</td>
<td>0.00</td>
<td>0.45</td>
<td>0.01</td>
<td>0.00</td>
<td>16.68</td>
<td>0.02</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>10 4x</td>
<td>0.00</td>
<td>0.00</td>
<td>6.20</td>
<td>0.01</td>
<td>1.00</td>
<td>8.20</td>
<td>0.01</td>
<td>1.57</td>
</tr>
</tbody>
</table>

Figure 29: Nutrient release of 10% clay and 90% clean sand from AuNPs interaction.

### 20% clay and 80% clean sand

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Na (µg/g)</th>
<th>Mg (µg/g)</th>
<th>Al (µg/g)</th>
<th>P (µg/g)</th>
<th>K (µg/g)</th>
<th>Ca (µg/g)</th>
<th>Mn (µg/g)</th>
<th>Fe (µg/g)</th>
<th>Cu (µg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Soil</strong></td>
<td><strong>Sand + clay</strong></td>
<td>0.01</td>
<td>1.11</td>
<td>58.37</td>
<td>30.29</td>
<td>51.66</td>
<td>4091.53</td>
<td>0.03</td>
<td>404.19</td>
</tr>
<tr>
<td><strong>Effluent</strong></td>
<td>20 Au0</td>
<td>0.00</td>
<td>0.00</td>
<td>34.85</td>
<td>0.02</td>
<td>0.23</td>
<td>52.39</td>
<td>0.00</td>
<td>3.18</td>
</tr>
<tr>
<td></td>
<td>20 pH20</td>
<td>0.00</td>
<td>0.00</td>
<td>6.06</td>
<td>0.03</td>
<td>0.00</td>
<td>11.84</td>
<td>0.00</td>
<td>2.18</td>
</tr>
<tr>
<td></td>
<td>20 2x</td>
<td>0.00</td>
<td>0.00</td>
<td>12.42</td>
<td>0.01</td>
<td>0.22</td>
<td>17.17</td>
<td>0.02</td>
<td>2.23</td>
</tr>
<tr>
<td></td>
<td>20 4x</td>
<td>0.00</td>
<td>0.00</td>
<td>4.64</td>
<td>0.01</td>
<td>0.24</td>
<td>8.30</td>
<td>0.01</td>
<td>1.84</td>
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</tbody>
</table>

Figure 30: Nutrient release of 20% clay and 80% clean sand from AuNPs interaction.
### 30% clay and 70% clean sand

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Na (µg/g)</th>
<th>Mg (µg/g)</th>
<th>Al (µg/g)</th>
<th>P (µg/g)</th>
<th>K (µg/g)</th>
<th>Ca (µg/g)</th>
<th>Mn (µg/g)</th>
<th>Fe (µg/g)</th>
<th>Cu (µg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil</td>
<td>Sand + clay</td>
<td>0.01</td>
<td>1.67</td>
<td>55.03</td>
<td>26.53</td>
<td>3581.80</td>
<td>0.05</td>
<td>358.09</td>
<td>0.11</td>
</tr>
<tr>
<td>Effluent</td>
<td>30 Au0</td>
<td>0.00</td>
<td>0.00</td>
<td>8.72</td>
<td>0.01</td>
<td>51.87</td>
<td>0.00</td>
<td>2.49</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>30 pH20</td>
<td>0.00</td>
<td>0.00</td>
<td>7.44</td>
<td>0.03</td>
<td>7.29</td>
<td>0.08</td>
<td>2.88</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>30 2x</td>
<td>0.00</td>
<td>0.00</td>
<td>1.09</td>
<td>0.00</td>
<td>17.11</td>
<td>0.01</td>
<td>0.42</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>30 4x</td>
<td>0.00</td>
<td>0.00</td>
<td>1.07</td>
<td>0.00</td>
<td>6.82</td>
<td>0.00</td>
<td>0.11</td>
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</table>

Figure 31: Nutrient release of 30% clay and 70% clean sand from AuNPs interaction.

### 40% clay and 60% clean sand

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Na (µg/g)</th>
<th>Mg (µg/g)</th>
<th>Al (µg/g)</th>
<th>P (µg/g)</th>
<th>K (µg/g)</th>
<th>Ca (µg/g)</th>
<th>Mn (µg/g)</th>
<th>Fe (µg/g)</th>
<th>Cu (µg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil</td>
<td>Sand + clay</td>
<td>0.02</td>
<td>2.23</td>
<td>51.69</td>
<td>22.78</td>
<td>3072.06</td>
<td>0.07</td>
<td>312.00</td>
<td>0.10</td>
</tr>
<tr>
<td>Effluent</td>
<td>40 Au0</td>
<td>0.00</td>
<td>0.00</td>
<td>5.13</td>
<td>0.00</td>
<td>47.76</td>
<td>0.00</td>
<td>1.09</td>
<td>0.00</td>
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<tr>
<td></td>
<td>40 pH20</td>
<td>0.00</td>
<td>0.00</td>
<td>11.79</td>
<td>0.05</td>
<td>24.41</td>
<td>0.00</td>
<td>4.14</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>40 2x</td>
<td>0.00</td>
<td>3.72</td>
<td>0.17</td>
<td>0.00</td>
<td>6.24</td>
<td>0.02</td>
<td>0.20</td>
<td>0.00</td>
</tr>
<tr>
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<td>1.00</td>
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<td>-0.03</td>
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<td>12.04</td>
<td>0.00</td>
<td>0.11</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Figure 32: Nutrient release of 40% clay and 60% clean sand from AuNPs interaction.