CLOUD SEEDING FOR SNOW AUGMENTATION: 566-73

LAND USE RAMIFICATIONS OF RESIDUAL SILVER IODIDE NUCLEATING AGENTS

By

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Introduction

A major goal of snow augmentation is to provide increased snowmelt water supplies for commercial, recreation, and domestic uses. In seeding winter storms in the Western USA, a possible concern in land use planning involves the potential effects residual silver iodide nucleating agents may have on soil microbial processes.

The total amounts of silver iodide which may be present in unseeded and seeded snows have been estimated by O'Rhea et al (1969) at Park Range, Colorado, to be approximately 0.000354 mg/l for 146 unseeded storms, and 0.000844 mg/liter for 175 seeded storms. Cooper and Jolly (1970) have estimated that if a seeding rate of 0.02 gram of silver/ha/cm of precipitation is accepted, then 60 cm of seeded precipitation could deliver 1.2 grams of silver as silver iodide/ha/year, or 0.12 mg of silver per surface square meter. Although these addition rates of themselves would appear to be of little concern, these should be considered in the context of silver retention in soils and aquatic muds, and the potential effects of more soluble silver forms on microbial decomposition processes at less than part per million levels.

Experimental Procedure

Soil Respiration Processes. Effects of varied silver forms on soil microbial respiration processes were carried out by use of a simplified respirameter (Klein, Mayeux, and Seaman, 1972) using undisturbed surface soil cores of 6.5 cm diameter and 8.0 cm depth obtained in the Fort Collins area. Silver in the forms of silver iodide and silver nitrate were added to soils as acetone and water solutions respectively, and respiration indices were carried out over 10 day periods at 25^{o} C in the dark. Soil microbial populations were assayed using standard procedures, with sodium caseinate agar used for total bacteria and actinomycete enumeration, and Rose Bengal agar used for fungal enumeration.

Soil Treatment Plots. The field plot at Nunn, Colorado, used in this study, involving the addition of silver iodide and silver nitrate to field plots at 1, 10, and 100 ppm in the top two centimeters of soil. Sub-plots of 1.5 x 1.5 meters size with 1.5 meters separation between individual plots were replicated on a 4-fold basis. The center 1 x 1 meter area is used for analysis to avoid border effects. Silver nitrate plots were completed using distilled water as a solvent, and silver iodide was solubilized by addition with sodium iodide in acetone. Appropriate solvent controls involving water and acetone additions, plus sodium iodide-acetone control plots were completed.

All plots were installed using spray bottles to provide a uniform addition of the treatment materials over the 1.5 x 1.5 meter areas. Analysis of respiration indices has been completed using standard procedures described previously.

Generator Site Analyses. A ground-based seeding generator site at Emerald Mountain, directly south of Steamboat Springs, Colorado, was used for this study. This generator site was in use for six years prior to 1968, and provides an established silver gradient around the actual generator site across which differences in microbial responses could be evaluated. Sampling sites at ground zero and in the cardinal directions, and at 5, 10, 20, 50, 100, 200, and 500 meters were used. Respiration analyses were carried out on samples from 0-2, 2-4, and 4-6 cm depths, using previously described procedures. Silver analyses were carried out using a persulfate oxidation procedure in a commercial laboratory.

Silver-Microbe Interaction Studies. Evaluation of microbial ability to transform silver originally present in a system as silver iodide to other forms was performed using

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both pure cultures, and natural populations present in field soils. Initial experiments were carried out using non-sterile soil-nutrient agar mixtures prepared by adding up to 10% w/w of either surface or sub-surface soils to molten nutrient agar before pouring plates where the medium would solidify. Upon incubation, the soil microorganisms are capable of producing a confluent lawn of mixed microorganisms.

Immediately after completion of the nutrient agar-soil plates, silver in the forms of silver nitrate (10 mm filter discs soaked in 0.1% w/w solutions), silver iodide (approximately 20 mg placed on the agar surface in a diameter of 4 mm, using a polyethylene funnel), or silver oxide (20 mg on agar over a circle of 4 mm) were placed on the agar surfaces. The plates were incubated in the dark at 27^{o} for up to 6 weeks using a humidified atmosphere.

Responses of soil microbial populations to the presence of gradients of free silver ion were completed by use of gradient plates. These were prepared by use of a first gradient of nutrient agar containing 0.1% w/w of silver oxide. After solidification, the plate was completed by use of a level layer of nutrient agar containing 10% w/w of a desired soil, or plain nutrient agar. Plates were streaked with 10^{-4} dilutions of desired soils and allowed to incubate in the dark before evaluation of microbe-silver interactions.

Ability of soil microbes to reduce silver by production of volatile materials was tested by addition of silver iodide or silver oxide on cover slips placed on completed soil agar plates. Silver on cover slips was tested for possible reduction using both dry forms, and the dry forms placed on water-saturated filter discs to determine if moisture was required for possible absorption of volatile materials.

Investigation of possible volatile material production also was carried out using surface and sub-surface samples. Possible amine-containing volatile materials were trapped using phenylisothiocyanate and 5% w/w hydrochloric acid solutions (Shriner, Fuson, and Curtin, 1956). These solutions were placed in watch glasses (0.1 ml of reagent) in the petri dish after completion of maximal growth. Absorption was allowed to proceed for a 2 week period before completion of derivatization procedures. All experiments were carried out at 27^{o} C in the dark.

Results

Soil-Silver Interaction Studies. Silver iodide added to soils directly as a fine powder will not have discernible effects on soil respiration processes when carried out over short-term experiments. Up to 1.0 gram of silver iodide added to 100 grams of soil was not able to cause discernible decreases in all-over microbial respiration rates. Addition of silver in the form of silver nitrate, a freely-soluble silver form, was capable of causing discernible decreases in soil respiration rates when added at 1.0 ppm, and essentially complete cessation of microbial respirations occurred when 100 ppm were used, indicating that the form of silver added to a natural environment is more important that the total amount added.

As silver ion is rapidly inactivated in the presence of many anions, including varied halides, additional studies of field condition effects on respiration processes have been completed.

For these studies, the soil treatment plot installed in the spring of 1971 was examined in the fall of 1972, after 18 months of microbial interactions with the added silver forms. The presence of 100 ppm of silver, either in the form of silver nitrate or silver iodide was not capable of causing decreased microbial respiration.

These results would indicate that silver presence at levels which would exceed accretion rates over extended seeding and snowmelt conditions should have minimal negative effects on soil microbial respiration rates.

To extend these results further in a more ecological time-dose context, the responses of microorganisms to a silver gradient in the vicinity of a seeding generator site were examined.

Results of these studies are shown in figure 1, for the east-west direction across the generator site at 0-2 and 2-4 cm depths, and in figure 2 for the 4-6 cm depth in an east-west direction and for the 0-2 cm depth in a north-south direction. The peak of silver in the 20 meter west location reflects a mis-alignment of the sampling grid in relation to the actual seeding generator site.

In general, the highest respiration rates and microbial populations were correlated with the higher silver levels. As noted in figure 1, the major correlation observed with the 0-2 cm soil depth is between the residual silver levels and the all-over respiration of the soils. Thus, it would appear that silver, instead of causing a direct inhibition of soil respiration processes, may by either direct or indirect means be related to increased levels of microbial activity. Correlated with this higher level of silver and microbial activity, a higher percent of water content and decreased pH were observed. This would indicate that these soils, with higher silver levels, were actually tending to go anaerobic where fermentation products might accumulate. The general levels of microbes per gram of soil were also higher in the high silver content zones. The similar east-west transect data for 2-4 cm depth again show the same series of relationships seen in the surface soils in spite of the generally lower silver levels.

The east-west data for the 4-6 cm depth are of greater interest (figure 2), in that the characteristic litter-humus character of the soil has been transformed to a more conventional soil profile. Even under these conditions with maximum silver concentration of 10 ppm, it is still possible to observe a similar set of respiration-organic matter-silver relationships. The pH and moisture level gradients also indicate that a major shift in conditions has occurred, which would reflect a higher organic matter, more acidic anaerobic environment.

The data for the surface transect in the north-south direction across the Emerald Mountain Ridge are given in the lower portion of figure 2. The general wind travel in the northerly direction toward Steamboat Springs can be correlated with the general increase of silver concentrations to 50 meters, followed by a 10-15 ppm residual silver level out to the 100 and 200 meters sampling points. Again, the general silver-organic matter-soil respiration relationship observed earlier is shown.

To summarize the general results at these generator sites, the presence of silver does not appear to cause a diminution of microbial activity, but may actually be related to increased respiration and accumulation of organic materials. The only postulation by which this might be expected to occur is if, in the presence of silver, there is a selective reduction in degradation rates for some plant material components. Thus, the organisms present per unit of organic matter may be decreased, and they may show a decreased oxygen use, and yet show a positive relationship with residual silver based on total soil weight.

Thus, the presence of increased amounts of silver may lead to increased microbial populations and soil organic matter instead of causing a decrease in these parameters. A retardation of anaerobic cellulose decomposition in aquatic muds with 1.0 ppm of added silver iodide has been noted (Sokol, Jarzyna, and Klein, 1973) and may indicate that under relatively higher rainfall conditions where soils would tend to be more anaerobic, that retardation of degradation rates for natural materials may occur. Increased sensitivity of anaerobic decomposition processes to the presence of silver has been postulated by Cooper and Jolly (1970).

<u>Silver-Microbe Transformation Interactions</u>. Silver added to soil in the form of silver iodide, or a burn mixture of complexed materials, has usually been considered to accumulate and reside in the soil predominantly in that form. To test for possible interaction of silver iodide with soil microorganisms a series of initial experiments using agarized soil plates and silver in the forms of silver nitrate, silver oxide, and silver iodide were completed.

It was hoped that these experiments would indicate an ability of higher soil levels to inactivate free silver, thus providing an index of silver toxicity suppression in the presence of soil constituents. Surprisingly, the result of this experiment was to indicate that soil microbes are capable of causing reduction of silver ions and silver iodie to

Figure 1. Microbial responses to a silver gradient at 0-2 and 2-4 cm depths in an east-west direction at the Emerald Mountain Seeding Generator Site.

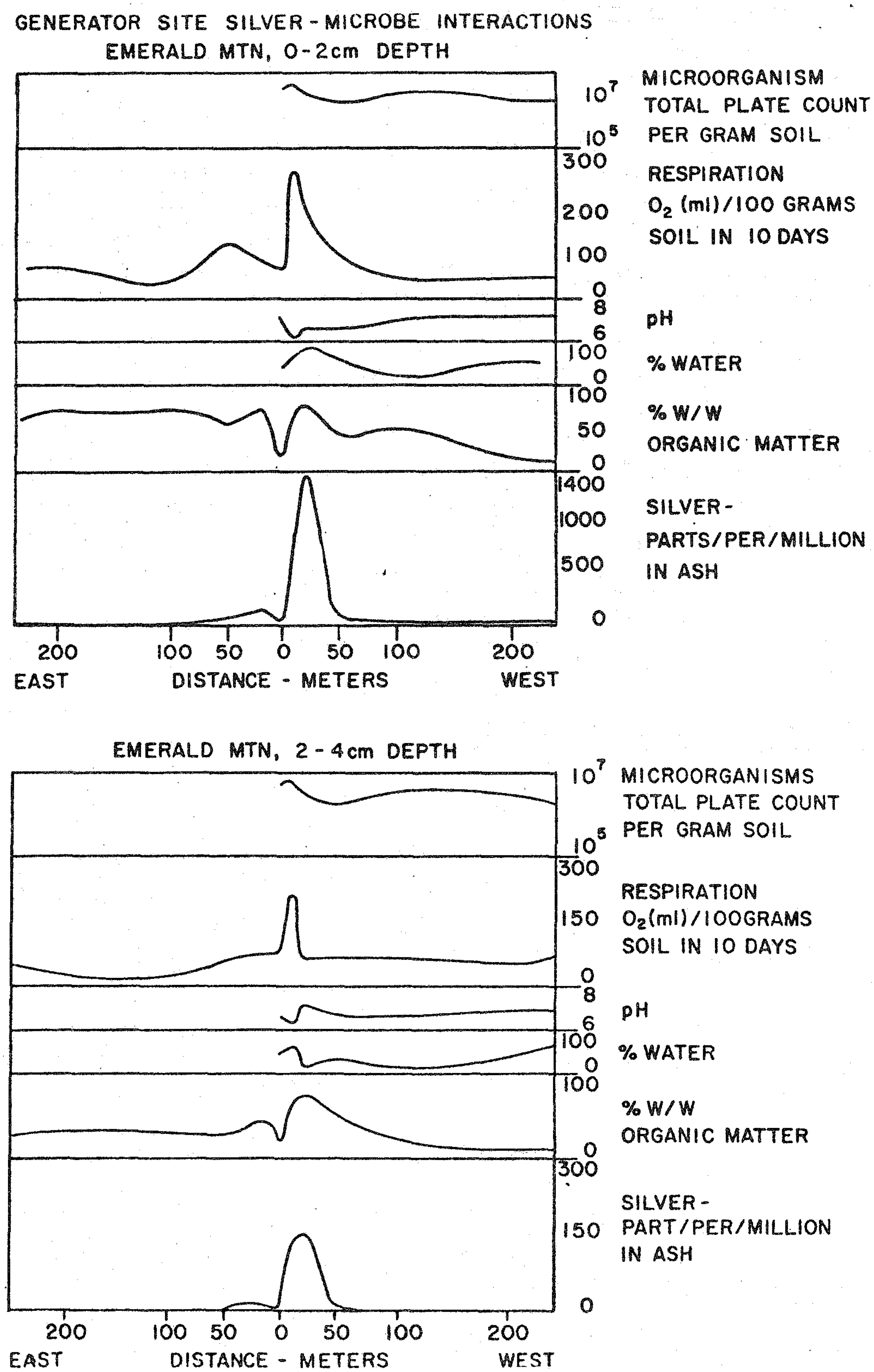
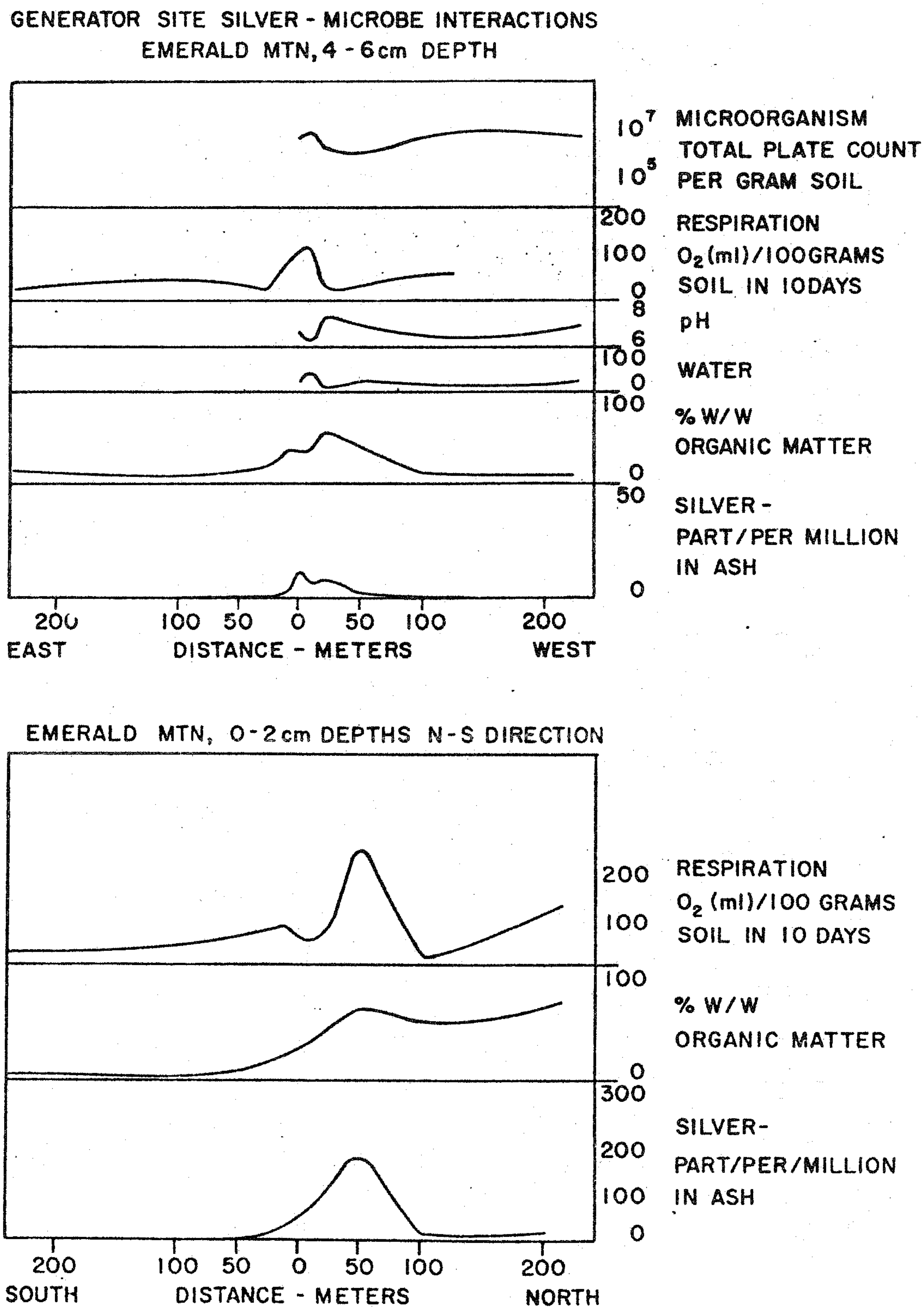


Figure 2. Microbial responses to a silver gradient at 4-6 cm depth in an east-west direction and at 0-2 cm depth in a north-south direction at the Emerald Mountain Seeding Generator Site.



metallic silver, and that silver reduction by microbial processes was stimulated in the presence of higher elvels of soil organic matter. This experiment also allowed observation of silver iodide inhibition of soil microorganisms, indicating that in spite of minimal solubilities quoted in the literature, sufficient free ion can be released, even in the presence of non-heated soil organic matter, to cause inhibition of microbial growth processes. This experiment was also repeated using silver oxide and metallic silver, where microbial growth inhibition and silver reduction could be observed.

Additional experiments were then set up using gradients of silver oxide, found to be an ideal source of low level free silver ion to test for the presence of specific microbes which will have a capability to reduce silver iodide and free silver ion to metallic silver. Soils from the seeding generator site ground zero area, and control soils from a 500 meter distance were used. Soils in both areas contained specific organisms capable of silver reduction.

During these studies, it was noted that all soil plates where active silver reduction was taking place had a strong amine or ammonia odor. Based on this organoleptic observation, test interaction systems between a series of aliphatic amines and silver nitrate, silver iodide and silver oxide were completed. Strong silver reduction in the presence of amines was observed.

This observation was also confirmed by examination of relevant inorganic chemistry literature (Gmelin, 1972), where silver iodide and free silver ion reduction by a wide range of amine-related compounds has been described.

Based on these observations experiments to trap microbially-produced volatile amines by derivatization were carried out. In the presence of phenylisothiocyanate, specific for trapping amines, a crystalline material has been recovered, tentatively an aliphatic amine of low molecular weight. Characterization of phenylisothiocyanate derivates by melting point determinations has indicated that methylamine and dimethylamine are produced by these microbes.

Thus, silver iodide will not be the only form of silver which can accumulate in a soil as a possible consequence of weather modification. It will be necessary to first determine the possible sequence of products which can accumulate under a given set of environmental conditions, and then to test the effects of that particular combination of silver forms on the biological system of concern.

Silver iodide dissociation to Ag and I^- is felt by various authors (Gmelin, 1972), to be either thermodyanamically prohibited, or at best only a slight possibility based on theoretical calculations.

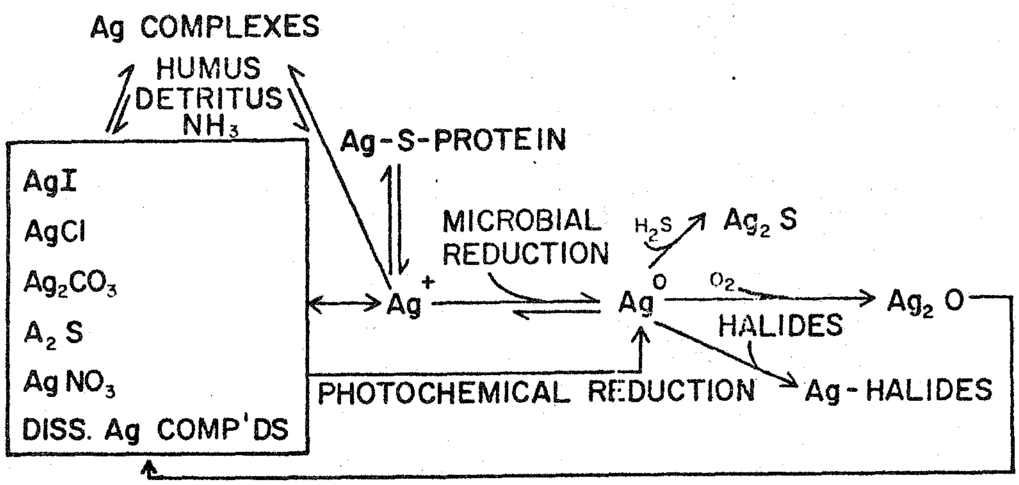
However, there is ample evidence cited (Gmelin, 1972) to indicate that silver iodide can react with zinc, cadmium, aluminum ion (under acidic or alkaline conditions), methylamines, pyrogallols and hydroquinones, to yield metallic silver at field soil temperatures. Other reduction reactions which have been described include interaction between heavy metals, salts and with ψ-amino-phenolic compounds.

Direct silver reduction in the presence of H_2 gas has been described, the known ability of diverse microbes to produce H_2 gas under reducing conditions should be considered (Brock, 1970).

Silver in the metallic form (Gmelin, 1972, A3, page 61) has been observed to be transformed in soil to the chloride form, followed by formation of silver sulfides. Formation of silver chloride can be quantitative in well-aerated soils. Silver sulfides can also be formed in the presence of sulfur-containing amino acids common to soil organic matter and microbial cells.

The forms of silver cited above are also known to be transformed to silver oxide, a readily ionizable form of silver, under a variety of conditions again described in Gmelin (1972) section B1. The description of Hydrogen peroxide-mediated silver oxide production from metallic silver is of interest as microorganisms are known to produce this oxidizing agent (Brock, 1970).

The following silver reactions can be postulated, based on information obtained to date:



Although there is no definitive evidence for the presence of free silver ion in soils, the existence of a series of reactions, both chemical and biological, which could yield the free ion makes it necessary to consider possible free ion effects on microbial processes in soil, even if at low and transient levels. The full significance of these silver transformation reactions for prediction of long-term ecological effects of weather modification-derived silver remains to be determined.

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