DIETARY SUPPLEMENT SILVER NANOPARTICLES: NO THREAT TO THE ENVIRONMENT

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ABSTRACT

Silver is an effective germ fighter, and silver nanoparticles are widely recognized as being especially effective because of their enormously high surface area to mass ratio. Due to the large number of manufacturers using silver nanoparticles in their products, some concern has arisen about the effects on the environment when these products are disposed of or washed. There even have been concerns expressed about whether or not colloidal silver should be considered a "drug" because of its biological properties. This report will demonstrate that silver nanoparticles do not exhibit harmful properties, nor do they remain "nanosize" when they come in contact with normal environmental samples, such as soil and water, but they agglomerate to form much larger, much less biologically effective, silver particles, which are non-toxic, non-ionic, and have no history of being harmful to the environment or aquatic life.

INTRODUCTION

Silver is a very well known metal. One would be hard pressed to find someone who did not know something about silver, nor who thought of silver as anything but harmless and desirable. It has become evident, however, that colloidal silver, because of the exceptionally small size of the particles, has certain pharmacological properties which may have an effect on environmental biosystems. Recently, the U.S. Environmental Protection Agency (EPA) issued a statement that they were planning to regulate companies that produce nanoparticles for use as anti-microbials. This gives rise to the question, why are the dietary supplement and nanoparticle industries being targeted at this time, and what is the rationale for new regulation of an industry which has previously had no reported harmful effects to humanity or the environment?

The EPA knows that silver nanoparticles are effective as antimicrobials. The reason given by the EPA for their current interest is that silver nanoparticles, or products claimed to be silver nanoparticles, are now being produced by a number of manufacturers. The EPA is concerned that, when these particles are disposed of, there might be an appreciable amount of silver nanoparticles suddenly appearing in the environment. The proposed concern is due to the fact that the silver nanoparticles are so small that their surface area per unit weight is very large: therefore, for a given weight of product, the biological effectiveness, which is proportional to surface area, is far beyond that which would be expected. This much is true and it is part of the reason that silver nanoparticles are so attractive for biological applications. The EPA is not questioning the fact that silver nanoparticles are effective in killing harmful bacteria. Its concern is that, by disposing these particles into sewers or waterways, might there be harmful effects to the environment by eliminating the bacteria which are useful in normal waste degradation?

The last statement shows a misunderstanding of what silver nanoparticles are and what they do. Nanoparticle technology is relatively new to the scientific community for good reasons: nanoparticles are difficult to produce; once they have been produced they are not stable and more significantly they are not stable enough to exist/persist in the wider natural environment for very long.

The purpose of this research is to show that normal interaction of nanoparticles with various constituents of the environment, such as soils and different water sources, is sufficient to cause growth of the particle size and dramatically decrease the biological activity. The observations reported here indicate that silver colloids, which start out as nanoparticles, upon contact with the environment "grow" to much larger clusters, as indicated by their average particle size distribution, (a nanoparticle size measurement),and zeta potential measurements. The zeta potential is altered to be outside of the range required for nanoparticle stability.

Several recent articles show misunderstandings about silver and its nanoparticles. At Arizona State University, Westerhoff and Benn [1] have reported "findings" which have never been observed during the last 15 years at Colloidal Science Laboratories (CSL) claiming that nanosilver particles produce ionic silver when exposed to moisture. This is NOT true! This is tantamount to saying that silver metal is water soluble. At CSL, various forms of silver, ranging from solid silver metal to fine silver powder, have been exposed to water for long periods of time with agitation. No increase in conductivity or silver ion concentration has ever been observed when silver metal in any form is treated with water. Silver metal requires chemical treatment with an oxidizing agent, such as nitric acid or Aqua Regia to produce silver ions. Nor is it true that only silver ions have antimicrobial properties. Colloidal silver is a wonderful antimicrobial by itself, which is a good thing, because silver cations are very reactive with chloride anions to form insoluble, and biologically inert, silver chloride. This happens in the stomach, the bloodstream and in waterways wherever halide and phosphate anions are present.

As this report will show, the high biological effectiveness of colloidal silver does not persist in nature, because the nanoparticles agglomerate as soon as they come in contact with the environment, specifically soil and water. Westerhoff and Benn admit that silver particles "clump" together in the (silver-impregnated) fabrics and in the wash water. That is precisely the point to be considered for environmental safety. How much "clumping" does it take so that the particles are no longer considered to be "nano", but much larger and eliminating their (original) high biological activity.

We examined three different environmental conditions which change the morphology and stability of silver colloids:

(i) the effect of drainage of silver colloids through several soil samples.
(ii) the effect of interaction of silver colloids with different water samples.
(iii) the effect of exposure of silver colloids to sunlight.

EXPERIMENTAL

Sample Selection

The first two questions to be addressed were what environmental samples should be used and to what concentration of colloidal silver should these samples be exposed.

It was decided to limit the environmental samples to the following:

Sand, taken from the New Jersey shore
Soil, taken from central New Jersey,
Soil, taken from Northern Pennsylvania
Local tap water from Westampton, NJ
Sea water, taken from the New Jersey shore
Water from a northern Pennsylvania well

The soil samples represent some of the most common types found on the Eastern Coast of the United States. The sand is essentially an Entisol, a type of soil that is not subject to a great deal of chemical change and is common to areas where natural deposition and removal occur at regular intervals. The New Jersey soil is primarily an Ultisol, containing clay, quartz, kaolinite and various iron oxides. The Pennsylvania soil is most likely a mixture of Alfisols and Inceptisols, which are clays suitable for growing most crops and common to many areas.[2]

The water samples are sea water, rich in many salts, NJ tap water, subjected to routine purification, and Pennsylvania well water, which most likely contains carbonates and nitrates. This range of samples should be sufficient to establish any effect of the environment on silver nanoparticles for this initial study.

Approximately 8 to 10 lbs of each environmental sample were collected. From these, 18 to 20 samples of 20.0 g each were selected, and these were randomized for the testing. The amount of colloidal silver to be used, it was decided that the initial tests should provide information with regard to an overabundance of nanoparticles being released to the environment, rather than just a trace amount. If the environment is not substantially altered by the overabundance, it seems reasonable to assume it will not be influenced by smaller amounts.

Preliminary studies indicated that, at concentrations of up to 6 ppm silver, and probably higher, based on the weight of soil samples, no nanoparticles would survive. Therefore, a more reasonable amount, but still an enormously high concentration for a natural occurrence, was selected.

Colloidal silver samples were dietary supplements and averaged at least 20 ppm silver. Most soil samples require 0.5 to 0.75 their weight in water to start draining. Colloidal silver was therefore diluted 10 to 1 (with de-ionized water) and then applied to each soil sample, so that each sample contained a minimum of 2 ppm of silver nanoparticles, based on the weight of the soil. This would correspond to dumping 27 liters of 20 ppm colloidal silver onto one ton of dirt. Since most consumers of dietary colloidal silver are concerned with teaspoon and tablespoon quantities, it also seems reasonable to assume that the quantities used for this experiment cover something well above the worst case scenario.

Measurements

In each experiment, the selected sample of colloidal silver was mixed with the environmental sample and the change in particle size and zeta potential recorded after a specified time using the Malvern Zetasizer, model Nano ZS. Since the samples in contact with soil contained very large macro particles and rocks, the samples all required vacuum filtration through grade 601 Ahlstrom filter paper to eliminate the natural particles which are 3 to 4 orders of magnitude greater in size than the ones of interest in this study. This filtration had no effect on silver nanoparticles in the absence of additives (soil, seawater, etc). For the tests using environmental water samples, the colloidal silver was diluted 10 to 1 in the water in question.

RESULTS

The initial data in this section shows the properties of the colloidal silver used in these trials. This sample, selected at random, had 81% of its particles with an average size of 1.74 nm, and a zeta potential of -31.7 mV. The data in tables 1 through 6 show the results for the particles found in the fluid after the specified time of contact with the environmental samples in question. For example, in Table 1, when DI water was filtered through the soil samples, no nanoparticles could be found, but only large particles of the order of 300 nm or more.

Table 2 shows that, after only 15 minutes of contact with the soil samples, a decrease in zeta potential, and the smallest particles have increased to the 3 to 8 nm range, and they still represent 80 to 90% of the total.

Table 3 indicates that, after a full 7 days of contact with the soil, but kept away from sunlight, the nano particles have increased 3 to 8 times in size. In Table 4, these results are more dramatic, since the samples were all exposed to the sunlight for the 7 days, with the increases in size being 7 to 20 fold, and the smallest particles now representing only 30 to 40 % of the total.

To obtain the data in Table 5, the colloidal silver was left in contact with the environmental water sample for 21 days in sunlight. The particle sizes have significantly increased (3 orders of magnitude), with a corresponding drop in the zeta potential.

In Table 6, the samples were left in contact with the water samples instead of the soil samples for 7 days in the sunlight. The results of these tests show that each water sample also decreased the zeta potential and increased the particle size.

Properties of Colloidal Silver Used in Testing

Smallest Part., nm	Zeta Potential, mV	Total silver, ppm	Ionic silver, ppm
1.74	-31.7	21.40	9.60

Table 1: Deionized Water (DI).

Filtering Medium	Smallest Part., nm	Zeta Potential, mV	Total silver, ppm	Ionic silver, ppm
Sand	none found	-20.2	0.00	0.00
NJ Soil	none found	-1.5	0.00	0.00
PA Soil	none found	-31.7	0.00	0.00

Table 2: Colloidal Silver - 15 min. contact -7 days later.

Filtering Medium	Smallest Part., nm	Zeta Potential, mV	Total silver, ppm	Ionic silver, ppm
Sand	3.53	-20.6	1.14	0.00
NJ Soil	4.35	-22.2	1.57	0.20

PA Soil	8.30	-21.7	1.05	0.20

Table 3: Colloidal Silver - 7 days contact, no sunlight.

Filtering Medium	Smallest Part., nm	Zeta Potential, mV	Total silver, ppm	Ionic silver, ppm
Sand	5.4	-15.7	1.27	0.00
NJ Soil	9.7	-20.8	0.56	0.00
PA Soil	14.7	-2.8	0.17	0.00

Table 4: Colloidal Silver - 7 days contact, sunlight.

Filtering Medium	Smallest Part., nm	Zeta Potential, mV	Total silver, ppm	Ionic silver, ppm
Sand	11.3	-22.8	0.94	0.00
NJ Soil	26.9	-22.2	0.41	0.00
PA Soil	34.2	-21.2	0.35	0.00

Table 5: Colloidal Silver - 21 days contact, sunlight.

Filtering Medium	Smallest Part., nm	Zeta Potential, mV	Total silver, ppm	Ionic silver, ppm
Sand	>2000	-12.7	0.54	0.00
NJ Soil	>1900	-6.1	0.24	0.00

PA Soil	>1700	-7.6	0.39	0.00

Table 6: Colloidal Silver - 7 days contact.

Filtering Medium	Smallest Part., nm	Zeta Potential, mV	Total silver, ppm	Ionic silver, ppm
Tap water	113	-11.3	0.03	0.00
Sea water	631	-4.6	1.14	0.00
Well water	32.1	-15.7	1.47	0.20

While some of the changes in particle size seem small, one must realize that they represent large changes in loss of surface area and, since biological activity is proportional to surface area, this would correspond to large losses in biological effectiveness. In Figure 1, it can be seen that a change in particle size from 2 to 10 nm represents at least an 80% loss in surface area for the same weight of particles. This is a crude approximation, since the exact morphology of the particles is not known. To make these calculations possible, an assumption has to be made that the particles are spherical and the spheres are close packed.

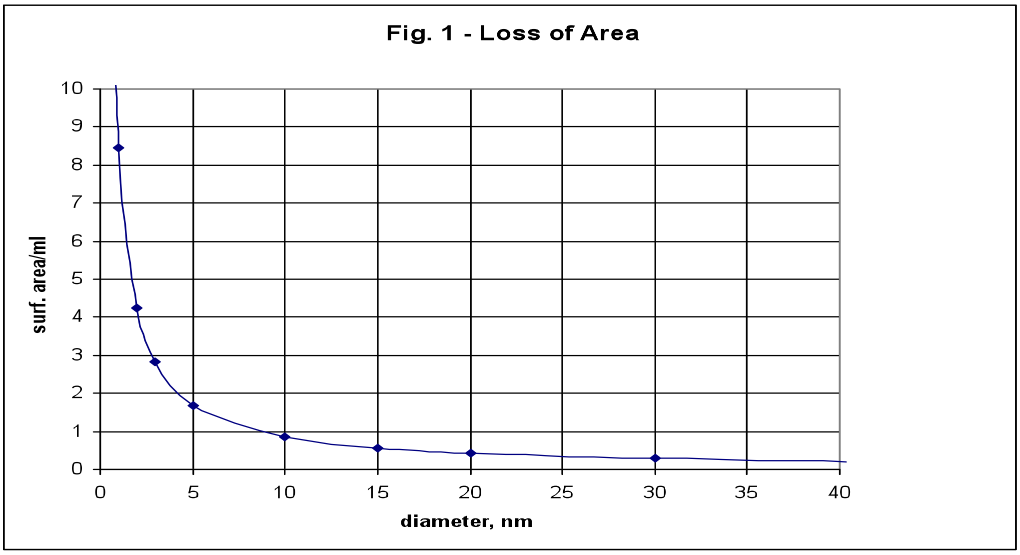
Fig. 1 - Loss of Area

In a previous paper by F. Key and G. Maass,[3] the nature of a colloid was described as being a suspension of very small particles which are stabilized by having a diffuse double layer of solution ions around them. The charge acquired by these particles gives rise to a potential difference (i.e., mutual repulsion) between them that keeps them separate and stabilizes the colloid. This potential difference is called the Zeta Potential, and has been described in countless books on electrolytic effects in solutions. When the colloid is composed of nanoparticles, the task of preventing their agglomeration is not an easy one.

As the previous paper pointed out, if the zeta potential is more negative than -30 mV, then the mutual repulsion between particles is sufficient to keep them separate and stabilize the colloid. However, when the zeta potential is between -15 mV and 0 mV, the particles agglomerate and flocculation or precipitation occurs.

In a 1996 report by t M. Elimelech and A. E. Childress,[4] it was pointed out that for world average fresh water rivers, the concentration of common anions and cations across all normal pH ranges is sufficient to change the zeta potential range from about -10 mV to +5 mV, promoting agglomeration of nanoparticles. In seawater, the agglomeration would be even more pronounced.

CONCLUSIONS

Theoretically, if a very large amount of silver nanoparticles from many sources were to be dispersed into the same part of the environment at the same time, it might be possible that the concentration of some good bacteria, as well as the bad bacteria, would be diminished, but this is not, at this time, considered a serious threat for the dietary supplement nanoparticles. The points to be remembered are as follows:

1. This report has demonstrated that silver nanoparticles will grow to biologically far less active “clumps” even if one dumps 27 liters of 20 ppm colloidal silver on each ton of soil. In practice, this is an enormously high quantity which could not be expected to be reached realistically.
2. In spite of the number of manufacturers producing silver nanoparticles or claiming to be silver nanoparticles, because of the low concentrations in which these products are sold, the total amount which could be released in any part of the environment would still be expected to be very low.

3. As shown by all the experiments above, nanoparticles do not persist as nanoparticles in nature for very long, but grow to harmless clumps of silver metal.
4. Silver nanoparticles are not water soluble, and, therefore, silver colloids will not release silver ions into the environment.

Once agglomeration of the silver nanoparticles occurs, the product is simply a harmless metal which has existed in nature from the beginning of our planet. Most people would not object to finding unreactive silver metal on their property.

REFERENCES

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