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THE TOXICITY OF SPENT PHOTOGRAPHIC SOLUTIONS AND OTHER SILVER COMPOUNDS AND THEIR MIGRATION IN SOIL

by

Claudine Ann Kasunic

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APPROVAL BY THESIS DIRECTOR

This thesis has been approved on the date shown below:

Dean E. Carter
DEAN E. CARTER
Associate Professor of Toxicology

November 3 1982
Date

To my father and mother,

Stephen G. Kasunic and Arlene G. Kasunic

and to my sisters,

Dorothy Anne Kasunic and Mary F. Kasunic

for their love, prayers, and encouragement

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ABSTRACT

The silver content of the waters, stream sediments, soils, and vegetation, in a canyon contaminated with spent photographic fixing bath solutions was determined. The total silver concentration in the canyon decreased with increasing distance from the mouth of the waste outfall. At a distance of approximately 300 m the silver levels of the vegetation approached those of the background. The silver content of the sediments and the soils, however, remained significantly higher than background for a distance of 420 m. Soil column experiments showed that silver solutions are attenuated by the soil at different rates and apparently by different mechanisms. The silver thiosulfate complex in the spent fixing bath solution is believed to be reduced to silver sulfide in the soils. The silver ion in silver nitrate and silver sulfate solutions probably replaces the Na^+ and/or K^+ ion in the clays present in clayey-skeletal Typic Eutroboralf soils. The phytotoxicity of the spent fixing bath solutions is due primarily to the presence of excess sodium ion. This reduces the ability of a plant to absorb water and essential mineral nutrients and leads to a decrease in productivity.

INTRODUCTION

Silver is ubiquitous in nature. It has been detected in rocks, soils, plants, animals, natural fresh waters, the sea, and the atmosphere. In biological systems, however, it is classified as a nonessential trace element and is known to be toxic to plants, animals, and man.

Although silver has been utilized by man in jewelry, artistic objects, and coinage for more than five thousand years, its recent use in industry has increased the environmental burden of silver contaminants. The average net industrial silver consumption is estimated at 150 million troy ounces of silver (1). Over half, approximately 80 million troy ounces, is lost to the environment annually (1). Most is disposed of onto the land in the form of innocuous minerals, metal, or alloys and is largely immobilized. However, up to 27 million troy ounces of silver enters the environment annualy as chemicals whose concentration, chemical, and/or physical properties increase its potential for pollution. A great deal of this silver is lost to the atmosphere in emissions from such sources as iron and steel production, cement manufacture, and fossil fuel combustion. The greater loss, however, is incurred during the disposal of photographic processing wastes. Approximately 16 million troy ounces of silver is lost annually as thiosulfate complexes in spent fixing baths discarded directly to municipal sewers by small photofinishers and amateurs (1).

Based on available data for the sedimentation values for copper, between 50% to 70% or more of the silver is removed from the sewage in the form of silver adsorbed to organic matter (1). This is eventually trapped in the sewage sludge. The remaining silver is discharged in the municipal treatment effluent where the silver is probably present as thiosulfate complexes, colloidal silver chloride and sulfide, or as soluble organic complexes (1).

The use of sewage sludge to fertilize cropland, and the use of sewage effluent for irrigation, is the most probable source of soil contamination by silver and one of its most likely points of entry into the food chain. Although present concentrations of silver found in the environment appear to offer little hazard to humans, food crops grown in sewage amended soils may accumulate silver in greater amounts (1). At present, little is known of the mobility, fixation, or plant bio-availability of silver in soils exposed to spent photographic solutions Few data are available on the response of plants grown in such soils or in other silver enriched soil.

Beginning in the late 1940's the Los Alamos National Laboratory at Los Alamos, New Mexico began discharging spent photographic solutions directly into a canyon situated within its grounds. For a period of 20 years, Canon de Valle received significant quantities of silver, $\geq$ 12 g/l (1) as silver thiosulfate complexes in untreated spent x-ray fixing baths. While there are no records on the total volume of waste discharged into the canyon, the discharges were more frequent in the late 1950's to mid 1960's when the Laboratory developed x-rays

24 hours a day. In the mid 1960s, the x-ray developing dropped to 16 hours a day for a few years before tapering off to a 8 hr/day, 5 day/ week schedule. Approximately 8 months prior to this survey, the Laboratory began recovering the silver from the x-ray fixing baths using ion-exchange columns before discharging the waste into the canyon.

The purpose of this study was four-fold: 1) the extent of contamination was determined by an investigation of the silver content of the waters, stream sediments, soils, and vegetation of Cañon de Valle; 2) the degree of mobility and fixation of various silver compounds in the soil was determined by a series of soil column effluent studies examining spent fixing bath solution ($Na_3Ag(S_2O_3)_2$), and silver nitrate ($AgNO_3$) and silver sulfate (Ag_2SO_4) solutions; 3) the phtotoxicity of these solutions and that of fixing bath solution ($Na_2S_2O_3$) was examined using germination, lethality, potential gross productivity and net productivity as indices of toxicity; 4) various digestion procedures were examined to determine a suitable method that would yield a sufficiently high percentage of silver recovery for the analysis of samples by atomic absorption spectrometry.

LITERATURE REVIEW

Silver Toxicity in Birds, Mammals, and Man

In man, silver is absorbed and retained by all tissues and accumulates in the body with age. The most common effect of chronic human exposure to silver is generalized argyria, characterized by a slate gray pigmentation of the skin and hair due to deposition of silver in the tissues. The average human dietary intake of silver from food is estimated at 0.088 mg/day (2). Argyria, however, has been found almost exclusively after occupational or therapeutic exposure to large amounts of silver (0.91 g total minimum necessary absorption) (1). Although argyria generally carries no recognizable health disturbances, some authorities have suggested that kidney lesions with consequent danger of secondary arteriosclerosis may be related to this condition (3,4).

Experiments with birds and mammals suggest that long term exposure to silver in the diet may have other adverse effects. These include lowered immunological activity (5), altered membrane permeability (6), enzyme inhibitions including antagonism to copper (7,8,9) and selenium metabolism (10,11,12), vascular hypertension (13), and growth suppression (7,14,15).

Sample Preparation and Storage

Analytical accuracy is dependent upon a number of factors, including the proper selection and cleaning of sample containers, the

correct handling and storage of sample material, and the inherent sensitivity of the method of analysis.

Because the sample container represents one of the earliest and potentially one of the largest sources of contamination, much of the analytical accuracy will depend on the proper selection and cleaning of sample and storage containers. Moody and Lindstrom (16) examined a number of plastic materials including bottles constructed of conventional polyethylene (CPE), linear polyethylene (LPE), polypropylene (PP), polymethylpentane (PMP), polycarbonate (PC), poly vinyl chloride (PVC), and several types of Teflon (TFE, FEP). Specimens of ethylene tetrafluoroethylene copolymer (Tefzel or ETFE), Teflon PFA, polystyrene (PS), and Teflon pipe sealing tape were also examined. Their studies included a gravimetric determination of water loss from the bottles, and an analysis of the impurities contained within and leached from the plastics. In the gravimetric study all of the bottles had water loss rates adequate for short term storage of aqueous samples with two of the bottles (PP and CPE) exhibiting rates of water loss compatible for storage over long time periods. Data previously obtained by Moody et al. (17) showed a similar low rate of water loss from 1-L Teflon FEP bottles. A comparison of the trace elemental contaminants present in the various plastics found CPE and Teflon TFE to have the least amount of impurities. This is in agreement with numerous other workers (18). The investigation of acid cleaning methods examined (1:1) mixtures of concentrated HCl or concentrated HNO_3 and water to determine their relative effectiveness in leaching various elements from the different plastics. Although, with

the exception of Teflon FEP, the (1:1) mixture of concentrated HCl and water was a better cleaning agent overall, the (1:1) mixture of concentrated HNO_3 and water was more effective in removing silver from the containers.

Conversely, the problem of metallic ion adsorption on container walls during sample collection, handling, and storage is another factor to be considered. The adsorption of silver by containers varies with concentration, pH, contact time, composition of dissolved salts, type of container, complexing agents, and light effects (19-24). Struempler (23) examined the adsorptive characteristics of silver in borosilicate glass, polyethylene (PE), and polypropylene (PP) containers at different acidities and varying temperature and light conditions. During a 36-day aging period, little silver was adsorbed on borosilicate glass or polyethylene container surfaces when the test solutions were maintained at pH 2. An increase in silver adsorption was noted, however, when the test solutions were raised to pH 4.5. When test solutions were maintained in polypropylene containers, there was a rapid loss of silver, irrespective of the acidity. In the study to determine the effect of temperature and light on silver adsorption, the test solutions were maintained at pH 2. Polypropylene containers were not included in this investigation. When the test solutions were exposed to light, there was a rapid and linear adsorption of silver ions on both the borosilicate glass and polyethylene containers. No adsorption loss was noted in those solutions maintained in the dark, except for the frozen polyethylene test sample, which sustained some adsorption loss after 8 days of aging. The erratic behavior of aged silver was also

investigated. Using test solutions maintained in the dark at pH 2, the percent relative standard deviation (n = 6) was determined for each of the test samples. The greatest deviations were noted in those solutions maintained in borosilicate glass at room temperature. The smallest deviations, obtained in the polyethylene test solutions, reflected precisions between 1 and 2 percent relative standard deviation. Consequently, of these three materials, polyethylene is the preferred container for work with silver ions. This study further recommended that test samples be acidified with HNO_3 to pH 2 and maintained in the dark to minimize container adsorption.

West, West and Iddings (24) studied the adsorption characteristics of traces of silver on selected surfaces in the presence of various complexing ligands. The materials examined were: Teflon, "Vycor" silica glass, polypropylene, polystyrene, and coatings of paraffin, acrylic spray, and Tygon paint applied to polypropylene beakers. The ligands considered in this study were: 0.1M solutions of ammonia, disodium salt of ethylenediaminetetraacetic acid (EDTA), and ethylenediamine, 0.1M and 1.0M solutions of sodium thiosulfate, and 0.1M, 0.01M and 0.001M solutions of sodium chloride. Silver concentrations studied were 0.05 mg/l-1.0 mg/l. Although Teflon adsorbed silver more rapidly from samples with lower concentrations of silver, of all the materials investigated, it exhibited the lowest and most delayed rate of silver adsorption. Of the ligands studied, 0.1 M $Na_2S_2O_3$ was most effective in preventing the adsorption of silver on all surfaces studied. An adsorption loss of less than 1% was found over a 30 day

contact period. The EDTA solution was an effective stabilizing agent for extended contact periods with Teflon and silica glass, but lost its effectiveness after a 64 hour contact period with any of the other materials. Ammonia was only partially effective as a stabilizing ligand, while ethylenediamine and sodium chloride acted to concentrate silver on surfaces.

To insure analytical accuracy and to reduce the possibility of contamination, nonaqueous samples, such as those of soil and organic matter must also be treated appropriately. Surface contamination of organic material by dusts and soils in a contaminated environment can result in elevated levels of the element in unwashed or poorly washed material (25). Van Loon reported washing vegetation by hand with a laboratory detergent solution, while Ward et al. (26) washed organic samples by agitation in slowly running tap water, followed by a distilled water rinse. Both soil and vegetative samples were subsequently dried for 3 days at 60°C (26). Due to the relatively small sample size used in analysis, 0.1-2.0 g for atomic absorption (26,27) and 0.5-1.0 g for neutron activation analysis (28,29), homogeneity of the sample is essential. Ward et al. (26) achieved this by sieving the soil samples and stream sediments to -60 mesh. Bea Barredo (26), however, used powdered rock samples, while Greig (29) ground dried organic samples with Teflon utensils to obtain a homogenous sample. These samples could then be further processed for silver analysis by atomic absorption spectroscopy or neutron activation analysis.

Atomic Absorption Spectroscopy and Neutron Activation Analysis

Several methods are employed in the dissolution of samples prior to analysis by atomic absorption spectroscopy. Ward et al. (26) digested 0.1 g samples of soil with 10 cm^3 of a 1:1 mixture of concentrated nitric and hydrofluoric acids in 50 cm^3 polypropylene squat beakers. The solutions were taken to dryness and the residues redissolved in 10 cm^3 amounts of hydrochloric acid. Bea Barredo et al. (27) prepared solutions using a modification of the Abbey method (30). In this procedure 5 ml of concentrated nitric acid, 5 ml of concentrated hydrochloric acid, 5 ml of 70% perchloric acid, and 15 ml of 40% hydrofluoric acid were added to 2 g of finely powdered rock sample. The mixture was heated on a hotplate at about 120°C until dense vapors from the decomposition of $HClO_4$ began to appear. Five milliliters of distilled water was added and the solution brought to dryness. To the residue, 5 ml of concentrated hydrochloric acid was added and the solution again evaporated to dryness. In the final step, 30 ml of 0.5 N HCl was added and the solution gently heated to dissolve the residue completely.

In the dissolution of organic material, Rooney (31) used a wet-oxidation method similar to that described by Nangiot (32). Up to 0.5 g of material was weighed into a 150 ml squat beaker to which 5 ml each of concentrated nitric and perchloric acids were added. The beaker was covered and the contents evaporated on a hot plate at a rate such that the nitric acid boiled off in 10-15 minutes and the perchloric acid began to fume. Following oxidation, the cover was removed and the

clear solution evaporated to dryness. The residue was then redissolved in 2 ml of a (1:1) mixture of nitric acid and distilled water, cooled, and transferred to a 25 ml calibrated flask where 2 milliliters of a 2% tartaric acid solution was added. The beaker was then rinsed with 5 ml of a (1:1) mixture of ammonia and distilled water, the solution added to the flask, and the mixture brought to volume with distilled water. Analysis of the dissolution samples were carried out using standard operating conditions for the particular atomic absorption spectrophotometer available.

Because neutron activation analysis (NAA) is inherently sensitive and is a simple and rapid method of analysis, requiring little if any sample preparation, it is one of the preferred methods for the detection of silver. Nadkarni and Morrison (28) analyzed 0.5-0.9 g geological samples sealed in high purity quartz vials along with approximately 5 µg silver standards. The samples were irradiated for 100 hrs at a thermal neutron flux of 2×10^{13} n cm^{-2} sec^{-1} or for 8 hours at a flux of 3.5×10^{12} n cm^{-2} sec^{-1} and then allowed to "cool" for several days before processing. Purely instrumental NAA was deemed impractical for determining the small silver content of the samples ($\leq$0.07 ppm) because the presence of high activity of major and other minor trace elements would swamp the small amount of silver activity produced after irradiation. Therefore, radiochemical separation, utilizing a resin- Srafion NMRR ion exchange column, was employed to concentrate the silver before analysis.

The isotope of silver generally used in neutron activation analysis is ^{110m}Ag with a half life of approximately 253 days. This silver isotope emits several gamma rays of which 0.658, 0.885, 0.937, 0.764, and 1.384 MeV are the most prominent (33). In their investigations, Nadkarni and Morrison (28) analyzed the samples for ^{110m}Ag nuclide utilizing a 56 cm^3 coaxial Ge(Li) detector at 0.658 MeV. At this photopeak the possible interfering nuclear reactions are $^{110}Cd(n,p)^{110m}Ag$ and $^{113}In(n,\alpha)^{110}Ag$. However, serious interference with the determination of silver is precluded due to the (a) low natural abundance of both ^{110}Cd and ^{113}In, (b) the poor cross sections of both these reactions compared with the $^{109}Ag(n,\gamma)^{110m}Ag$ reactions, and (c) the high thermal-to-fast neutron ratio in the irradiation positions used.

In Greig's investigations (29), up to 1 g of dried organic matter sealed in quartz tubing was bombarded with neutrons at a flux of approximately 2×10^{13} n $cm^{-2}sec^{-1}$ for a total of 10 hours. However, unlike Nadkarni and Morrison (28), Greig (29) did not concentrate the silver before analysis, but instead left the samples to "cool" for 3-5 weeks to allow the short-lived isotopes to decay to a point where interference with the silver nuclide was negligible. The samples were then analyzed for ^{110m}Ag nuclides with a lithium-drifted germanium detector.

Environmental Investigations

The average silver content of all types of soils, excepting those over mineralized zones, is approximately 0.30 ppm (34), ranging from 0.01 to 5 ppm (35). The silver content of plants similarly spans a wide range, varying with location and species (36-38). In general, plants growing in regions of silver mineralization have higher silver content; a fact which has been profitably exploited as a means of geochemical prospecting (37,39,40). The most effective methods, however, appear to be those based on the sampling of stream sediments and soils, as in some cases, there may be no correlation between the amount of silver in a plant and the content of the element in its soil substrate (36). Although investigations of environmental contamination from various heavy metals such as cadmium, copper, lead, and zinc have been reported (41,42), very few studies have concentrated on silver pollution from industrial or mining activities. Ellis (43), however, reported significant accumulations of copper, zinc, lead, and silver in trees growing in several drainage areas of the highly mineralized area of northwestern Washington and northern Idaho, while Ward et al. (26) investigated the silver content of soils, stream sediments, waters, and vegetation near a silver mine and treatment plant. In their investigations several sample collection sites were selected and their distance from the source of contamination measured. Non-affected areas were also included to provide comparison data on the natural abundance levels of the element. From these data the degree and extent of contamination

was effectively assessed. In general, the level of silver concentration decreased with increasing distance from the source of pollution (26).

Soil Studies

The soil is a dynamic system where numerous reactions take place at any one time and where conditions constantly change (44). Chemicals that enter the soil are subject to the influence of several interrelated and interacting factors that operate to retain or mobilize a particular element. Principal among these are: soil drainage conditions, pH and normal redox potentials, the presence of complexing agents, and the presence of precipitating constituents (34,44). In soil/chemical evaluations, a customary starting point is the determination of the relative mobility of a particular chemical or element within the soil. As an index of response, mobility measurements provide the investigator with a means of comparing many different chemicals whose mecshanism of attenuation may differ (44). From these studies other important information may be gathered. With a knowledge of the basic chemical character of the soil, data on the rate of migration of a particular element, along with any observed change in pH of the solution as it passes through the soil, assists the investigator in determining which chemical reactions may or may not be operative. The information thus gathered serves to designate the direction of future soil/chemical studies.

Several investigators (45-48) have examined the movement of trace elements through different types of soils. Prior to their elution studies the soils were characterized as to type, including percentage

of clay, sand, etc., pH, surface area, electrical conductivity, cation exchange capacity, and trace element concentration. The soils were then passed through a 2 mm sieve and uniformly packed in 5 cm or 10 cm diameter PVC columns to a depth twice that of the diameter (i.e. 5 cm dia x 10 cm depth). Test solution reservoirs were subsequently attached to the columns and the flow adjusted to maintain as uniform an elution rate as possible. Throughout the experiments, sample effluents were periodically collected and analyzed for trace element content, and the sample elution continued until one of three conditions was met: breakthrough (effluent concentration = influent concentration), steady state (unchanging or very slowly changing effluent concentration at a value below that of the influent concentration), or continued absence of the element after extended leaching. From these data the migration and/or attenuation of the trace elements, i.e. mass adsorbed per gram of soil per milliliters of added eluent, could be determined.

Productivity Measurements

The phytotoxicity of a particular compound or element may be determined from measurements of productivity, germination, root growth, and/or lethality.

Basic or primary productivity is defined as the rate at which energy is stored by photosynthetic and chemosynthetic activity of producer organisms (chiefly green plants) in the form of organic substances that can be used as food materials (49). The overall equation for this photosynthetic process is:

$$H_2O + CO_2 \xrightarrow{\text{light}} (CH_2O) + O_2$$

where (CH_2O) designates the carbohydrate formed as the end product (50). Productivity is defined in two different ways (49). Gross primary productivity is the total rate of photosynthesis, including the energy used in respiration. Net primary productivity is the rate of storage of energy in excess of respiration losses.

Several methods are used in the measurement of productivity. Where there is little or no consumption of plants and where a steady state is never reached, the harvest method is commonly employed. By simply "censusing" or counting and weighing the plants present at any one time, the net productivity of a system may be determined (49). Chlorophyll content serves as an index to potential gross primary productivity (49). All photosynthetic cells contain one or more of the light absorbing pigments known as chlorophylls. In green plants there are two forms of chlorophyll: chlorophyll a and chlorophyll b. Accessory pigments such as the carotenoids and phycobilins, having absorption maxima at wavelengths other than that of chlorophyll, serve as supplementary light receptors for portions of the visible spectrum not completely covered by chlorophyll (50). However, whenever light energy is absorbed by these pigments, it must be transferred as excitation energy to chlorophyll molecules before it can be used for photosynthesis (50). Chlorophyll, the major light-absorbing pigment in most green cells, is, thus, indispensible to the photosynthetic process (50). Because there is a strong correlation between

chlorophyll content and photosynthesis (50), chlorophyll determination is a useful tool in assessing potential gross primary productivity (49).

Chlorophyll concentrations are relatively easy to determine. The pigment may be readily extracted from plant material with acetone and measured by a spectrophotometer at specific wavelengths. From these data a quantitative measure of chlorophyll may be determined. Vernon (51) described such a spectrophotometric procedure for the determination of chlorophyll. In a typical experiment, 70 g vegetative samples were diced and placed in separate Waring blenders. A 250 ml aliquot of acetone was added and the samples were homogenized and filtered. The filter cake residues were then washed with aqueous 80% acetone and the filtrates brought to a final volume of 500 ml with 80% acetone. This solvent was selected because small variations in plant water content would have less effect on the calculated percentages when using 80% acetone rather than either 90% or 100% acetone as a baseline. The absorbances of each extract were then measured at 665µm and 649µm using 80% acetone as a reference. The chlorophyll content was then calculated using the following equations:

chlorophyll a (mg/liter) = 11.63(A665) - 2.39(A649)

chlorophyll b (mg/liter) = 20.11(A649) - 5.18(A665)

total chlorophyll (mg/liter) = 6.45(A665) + 17.72(A649)

While productivity and germination may serve as useful indices of phytotoxicity, they are influenced by a number of potentially limiting factors, including temperature, water, the quality, intensity

and duration of light exposure, and the availability of essential mineral nutrients (49). Ten of these mineral nutrients, iron, manganese, copper, zinc, boron, sodium, molybdenum, chlorine, vanadium, and cobalt, although required only in minute quantities, are essential to plants. Those elements and their compounds required in relatively large amounts include nitrogen and phosphorus, as well as potassium, calcium, sulfur, and magnesium (49).

Phytotoxicity of Silver

The phytotoxicity of silver has been demonstrated by its ability to effectively reduce the rates of germination and productivity, limit the uptake of essential mineral nutrients, and alter the soil microbial environment of the plant.

The toxicity of a specified amount of silver is related to the concentration of silver ions in solution rather than to the chemical or physical nature of its source (52). Therefore, those compounds that are very insoluble and/or those that ionize very weakly are relatively non-toxic. Although ionic silver is strongly electronegative and can displace other cations from electropositive sites (53), the principal method of toxic action is believed due to reversible chemical bonding with enzymes and other active molecules at the cell surface (54). Because the binding is highly reversible, an excess of silver is apparently required for sufficient penetration into the cell to cause irreversible denaturation (52).

An interest in the use of silver as a protective fungicide for seed resulted in numerous papers on its phytotoxic effects. While a

silver nitrate dip can be successfully employed to disinfest seed from adhering saprophytes (55,56,57) and pathogens (58,59), because of its thorough action, it is of no value in treating organisms embedded in the tissues (56). Should the silver nitrate penetrate beyond the seed coat to any appreciable extent, the plant embryo is destroyed (55). Thus, the plant embryos of wheat and barley seed with broken seed coats, as well as the embryos of those seeds with permeable seed coats (i.e., peas, beans), are destroyed by the silver nitrate dip (57). Therefore, the toxic effect of silver depends not only on the concentration of silver and the duration of treatment or exposure, but also upon the integrity and/or permeability of the seed coat. However, not all seed coats are as permeable to silver nitrate. Schroeder (57,60) found that the embryos of rye, wheat and barley seed with sound seed coats are uninjured by a 18-24 hour dip in a 5 percent silver nitrate solution. Mead (56) and Nielson and Massey (55) have shown that the embryos of wheat and barley seed dipped for shorter periods of time to be similarly unaffected. The reduced germination rates of these grains reported by other investigators have therefore been attributed to injured seed coats (55).

Alternatively, the silver nitrate treatment may affect the onset of germination and the development of the young seedlings. Burk (58) found that wheat seeds treated with silver nitrate have a delayed onset of germination. The converse was noted with tobacco seeds, because the treatment hastened germination and the development of the cotyledons and primary leaf, yet retarded the development of the root (55).

Several inorganic silver salts and some organic silver mixtures have been tested for their use as eradicative or protective fungicidal agents in spray applied to plants. Although many of these silver solutions proved toxic to the various fungal spores, several produced visible foliar damage to the plants to which they were applied (55). Nielson and Massey (55) found silver nitrate solutions containing 100 ppm and 1000 ppm silver to be toxic to the leaves of young tomato plants six nodes in height and to bean plants in the primary leaf stage of development. However, of all the silver sprays investigated, silver chloride sprays containing a wetting agent and those sprays prepared by admixing silver nitrate with sodium lauryl sulfate, and particularly sodium oleyl sulfate, were most likely to produce injury (55).

Investigations into the phytotoxic effect of silver to higher plants grown in nutrient solution culture or planted in sand substratum have provided information on the uptake of silver, its distribution, and possible mechanism of toxicity. Jensen (61) examined the effects of various silver nitrate concentrations on the transpiration, sprout length, and green and dry weights of wheat plants grown in both nutrient solution culture and in soil (quartz sand) culture. The silver concentrations tested ranged from 10 ppm to 100 ppm $AgNO_3$ in the solution culture and from 100 ppm to 0.4% $AgNO_3$ in the soil culture study. In the solution series, a gradual increase in sprout length and green and dry weight was observed as the concentration of $AgNO_3$ was increased from control (H_2O) to 20 ppm $AgNO_3$. At 40 ppm $AgNO_3$, the sprout length and dry weight was less than the control and continued to drop as the level of $AgNO_3$ increased. A more gradual decrease in green weight was

observed until it fell below the control at 100 ppm $AgNO_3$. A similar pattern was observed in the soil culture series. The sprout length, transpiration rate, and green and dry weights peaked at 2,000 ppm $AgNO_3$ and then decreased with increasing $AgNO_3$ concentration. At 5,000 ppm $AgNO_3$, the sprout length, transpiration rate, and green weight fell below the control. The total dry weight, however, did not drop below the control until the cncentration of $AgNO_3$ had reached 0.01%.

Wallace et al. (62) and Koontz and Berle (63) examined the phytotoxic effect of silver to higher plants grown in nutrient solution to determine the uptake and distribution of silver and its effect on the ability of plants to concentrate essential mineral nutrients. Wallace and his coworkers (62) grew bush bean plants for 13 days in 3700-ml nutrient solution with 0, 10^{-6}, 10^{-5}, and 10^{-4} M $AgNO_3$. In the 10^{-4} M Ag the plants remained green, but very little growth occurred. Although the silver content of all parts of the plant increased with an increase in $AgNO_3$ in solution, most of the silver remained in the roots. A mineral composition analysis of the leaves showed no change in the iron, calcium, copper, or zinc levels for those plants grown in 10^{-6} M Ag solution. At 10^{-5} M Ag the levels of iron, copper, and zinc were greater than those of the control. The calcium level was lower, however. Manganese levels in the leaves gradually decreased with increasing silver concentration. Koontz and Berle (63) showed that silver effectively inhibits the uptake of phosphorus in bean, corn, and tomato plants. Although the uptake of phosphorus was decreased in the root, the effect was greatest in the shoots where the lowest Ag^+ concentration tested (0.1 μM Ag) produced a 64 to 75 percent

reduction in phosphorus uptake. Higher concentrations were more inhibitory. Sulfur uptake by the corn plant was reduced by 39% in the root and 61% in the shoot at 0.05 μM Ag and by 83% and 96% in the root and shoot respectively at 0.5 μM Ag concentrations. In contrast, as the Ag^+ concentration in solution was increased, the calcium uptake of bean plants increased in the roots and decreased in the shoots.

Hendrix and Higinbothan (64) showed that while very low concentrations of Ag^+ (0.001-0.1 μM $AgNO_3$) stimulate potassium uptake in etiolated pea stem cells, slightly higher concentrations (0.5-0.6 μM Ag) strongly depress K^+ uptake and slightly stimulate respiration. Since the higher concentrations of silver ion induce and uncoupling of of respiration from K^+ uptake, Hendrix and Higinbothan (64) hypothesized that at these concentrations Ag^+ is acting primarily at the plasma membrane rather than as a metabolic inhibitor or as a mitochondrial poison. Silver is known to react selectively with sulfhydral groups to form silver mercaptides (65,66). Since these reagents have long been known to interfere with cation movement in cells and with membrane bound enzymes (65,67), the formation of these mercaptides is believed to interfere with cation recognition (or pump) sites in the plasma membrane (64,68).

In an effort to gain information on the mobility and translocation of silver within the plant, Koontz and Berle (63) placed bean plants in nutrient solution labeled with 0.05 μM $^{110}AgNO_3$ for 24 hours. Following a transfer to $AgNO_3$-free nutrient solution, the plants continued to translocate Ag^+ into new growth. Although the roots still

retained 94 percent of the Ag^+, approximately 5 percent was lost to the "$AgNO_3$- free" nutrient solution, these data indicated that not all of the Ag^+ are bound or incorporated into root tissue as Petterson (69) has suggested. While most of this movement could be interpreted as xylarly, experiments demonstrating ^{110m}Ag export from a truncated leaf (63) indicate that Ag^+ is also transported through the phloem.

In plant tissue ionic silver may be precipitated as Ag_2S, AgCl, or reduced to metallic silver (63). Silver chloride granules have been located in both xylem and phloem elements, particularly in the plasmodesmata and endoplasmic reticulum (63,70). Brown et al. (71), Jensen and Kavaljian (72), and Weier (73) have suggested that the discoloration of tissue, most notable in the roots, is due to the reduction of Ag^+ to its metallic form by endogenous ascorbic acid. Since some Ag^+-resistant microorganisms produce more dark metallic silver than strains that are Ag^+ sensitive (74), the reduction of Ag^+ to metallic silver may well be a mechanism by which higher plants render the element non-toxic (63).

The vitality of a plant is integrally dependent upon the numerous soil microbial processes which provide essential nutrients for plant utilization. The introduction of silver to soils may affect microbial proliferation and enzymatic activities and possibly lead to a decrease in the rates of biochemical processes in the soil environment (75).

Because the amount of plant-available nitrogen is completely dependent upon nitrogen-fixing bacteria and/or decomposed bacteria in

the soil environment (49), the toxicity of silver to these microorganisms may effectively limit productivity. Liang and Tabatabai (75,76) found that silver sulfate is an effective inhibitor of nitrogen mineralization in soils. Their studies showed that, under aerobic conditions, silver reduces the amount of NH_4^+-N oxidized to NO_3^--N, the form of nitrogen available for plant uptake (75,76). In one of the soils studied, silver also inhibited Nitrobacter (the organism responsible for conversion of NO_2^- to NO_3^-) leading to a possible accumulation of the intermediate nitrite (NO_2^--N) (76). Sokol and Klein (77) examined the effects of added silver compounds on microbial growth, anaerobic cellulose degradation, and the soil environment immediately adjacent to a cloud seeding generator. Their studies showed that in a laboratory culture, both silver ions, added as $AgNO_3$ and AgI, effectively inhibit the growth of Anthrobacter, a soil bacterium involved in the degradation of organic matter. The rate of anaerobic degradation of cellulose in a mud environment containing AgI at concentrations of 100 μg/g were also decreased. Environmental observation appeared to confirm these data. A strong positive correlation was demonstrated between organic matter content and silver concentration in soils cntaining 50 μg/g silver or less. Higher silver concentrations had very little further influence on organic matter content. In addition, soils with high silver content also had higher water content, lower pHs, more microorganisms including bacteria, actinomycetes, and fungi, and higher respiration rates. The enhanced microbial growth is believed due to

laboratory manipulation of the soils, stimulating aerobic activity at the expense of anaerobic activity (78,79). The results of these data (78) and those of Laing and Tobatabai (75,76) suggest that silver accumulation in soils may greatly alter the soil microbial environment affecting various parameters including pH, water retention, the amount of organic matter, and the level of plant available nitrogen.

Phytotoxicity of Thiosulfates

The toxic action of thiosulfates is also of importance in determining the phytotoxicity of spent photographic effluent. In their investigations on the effects of low concentrations (0.001 M, 0.01 M, and 0.1 M) of sodium thiosulfate on the germination and subsequent root growth of a number of plants in nutrient solution cultures, Audus and Quastel (80) found that sodium thiosulfate markedly inhibits root growth. Higher concentrations were generally required to produce the same degree of inhibition of germination. The most sensitive plant, judged by root growth, was the pea, where concentrations of 0.004 M and 0.031 M were necessary to produce 50 percent inhibition of root growth and germination, respectively. In contrast, the germination of the mustard seed was inhibited at concentrations lower than those required to produce the same degree of inhibition of root growth. Concentrations of 0.027 M thiosulfate were required for 50 percent inhibition of root growth, while 0.015 M was necessary for a 50 percent reduction in germination. A considerable range of sensitivity was observed in the investigations.

Quastel and coworkers (81) examined the effects of calcium and sodium thiosulfate complexes on crops grown on manganese-deficient soils. Their experiments showed that the addition of these complexes to the soil did, in fact, increase the soluble manganese content in the tissue of the oat, beet, and pea, and reduce the symptoms of manganese deficiency. A significant increase in plant vigor accompanied these additions when the thiosulfate solutions were placed one inch below the seed level. However, when the highest concentrations of thiosulfate, 10 cwt/acre, were applied in solution as spray to the soil surface, the vigor of the plants was reduced below that of the control (untreated plants grown in Mn-deficient soils). Apparently the manner in which these solutions are administered to the soil determine whether thiosulfate complexes have a beneficial or toxic effect.

Effects of Sodium on Soils and on Plant Productivity

Excess sodium present as $Na_3Ag(S_2O_3)_2$ in spent photographic processing solution (1) can have a marked effect on the soil, soil microbial processes, and plant productivity. The main cause of salination in normal agricultural soils is the adsorption of sodium on particles of clay. When this occurs, the clay particles swell and the space between the particles of soil is reduced. The soil becomes less permeable, and toxic levels of the salts may accumulate (82). Because these soils are relatively impermeable, water tends to remain at the surface (83). If there is a high evaporative demand, these soils exhibit initially higher evaporative losses than soils with

lower sodium content. Subsequent water loss is diminished, however, since soils with higher sodium content exhibit a decrease in hydrolic conductivity (83). The reduced upward water flux to replenish the loss occurring at the surface under a high evaporative demand results in a desiccation of the surface zone where seeds generally lie. In contrast, a low evaporative demand results in excess water inthe surface layers. The soil surface remains wet, resulting in a prolonged first stage of drying (83). Due to the poor downward mobility and decreased hydraulic conductivity of these soils, water below the soil surface will tend to stagnate. The soil will be less well aerated and the amount of oxygen available for aerobic respiration will be reduced (82). Since decomposition rates are reduced under anaerobic conditions (84), the organic matter turnover rate will be similarly slowed (77) leading to a possible reduction in plant available nitrogen (78). More importantly, however, the reduced atmosphere limits the ability of a plant or microorganism to handle excess sodium present in its environment. Since the sodium-potassium pump derives its energy from the hydrolysis of adenosine triphosphate (ATP) (68), a cell (individual microorganism or plant hair cell) will consume oxygen as fast as needed to regenerate ATP (85). In the absence of molecular oxygen, the activity of the pump generally declines as the cell must rely on the energy liberated from glycolysis (68). High concentrations of sodium may then readily saturate the pump resulting in a net influx of Na^+ into the cell until osmotic equilibrium is established. Because high external concentrations of sodium also depolarize the

cell, the resulting loss in electrical current flow combined with the maintained osmotic equilibrium effects a loss in net water movement into the cell (68). Therefore, the ability of a plant to absorb water from soils containing high levels of sodium is greatly reduced.

GEOCHEMISTRY OF SILVER (34)

The mobility and precipitation of silver in soils is dependent upon a number of factors including soil drainage conditions, the pH and normal redox potential (Eh) of the solutions and environment, the presence of complexing agents, and the presence of precipitating constituents such as H_2S, Cl, Br, I, primary sulfides, and carbonaceous material.

Since all silver compounds are slightly soluble and are removed from the various soil horizons with time, the drainage coindition of a soil will determine its relative silver content. Therefore, soils which are well drained tend to have lower silver content than poorly drained soils in the same area.

The pH and Eh of the solutions and environment have a marked influence on the chemistry of silver. While silver normally has only one oxidation state and can not be directly affected by the normal oxidation reduction potentials in soil, its chemistry can be influenced by other elements sensitive to changes in Eh. The ability of soil pH to influence the mobility of silver is similarly affected by these elements. In general, silver compounds are more soluble and therefore more mobile in an acid environment. As the acidity decreases the silver ion (Ag^+) becomes slightly hydrolyzed, which may result in the precipitation of acid and basic compounds. In alkaline conditions silver may precipitate as the oxide or hydrated oxide. These simple reactions, however, rarely if ever occur in the soil because iron,

manganese, alumina, and organic matter greatly modify the course of events.

The reduction potentials of the following couples in alkaline and acid conditions are therefore important to a basic understanding of the geochemistry of silver.

Alkaline Solutions

$Fe(OH)_3 + e^- = Fe(OH)_2 + OH^-$	$E^o = -0.56$
$S + 2\ e^- = S^{2-}$	$E^o = -0.48$
$MnO_2 + 2\ H_2O = 2\ e^- = Mn(OH)_2 + 2\ OH^-$	$E^o = -0.05$
$Mn(OH)_3 + e^- = Mn(OH)_2 + OH^-$	$E^o = +0.1$
$Ag_2O + H_2O + 2\ e^- = 2\ Ag + 2\ OH^-$	$E^o = +0.344$
$O_2 + 2\ H_2O + 4\ e^- = 4\ OH^-$	$E^o = +0.401$

Acid Solutions

$S + 2\ H^+ + 2\ e^- = H_2S$	$E^o = +0.141$
$Fe^{3+} + e^- = Fe^{2+}$	$E^o = +0.771$
$Ag^+ + e^- = Ag$	$E^o = +0.799$
$O_2 + 4\ H^+ + 4\ e^- = 2\ H_2O$	$E^o = +1.229$
$MnO_2 + 4\ H^+ + 2\ e^- = Mn^{2+} + 2H_2O$	$E^o = +1.23$

The potentials of these couples, from Latimer (48) are referred to the standard hydrogen electrode. A negative value for E indicates that the reduced form of the couple is a better reducing agent than H_2. A positive E^o indicates that the oxidized form of the couple is a better oxidizing agent than H^+. The couples are given in order of decreasing reducing power and increasing oxidizing power.

The above potentials show that in both an acid and an alkaline environment the ferrous ion (Fe^{2+}) will be oxidized to the ferric state (Fe^{3+}) by atmospheric oxygen. Although the silver ion is reduced to the metal by Fe^{2+} in acid solutions, the reduction occurs with greater facility with $Fe(OH)_2$ in basic solutions because $Fe(OH)_2$, ($E^o = -0.56$) is a better reducing agent than the ferrous ion (Fe^{2+}), ($E^o = +0.771$). $Mn(OH)_2$ has a similar effect on Ag^+ in an alkaline environment. As regards the manganous-manganese dioxide couples, the potential developed by the oxygen couple is not sufficient to oxidize Mn^{2+} to MnO_2 in an acid environment, but is adequate in a basic medium. Hydrogen sulfide and other sulfide ions are similarly oxidized. The formation of sulfur is facilitated by atmospheric oxygen in an alkaline environment and by both atmospheric oxygen and ferric ion in an acid medium.

As silver bearing solutions migrate through the soil, the elements behave in accordance with the oxidiation-reduction potentials and pH of the environment. In near surface processes the acid reaction, $Fe^{2+} + Ag^+ \rightleftharpoons Ag + Fe^{3+}$, is one of the most important. Near the soil surface oxygen is abundant and the oxidation potential is high. Iron, if present in the ferrous state (Fe^{2+}) is rapidly oxidized to the ferric state (Fe^{3+}). This results in a shift in the Fe^{2+}/Fe^{3+} ratio, thereby mobilizing silver. As the solutions pass downward, atmospheric oxygen is consumed and the oxidation potential gradually decreases. The pH of the solutions will also increase at a gradual rate. This is due mainly to neutralization by carbonates, silicates,

and/or alkaline waters. In the next immediate soil horizon there is a decrease in acidity, yet a relatively high Eh still prevails. Under these conditions the ferric ion may be hydrolyzed and precipitated as a basic salt or as the hydrated oxide, $FeO(OH)\cdot nH_2O$, effectively removing it from the oxidation-reduction reactions. The hydrated ferric oxide is a poor carrier of silver since its colloid bears a positive charge. However, elements such as PO_4^{3-}, AsO_4^{3-}, hydrated MnO_2, silica, and humic colloids, when present in the soil, are attracted to the hydrate giving the combined colloidal complex a negative charge. The complex then serves to adsorb and coprecipitate Ag^+. Silver may also be precipitated in this environment by the manganous ion according to the oxidation-reduction reaction:

$$2\ Ag^+ + Mn^{2+} + 4\ OH^- = 2\ Ag + MnO_2 + H_2O$$

A further decrease in acidity results in the precipitation of hydrated manganese oxides which, due to their negative charge, may adsorb and coprecipitate any availabel Ag^+. In this soil horizon alumina may also influence the chemistry of silver. With a decrease in acidity, alumina undergoes hydrolysis forming a complex series of hydroxides and alumina-silicates. These attract Na^+ and K^+, forming the familiar sodium-, potassium-rich clay minerals. The silver ion (Ag^+), similar to Na^+ and K^+ in ionic radii and adsorption characteristics, is then scavenged and removed from circulation by the clay minerals.

In the next soil horizon the oxidation potential is further reduced resulting in a stabilization and concentration of the ferrous

ion (Fe^{2+}) in solution. In this environment native silver is precipitated according to the equation:

$$Fe^{2+} + Ag^{+} \rightleftharpoons Ag + Fe^{3+}$$

The reduced oxidation potential also allows for the precipitation of silver as the sulfide according to the following reaction:

$$2\ Ag^{+} + S^{2-} = Ag_2S$$

The presence of complexing agents in the soil act to either increase or decrease the mobility of silver. Anions such as SO_4^{-}, NO_3^{-}, HCO_3^{-}, $(S_2O_3)^{2-}$, and certain organic acids render silver relatively soluble, increasing its mobility. Sulfuric acid enhances the mobility of silver in several ways. The sulfate may react with native silver or silver sulfides and sulphosalts to give soluble silver sulfate:

$$2\ Ag + 2\ H_2SO_4 = Ag_2SO_4 + 2\ H_2O + SO_2$$

$$Ag_2S + H_2SO_4 = Ag_2SO_4 + H_2S$$

Or, sulfuric acid may act on carbonates in the soil yielding an abundance of bicarbonate ion (HCO_3^{-}) which further enhances the solubility of silver as the hydrogen carbonate. Thiosulfate ions $(S_2O_3)^{2-}$ yield soluble silver complexes of the type $[Ag(S_2O_3)_2]^{3-}$ in neutral or alkaline conditions:

$$Ag^{+} + 2\ (S_2O_3)^{2-} \rightleftharpoons Ag(S_2O_3)_2^{3-}$$

The silver complex dissociates, however, with the formation of S and AgS when there is an increase in acidity or when the solution comes in contact with reducing substances such as carbonaceous matter.

Anions such as PO_4^{3-}, Cl^-, Br^-, I^-, CrO_4^{3-}, and AsO_4^{3-} precipitate insoluble compounds and reduce the mobility of silver. An excess of Cl^- ions, however, will yield soluble complexes such as $[AgCl_2]^-$ and $[AgCl_3]^{2-}$, rendering the element more mobile.

Organic matter, in particular the humic substances, also serve to immobilize silver. Organic compounds strongly adsorb silver possibly forming chelated complexes with the metal. Although silver may be liberated under a high oxidation potential as the humic complexes are oxidized to CO_2 and H_2O etc., the element is generally seized by the remaining human complexes. This process, repeated ad infinitum, finally leads to the enrichment of silver noted in some of the organic horizons of many soils.

DESCRIPTION OF SITE USED IN ENVIRONMENTAL INVESTIGATION

Physical and Environmental Setting (86,87)

The Los Alamos National Laboratory is located in Los Alamos County in north-central New Mexico about 100 km (60 mi) north-northeast of Albuquerque and 40 km (25 mi) northwest of Santa Fe by air (Fig. 1). The Laboratory and the adjacent residential area of Los Alamos are situated on the Pajarito Plateau between the Jemez Mountains to the west and the Rio Grande Valley to the east. The plateau, 16 to 24 km (10-15 mi) wide and 40 to 48 km (25-31) mi long, slopes eastward from an altitude of about 2400 m (7800 ft) along its western margin to about 1800 m (6200 ft) to the east, where it terminates 90 to 300 m (300-1000 ft) above the Rio Grande at the Puye Escarpment and the rim of the White Rock Canyon. Cañon de Valle is one of a series of steep-sided canyons cut by intermittent streams that trend east-southeast to the Rio Grande and dissect the plateau into numerous finger mesas (Fig. 2). The headwaters of the canyon originate from springs located between 2400 m and 2700 m (7900 and 8900 ft) elevation on the slopes of the Sierra de los Valles. Although the springs supply base flow throughout the year to the upper reaches of the canyon, the volume of flow is insufficient to maintain surface flow across the Laboratory area before it is depleted by evaporation, transpiration, and infiltration into the underlying alluvium. Runoff from heavy thunderstorms or unusually heavy snowmelt, however, will reach the Rio Grande several times a year.

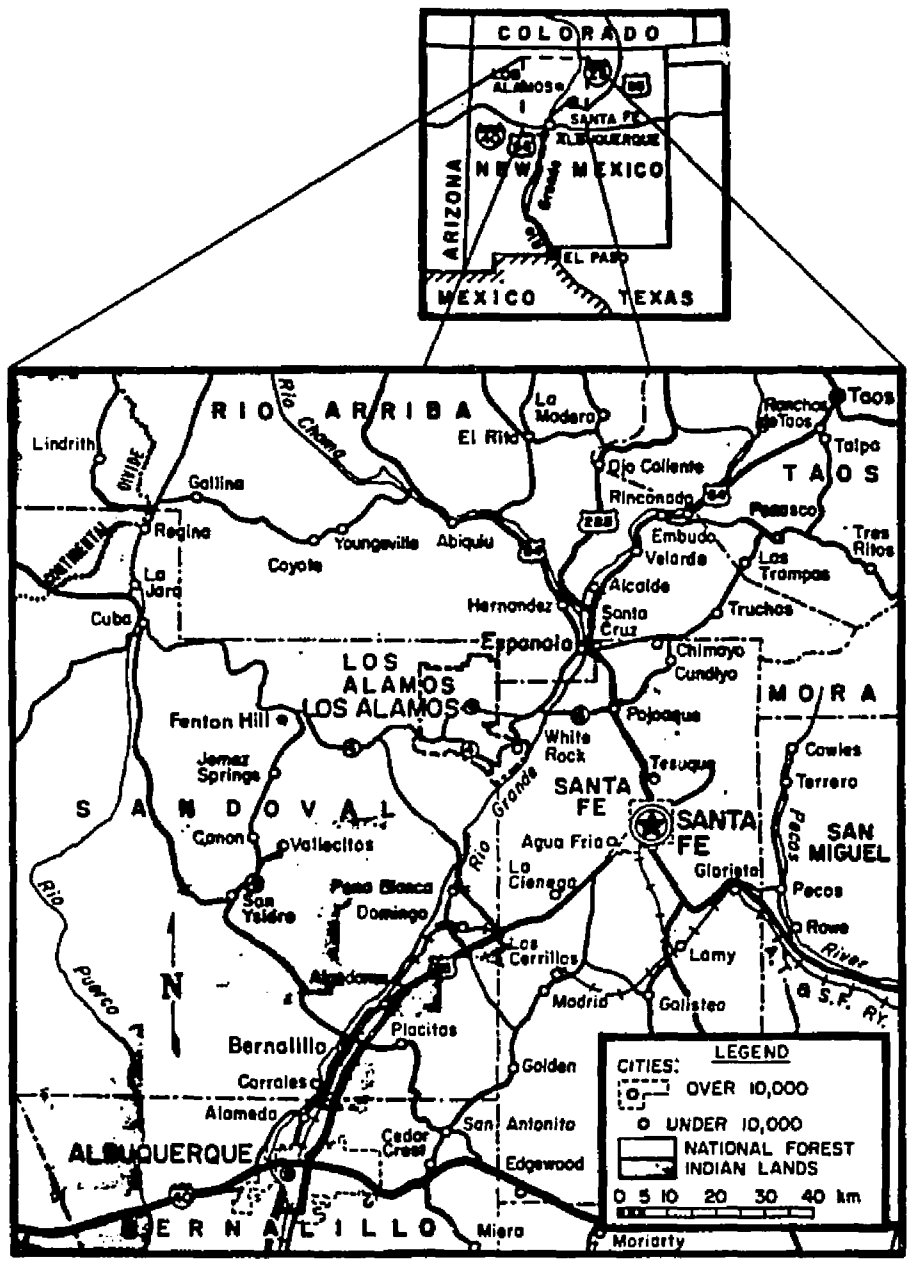


Figure 1. North-central New Mexico. (86)

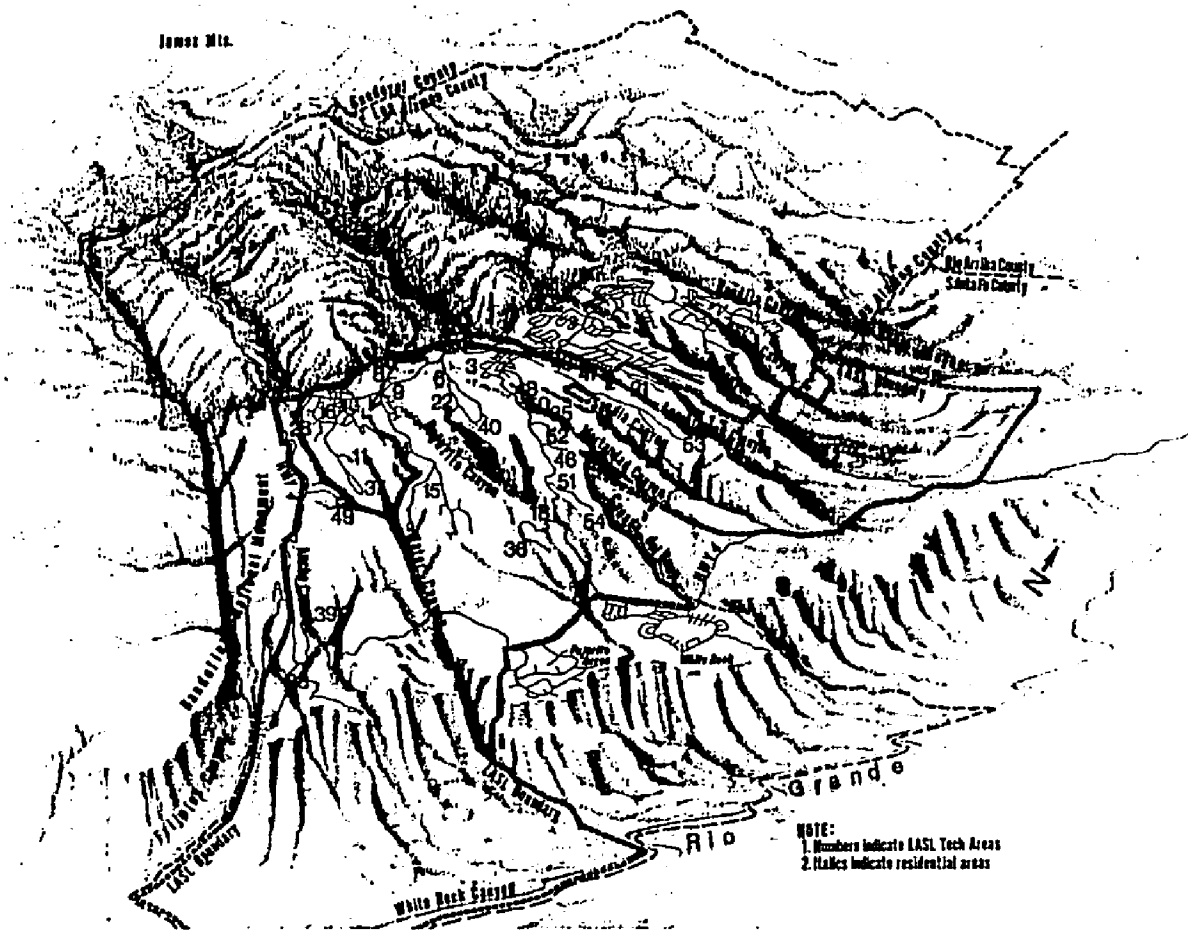


Figure 2. Topography of the Los Alamos, New Mexico area. -- Arrow points to Cañon de Valle. (86).

The alluvium deposited in the stream beds of the canyons of the plateau is composed of sands, gravels, and cobbles derived from the Tshirege member of the Bandelier Tuff. It ranges from less than 1 m to as much as 30 m in thickness and is quite permeable, allowing rapid infiltration of rainfall and streamflow. However, since the alluvium generally overlies the less permeable volcanic tuff and sediments, the downward movement of water is impeded. This results in the formation of a shallow alluvial ground water body which then moves downgradient in the alluvium at a rate of 1 to 20 m/day (3-60 ft/day). This perched alluvial water is then depleted by evapotranspiration and infiltration into the underlying tuff. The main aquifer in the Los Alamos area is situated within the Tesuque Formation beneath the entire plateau and the Rio Grande Valley. Because perched water has not been found in the tuff, volcanic sediments, or basalts above this aquifer in either the western or central portions of the plateau, there is virtually no potential for alluvial waters in waste discharge areas to infiltrate to the deep aquifers used for human consumption.

Meteorology (86,87)

Located at an approximate altitude of 2662 m (7300 ft), Los Alamos has a semiarid continental climate. The annual precipitation is 46 cm (18 in), 75% of which falls between May and October, primarily as thunderstorms. With an annual average of 62 thunderstorm-days per year, the Los Alamos area is equivalent to the Gulf Coast States in thundershower occurrence. In the winter, precipitation falls primarily as snow with annual accumulations of 1.3 m (4.3 ft). Maximum

temperatures in the summar are generally below 32°C (90°C) with nocturnal temperatures ranging from 12°C to 15°C (54°F-59°F). During the winter temperatures range from -10°C to 5°C (14°F-41°F). The relative humidity averages 40% and ranges from 30% in May and June to above 50% in January, February, and July.

Ecology (86,87)

There are six major vegetative overstory complexes found in Los Alamos County. These are the juniper-grassland, pinon-juniper, ponderosa pine, mixed conifer, spruce-fir, and subalpine grassland. However, the pronounced east-west canyon and mesa orientation with the accompanying differences in soils, moisture, and solar radiation, produces an interlocking finger effect which results in transistional overlaps of plant and animal communities within a small area. In general, the vegetative understory is sparse, although canyon bottoms and some south slopes harbor a wide variety of shrubs, grasses, and forbs.

Waste Outfall Location, Soils, and Ecology (86,87,88)

The mouth of the outfall for the spent X-ray fixing bath solution is located on the Pajarito Plateau at approximately 2785 m (7640 ft) elevation in a mixed ponderosa pine/pinon pine-juniper overstory. The outfall trends south for approximately 85 to 95 m before it converges with Cañon de Valle approximately 48 km (30 mi) from the headwaters of the canyon, 5 km (3 mi) upstream of the confluence with Water Canyon and 11 km (7 mi) from the Rio Grande River (Fig. 2). The soils of this

area are comprised of 10% Tocal and Carjo soils and 90% clayey-skeletal Typic Eutroboralfs of the Alfisol order. These Typic Eutroboralfs occur on nearly level to moderately sloping mesas (1-8% slope) and are deep, well-drained soils that formed in gravelly fan material originating close to the mountains. Permeability of these soils is slow (0.15-0.50 cm/hr) and although the effective rooting depth is 120 m, the available water capacity is low (9.5-13 cm). Runoff is slow to medium (0.00-0.13 to 0.14--0.51 cm) and the erosion hazard is moderate (0.65-1.8 cm soil/year). Profiles of the three soil series found in this area are represented in Figure 3. Generally, the surface layer (A2) of these clayey-skeletal Typic Eutroboralfs is about 15 cm thick and is comprised of a light gray silt loam or loam. These soils have very fine vesicular pores (0.1-0.5 mm) and contain about 10% gravel. The soils in the next horizon (A/B) extend from approximately 15 cm to 30 cm in depth and are comprised of a very gravelly loam, pinkish grey and/or reddish-brown in color. Medium and coarse gravel account for 55% of the soils material and fine black iron and manganese concretions are common. The next horizon (B1t) extends from 30 cm to 46 cm in depth and is comprised of a vary gravelly reddish-brown clay. The soils in this horizon contain approximately 75% gravel and cobble. Fine black iron and manganese concretions are common and thin clay films are found in the pores and on pebbles. The last soil horizon (B2t) is a very gravelly brown clay which extends from 46 to 122+ cm. Thin clay films are found in the pores and on pebbles in this region.

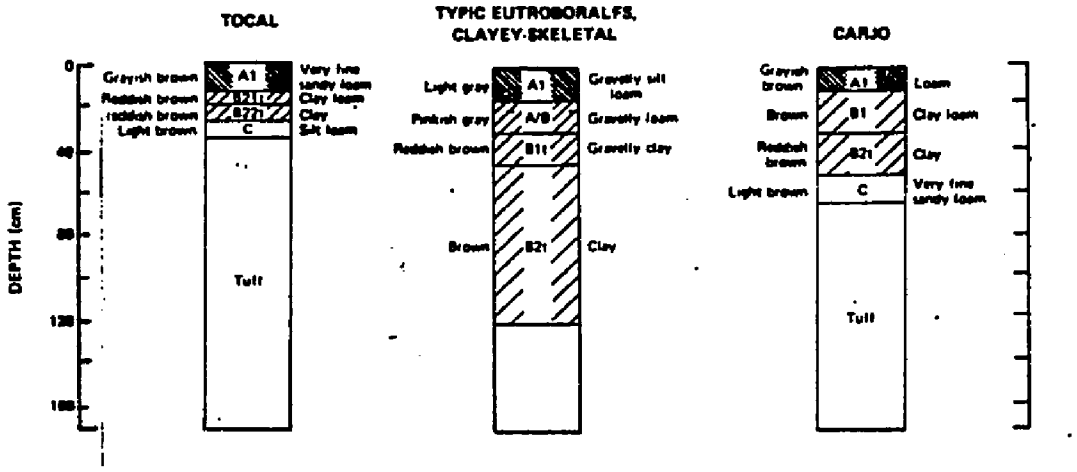


Figure 3. Profiles of soil series in Canyon del Valle. -- (88).

These Typic Eutroboralfs are the principal soils (~90%) in the waste outfall area and extend for approximately 200 m down the canyon from the discharge site (Fig. 4). At 200 m from the outfall and for the remaining distance of the canyon the land and soil type are of a different character. In this area of the canyon the land type has slopes greater than 30% on steep to very steep mesa breaks and canyon walls and consists of about 90% rock outcrop. The soils, shallow and undeveloped, are found on tuff, mesic rock outcrop (5-30% slope) and frigid rock outcrop (5-30% slope).

Because Cañon de Valle is isolated from human traffic and has had no other waste discharged either upstream or within the area investigated, it offered a unique opportunity to study the problem of the transport of silver in an environment contaminated with spent photographic fixing solution.

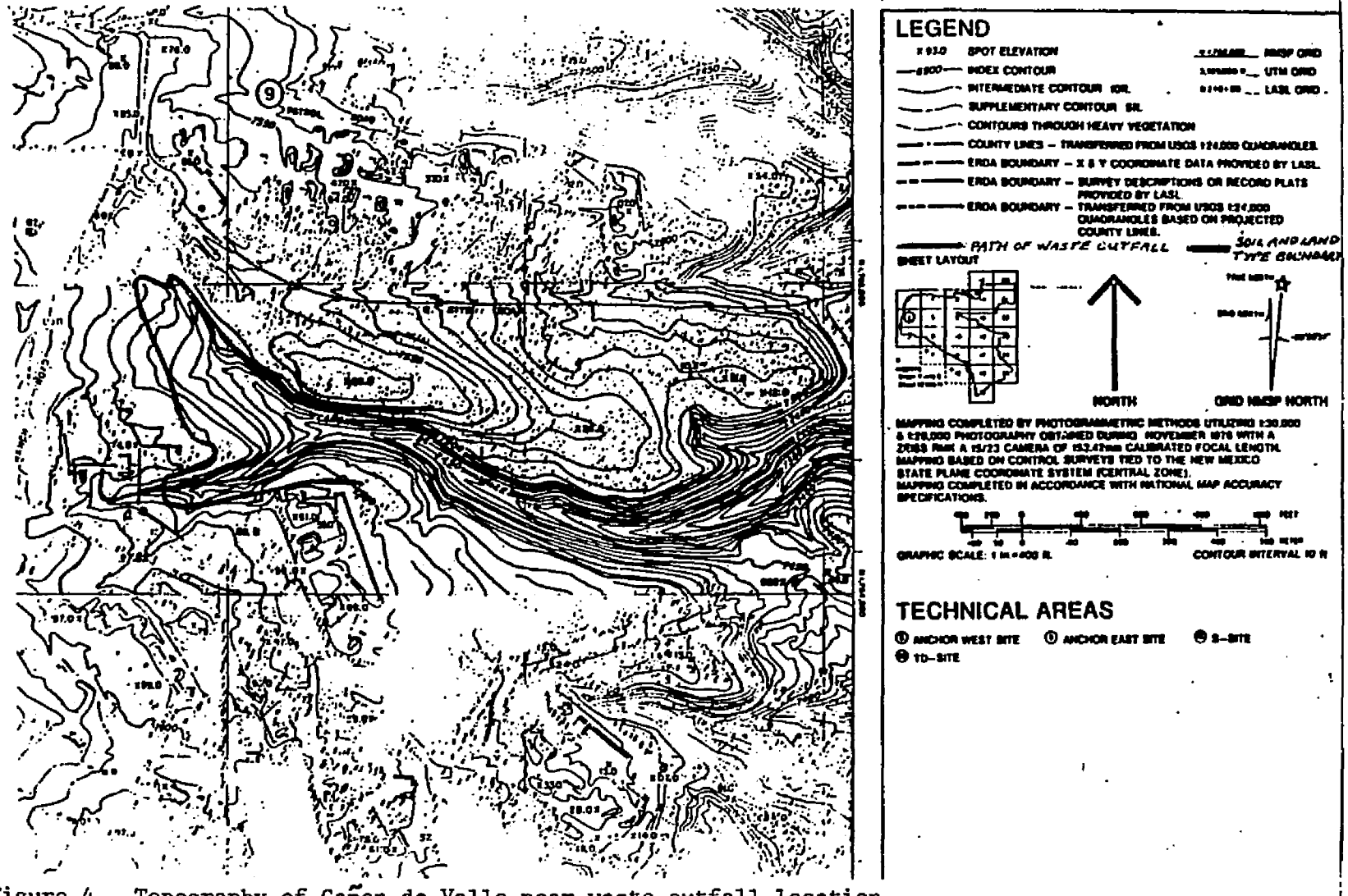


Figure 4. Topography of Cañon de Valle near waste outfall location.

MATERIALS AND METHODS

Sample Preparation and Analysis for Silver Content

All sample bottles and containers used throughout these investigations were cleaned by a 24 hour soak in a (1:1) mixture of concentrated nitric acid and deionized water followed by three 24 hour rinses in deionized water.

In order to insure against silver loss due to photooxidation or adsorption (27), water samples were collected in black-taped linear polyethylene bottles, labeled, and removed to the lab where they were immediately filtered. A 200 ml volume of the filtered sample was then returned to the sample bottle which had been rinsed in deionized water to remove any adhering sediment. The pH of the sample was measured and recorded and 15 ml of concentrated HNO_3 added to bring the sample solution to less than pH 1.0.

Plant material was rinsed free of adhering dusts and soil by placing each sample in a wide mouth polyethylene bottle and shaking the sample with three rinses of deionized water. The plant samples were then placed in labeled brown paper bags and dried in an oven for two days at 65°C. The dried samples were cut into smaller sections and then ground to approximately 325 mesh in an alumina ceramic-lined Shatterbox grinder.

Soil and sediment samples were also placed in labeled brown paper bags and dried in the oven at 65°C for two days. The dried samples werethen passed through a #10 U.S.A. Standard Test mesh screen

to remove any large rocks, twigs, etc. and ground to approximately 325 mesh in the Shatterbox grinder. Care was taken to rinse and dry the mortar and pestle of the grinder between samples to prevent cross contamination.

Water samples were analyzed with a Perkin-Elmer Model 603 flameless atomic absorption spectrophotometer with a Perkin-Elmer Model 2000 graphite furnace. Soil column effluent samples were analyzed with either a Perkin-Elmer Model 306 or a Varian Techtron Model AA-5 flame spectrophotometer. Operating conditions were those recommended by the instrument manufacturer with the wavelength, lamp position, and atomizing parameters optimized for maximum absorbance and linear response while atomizing silver standards prepared with reagent grade silver nitrate in 2.5% HNO_3/deionized water.

Vegetative and geological materials were analyzed by instrumental thermal neutron activation analysis by Dr. Ernest Anderson of the Environmental Surveillance Group at the Los Alamos National Laboratory (89). Approximately 200 mg quantity of each powdered sample was weighed into a small BEEM snap-cap polyethylene vial, four of which were fitted end to end in a 4 cm^3 polyethylene rabbit. The rabbits were irradiated two at a time for 1 hour in a thermal neutron flux of 1×10^{13} $n/cm^2/sec$. Standards were prepared from stock solutions of reagent grade silver nitrate dissolved in 2.5% HNO_3/deionized water. After diluting the stock solution to appropriate concentration with deionized water, a 50 μl aliquot of the standard was pipetted onto a 2 cm diameter Whatman No. 2 or No. 41 filter paper. The standards were

therefore not subject to errors which could occur when irradiating solutions directly. There was no loss of sample due to leakage from the container and the samples were not contaminated by elements which could leach into solution (89). In order to mimic the cross section of the samples and to reduce the possibility of any error due to self-shielding effects, the filters were folded to approximate the size and shape of the sample to be analyzed and fitted into a small BEEM snap-cap polyethylene vial. Flux monitors, used to measure any variation in the thermal neutron flux, were prepared in a similar fashion using stock solutions of cobalt dissolved in concentrated nitric acid. Following irradiation, the samples were allowed to "cool" for 3-4 weeks before analysis to allow the short-lived isotopes time to decay to a point where interference with the silver nuclide was negligible (29). The samples were then counted for 1 hour each on a large Lithium-drifted Germanium detector using the 658 keV line from ^{110m}Ag. At this photo-peak, the possible interfering nuclear reactions are $^{110}Cd(n,p)^{110}Ag$ and $^{113}In(n,\alpha)^{110m}Ag$. However, serious interference with the determination of silver was precluded due to the (a) low natural abundance of both ^{110}Cd and ^{113}In, (b) the poor cross-sections of both these reactions compared with the $^{109}Ag(n,\gamma)^{110m}Ag$ reactions, and (c) the high thermal-to-fast neutron ratio in the irradiation position used (28). The data analysis program GAMSPEC (90) was used in the computer reduction and identification of the γ-ray spectral data. All data was corrected for observed differences in flux.

Since vegetative and geological samples are generally solubilized prior to analysis by atomic absorption spectroscopy, several dissolution methods were investigated. Radioactive silver was employed to determine rates of recovery. The radioisotope ^{110m}Ag, was obtained from New England Nuclear (Boston, Massachusetts) in the form of silver nitrate in nitric acid. Because the specific activity of the tracer was sufficiently high (3-20 curies/gm silver), the ^{110m}Ag stock solution was diluted with 50% aqueous nitric acid to obtain a solution with silver content below the ppb range which yielded a few thousand counts/ml. Since sediment samples were found to be more difficult to dissolve than either plant or soil samples, a sediment sample containing a relatively high silver content (previously determined from a digestion procedure yielding incomplete dissolution) was chosen as a representative sample. Prior to dissolution, 1 ml of the diluted ^{110m}Ag solution was added to 1 gm quantities of the powdered sample. In order to avoid decay corrections, a reference sample was prepared at the same time. This was made by taking 1 ml diluted ^{110m}Ag solution and diluting it to 50 ml volume with 50% aqueous nitric acid. Upon completion of the digestion, the samples were filtered. The filters were placed in labeled plastic holders and the filtrates removed to labeled linear polyethylene bottles. The beakers, filters, and filtrates were then counted three times for one minute each in a NaI well counter. The counts were averaged and corrected for background radiation, determined by counts of a "clean" beaker, filter, and a linear polyethylene bottle containing 50 ml of 50% aqueous nitric acid. the reference sample

prepared at the beginning of the dissolution procedures was similarly counted and the count average assigned 100% recovery. Silver recovery is reported in percent and was determined by dividing the average of the sample counts by the average count for the reference sample.

All digestion procedures were carried out in triplicate with reagent grade chemicals in 500 ml Teflon beakers heated at moderate temperatures on hot plates. In the first method, 10 ml of concentrated HNO_3, 5 ml of concentrated HCl, and 15 ml of concentrated HF were added to 1 gm powdered samples. The solutions were evaporated to dryness and the residues dissolved in 5 ml of concentrated HNO_3 and 10 ml of concentrated HF. A small amount of H_2O_2 was added with a squirt bottle. The solutions were again evaporated to dryness and 5 ml of concentrated HF and 5 ml of concentrated H_2O_2 added to the residues. In order to aid dissolution of the sample, this last step was repeated a second time before the final residues were each dissolved in 1.25 ml of HNO_3 and brought to 50 ml volume with deionized water. In the second procedure, 15 ml of concentrated HNO_3 and 15 ml of concentrated HF were added to 1 gm powdered samples. When the nitric acid started fuming, concentrated H_2O_2 was added with a squirt bottle. In order to complete the oxidation of the organics, this was repeated several times before the solutions were taken to dryness. The residues were redissolved in 10 ml of concentrated HNO_3 and evaporated to dryness. In the final step the resulting residues were dissolved in 1.25 ml of concentrated nitric acid and diluted to 50 ml volume with deionized water. In the third dissolution procedure 15 ml of concentrated HNO_3 was added to 1 gm powdered

samples. The solutions were evaporated to dryness and the residues dissolved in 15 ml of concentrated HF. After the solutions were evaporated, 5 ml of boric acid were added and solutions were evaporated, 5 ml of boric acid were added and the solutions again evaporated to dryness. The residues were redissolved in 1.25 ml of concentrated HNO_3 and diluted to 50 ml volume with deionized water. In the fourth oxidation procedure, the samples were heated with 15 ml of concentrated HNO_3 and evaporated to dryness. Twenty five milliliters of concentrated HNO_3 and 10 ml of concentrated $HClO_4$ were added to the residue. The solutions were then evaporated to a moist salt state and 10 ml of concentrated HNO_3 was added. The solutions were again heated on the hot plate until a small volume of fuming HNO_3 just covered the bottom of the beaker. At this stage a small amount of H_2O_2 was squirted around the inside of the beakers. The beakers were immediately covered by Teflon "watch glasses" to minimize silver loss due to spray following the H_2O_2 addition. Several additions of H_2O_2 were generally required to complete the oxidation of the organics and to remove the "bathtub" ring formed by the oils in the sample. When necessary, additional HNO_3 was added to aid dissolution. After the organics had been oxidized, the solutions were evaporated to dryness. A 15 ml aliquot of concentrated HF was then added and the solutions again evaporated to dryness. This last step was repeated as often as necessary until the silicates had been digested and a clear solution remained. The solutions were once again evaporated to dryness and 15 ml of concentrated HNO_3 was added. After a final evaporation, 1.25 ml of concentrated HNO_3 was added to each residue and the rsulting solutions were diluted to 50 ml volume with

deionized water. The fifth, sixth, and seventh digestion procedures were basically identical to the fourth, varying only in the solution in which the final residues were dissolved. In the fifth oxidation method the final residues were dissolved in 1.25 ml of concentrated HNO_3 and diluted to 50 ml volume with 2% EDTA. The final residues in the sixth digestion procedure were dissolved in concentrated HCl. In the seventh digestion procedure the residues were dissolved in 1.25 ml of concentrated HNO_3. Then a small amount of deionized water was added and the resulting solutions were gently warmed to aid dissolution. After the residues had redissolved completely, 1 ml of NH_4OH was added to each followed by 5 ml of Process E-6 Kodak Fixer and Replenisher ($NH_4S_2O_3$). The resultant mixtures were then diluted to 50 ml volume with deionized water.

Collection of Environmental Samples

Prior to collecting samples, the general appearance of the Canon de Valle environment and the type of vegetation available for sampling was studied. The waste stream channel was measured with a tape measure and flagged every 10 m for the first 30 m and every 30 m thereafter for 450 m down the canyon. Water, stream sediment, soil, and vegetation samples were collected at each site. Water samples were collected in labeled black-taped linear polyethylene bottles and treated for silver analysis as described previously. Stream sediment samples were collected with a hand spade and placed in labeled zip-lock polyethylene bags. Soil samples were taken approximately 1 m from the center of the

stream channel using a 4 foot auger with a 6 inch head. Surface to 6 inch deep samples of soil were acquired from each location and placed in labeled zip-lock polyethylene bags. A vertical soil profile extending to 3 feet beneath the soil surface was obtained 10 m from the mouth of the outfall with 6 inch samples. A similar soil profile was obtained 20 m from the mouth of the outfall and extended to 1 ft beneath the soil surface. Organic detritus was brushed from the surface prior to removal of all soil samples. Vegetative samples were obtained at each location using shears. In order not to bias the sample, care was taken to include both large and small leaves of the paritcular plant in each individual sample. The approximate distance of these samples from the center of the stream channel was noted and recorded and the samples placed in labeled zip-lock polyethylene bags. For comparison data, stream sediment, soil, and vegetation samples were obtained in a similar manner from a non-contaminated canyon with the same soil type located adjacent to the study canyon. All material was then removed to the laboratory and prepared and analyzed for silver content as described previously.

Soil Column Studies

The columns, sample bottles, and containers used in this investigation were cleaned by a 24 hr soak in a (1:1) mixture of concentrated nitric acid and deionized water followed by three 24 hour rinses in deionized water (16).

Clayey-skeletal Typic Eutroboralf soils were collected from a control canyon in the Los Alamos area. Organic detritus was brushed

from the surface and the first two feet of soil was removed by shovel. The soil was spread 1-2 inches deep on large trays and allowed to air dry. When dry, the larger clumps of soil were broken and the soil was passed through a #10 U.S.A. Standard Test mesh screen to remove any large rocks, twigs, etc. Pine needles, twigs, etc. greater than ~20 cm in length that had passed through the sieve were then removed from the soil samples. The soil was mixed together and uniformly packed into Teflon columns. Packing of the columns was done approximately 20 cm at a time by adding a small amount of soil and then tamping the bottom of the column several times on a flat surface. The upper 2 to 2½ inches of the column were left empty. This area served as a partial sample reservoir for the applied silver solutions.

The silver solutions were prepared in linear polyethylene bottles. Stock solutions were made fresh every time at silver concentrations 100 times greater than those solutions applied to the soil. Stock solutions of silver thiosulfate ($Na_3Ag(S_2O_3)_2$) were prepared by dissolving reagent grade silver bromide (AgBr) in Kodak Rapid Fixer with Hardener for Films, Plates, and Papers ($Na_2S_2O_3$). The stock solutions of silver nitrate and silver sulfate were made by dissolving the appropriate analytical reagent in deionized water. A predetermined volume of sample solution was prepared for each column by diluting the stock solutions to concentration with deionized water. In order to minimize disturbance of the top layers of soil, these sample solutions were introduced into the columns by pouring each down a glass rod. The solutions were allowed to gravitate through the soil and were

subsequently collected in 500 ml Teflon beakers. As the partial sample reservoirs at the top of the columns were depleted, additional solution was added until the total sample volume for each column had been applied to the soil. Plastic was then placed over the heads of the columns and the collection beakers to prevent contamination and to reduce evaporation of the samples. After the entire sample volume for each column had eluted through the soils, the effluent was then transferred from the beakers to 500 ml linear polyethylene bottles. The silver nitrate and the silver sulfate eluents were acidified with 28 ml of concentrated nitric acid and all eluent samples were analyzed for silver content by atomic absorption spectroscopy as described previously. Consecutive volumes of silver solution were then applied to the soil until one of three conditions was met: breaktrhough (effluent silver concentration $\geq$1% influent silver concentration for two to three consecutive sample volumes), steady state (unchanging or slowly changing effluent silver concentration at or below that of influent silver concentration), or continued absence of the element after numerous sample volume applications. After one of these conditions had been met, soil from the columns demonstrating silver attenuation was removed by spatula in one inch deep increments and prepared and analyzed for silver content by thermal neutron activation analysis as described previously.

In the first experiment, six 2½ inch diameter Teflon columns were packed to a depth of 6 inches. Every two days, each of two columns received a 500 ml sample volume of 20 ppm Ag as silver sulfate, or 10 ppm Ag as silver nitrate or as silver thiosulfate.

In the second experiment, 280 g of soil were packed in each of nine 2 inch diameter Teflon columns to a depth of 4 inches. Each of three columns received varied volumes of either 10 ppm, 50 ppm, or 100 ppm silver as silver thiosulfate. The volume of solution remaining on each column following elution was calculated and the pH of the sample solutions were measured and recorded prior to and following elution from the columns.

Phytotoxicity Studies

All plastic sample bottles and containers used in this investigation were cleaned by a 24 hour soak in a (1:1) mixture of concentrated nitric acid and deionized water followed by three 24 hour rinses in deionized water (16). The soils and solutions were prepared in the manner described previously.

Several 7 oz. styrofoam cups were used as planters. To allow for drainage, a hole was cut into the bottom of each with a cork borer and covered with a No. 2 Whatman filter paper. Each cup was loosely packed with soil. Packing of the cups was accomplished by adding as much soil as possible and then tamping the bottom of the cup several times on a flat surface. Additional soil was then added and the cup tamped again until the surface of the soil was within one half inch of the top of the cup. Approximately 50 seeds of western wheat grass (Agropyron smithii) were then counted, distributed evenly over the surface of the soil in each cup, and covered by a 1/4 inch sprinkling of soil.

The cups and seeds were divided into several groups, each containing 14 to 18 cups. The period of study lasted a total of 49 days.

The germination group received daily aliquots of either sodium thiosulfate, 10 ppm Ag as silver thiosulfate or silver nitrate, or 20 ppm Ag as silver sulfate for the entire study. The post germination group received daily aliquots of deionized water for the first 24 days and then daily aliquots of either sodium thiosulfate, 10 ppm Ag as silver thiosulfate or silver nitrate, or 20 ppm Ag as silver sulfate for the remaining 25 days. To insure that the lack of available essential mineral nutrients would not be a limiting factor (49), plant food was added periodically to replenish any nutrients depleted from the soil during the course of this investigation. Beginning on the 25th day from the initiation of the experiment and once a week thereafter, all solutions applied to the seedlings were diluted to concentration in Sterns Miracle Gro plant food.

To help insure germination, the soil must be kept damp. However, to maintain consistency, each cup should receive the same volume as solution. The volume of water applied to each cup within the control group was therefore used as an index for the volume of solution applied to each cup within the other groups. Solutions were measured into the cups with graduated 60 ml linear polyethylene squeeze bottles. After germination care was taken to apply the solutions to the soil around the base of the plants. This precautionary measure eliminated the possibility of foliar damage to the plants (55) and insured that the measured silver content of the plants was due to uptake and not to foliar absorption (25). In order to simulate spring, when daylight hours lengthen and most plants germinate, the cups were exposed to Vita Lite

from Duro-Light Lamps, Inc. for 14 hours a day every day. On the 24th day from the initiation of the experiment, all cups were thinned to 20 plants each.

To determine rates of germination, the number of plants per cup was counted daily and the average percent germination calculated. Lethality calculations were handled in a similar manner. The average percent lethality was calculated from the number of deaths per number of plants germinated per cup per day.

Potential gross productivity was assessed by spectrophotometrically determining chlorophyll content (51). On the 50th day from the initiation of this investigation, one or more plants per cup were cut into quarter inch length pieces and 0.1 gm of each placed into 10 ml test tubes. A 10 ml aliquot of 80% acetone was added to each and all were placed in the dark at room temperature for a period of 48 hours. During this time the tubes were periodically removed and shaken. After 48 hours the extracts of each were pipetted into cuvettes and each one was quickly measured on a spectrophotometer at 665 m and 649 m using 80% acetone as a reference. The chlorophyll content was then calculated using the following equations (51):

$$\text{chlorophyll a (mg/liter)} = 11.63(A665) - 2.39(A649)$$

$$\text{chlorophyll b (mg/liter)} = 20.11(A649) - 5.18(A665)$$

$$\text{total chlorophyll (mg/liter)} = 6.45(A665) + 17.72(A649)$$

Net productivity was determined by "censusing" or counting and weighing the remainder of the plants per cup. As the plants were counted, each sample group was split into two equal factions. In each

group, the number of cups was divided evenly. The plants in one half the total number of cups were included in one faction, and the plants in the remaining half of the cups placed in the second faction. Both factions per group were then prepared and analyzed for silver content by thermal neutron activation analysis as described previously.

RESULTS AND DISCUSSION

Sample Preparation and Analysis for Silver Content

Several problems were encountered in the development of a suitable wet oxidation procedure that would yield a sufficiently high percentage of silver recovery. Although the procedure and the acids used were important factors in determining the amount of silver recovered, technique was found to be equally important. Improper handling of the sample may result in significant silver loss. If the residues were heated past the dry stage and allowed to char, even slightly, the silver compounds that formed were often insoluble and never redissolved. In general, if the charring occurred in the final stages of the procedure, more silver would be lost to the solution than if the charring occurred during the first part of the procedure. A significant amount of silver can also be lost in the spray formed during the particularly ebullient reaction following the addition of hydrogen peroxide to fuming nitric acid. Although Teflon "watch glasses" reduced this problem, the relative speed with which the beakers were covered often determined the amount of silver lost. The data presented herein were obtained after a careful monitoring of the entire digestion procedures. Extreme care was taken to avoid any loss of silver due to manipulative errors.

Several wet oxidation procedures were investigated. Because the nitric acid-perchloric acid digestion procedure was recognized as hazardous, an effort was made to develop a digestion procedure that would avoid the use of perchloric acid. However, when $HClO_4$ was

ommitted from the oxidation reactions, there was a decrease in silver recovery. In the absence of perchloric acid, oils in the sample separated and formed a separate upper phase that reacted only to a limited extent with the nitric acid (31). The oils therefore remained relatively inert and eventually adhered to the beaker in the form of an oily ring. Silver, which is strongly lipophilic (91), adsorbed onto the oils and was lost from the solution. The relatively high percentage of silver found on the beakers in procedures two and three reflect this loss (Table 1). Silver was also lost from the solution as insoluble silver compounds. These were either formed during the digestion procedure or were the result of incomplete dissolution of sample material. Their presence is reflected by the higher silver content found on the filters, and to some degree, that found on the beakers. Significant amounts of insoluble silver compounds were present when procedures two, three, and five were examined (Table 1). However, three digestion procedures were found to yield satisfactory rates of silver recovery. Procedure four yielded a total silver recovery of 89.7% (Table 1). The majority of silver lost in this procedure, 6%, was in the form of insoluble silver compounds, and is believed due to a slight charring of the final residue before it was redissolved and brought to volume. Procedure six demonstrated excellent silver recovery, 94.4% (Table 1). However, the acidity of the solution may cause damage to the atomic absorption spectrophotometer should a larbe number of samples be analyzed. Although procedure seven exhibited the greatest percentage of silver recovered, 97.4% (Table 1), the copious amount of non-silver

Table 1. Average percent of silver recovered in digestion procedures. -- All data represent the average for three samples.

No.	Procedure	% Ag on Beaker	% Ag unfiltered Solution	% Ag on Filter	Total % Ag recovered Filtrate
1.	HNO_3 + HCl + HF - HNO_3 + HF + H_2O_2 - HF + H_2O_2 - HF + H_2O_2 - 2.5% HNO_3/H_2O		<50		
2.	HNO_3 + HF + H_2O_2 - HNO_3 - 2.5% HNO_3/H_2O	9.0	80.3	26.4	53.9
3.	HNO_3 - HF - H_3BO_3 - 2.5% HNO_3/H_2O	11.0	81.6	18.1	63.5
4.	HNO_3 - HNO_3 + $HClO_4$ - HNO_3 + H_2O_2 - HF - 2.5% HNO_3/H_2O	0.5	95.7	6.0	89.7
5.	HNO_3 - HNO_3 + $HClO_4$ - HNO_3 + H_2O_2 - HF - 2.5% HNO_3/2% EDTA	1.4	91.7	34.5	57.2
6.	HNO_3 - HNO_3 + $HClO_4$ - HNO_3 + H_2O_2 - HF - HCl	0.3	96.5	2.1	94.4
7.	HNO_3 - HNO_3 + $HClO_4$ - HNO_3 + H_2O_2 - HF - HNO_3 + NH_4OH + $NH_4S_2O_3/H_2O$	0.2	99.0	1.6	97.4

precipitates formed following the addition of ammonium hydroxide and Process E-6 Kodak Fixer and Replenisher made simple filtering of the samples difficult. Thus, centrifugation of the samples and filtration of the decanted solution may prove to be advantageous.

Because of the time and the extreme care required in the preparation of samples for atomic absorption spectroscopy analysis, thermal neutron activation analysis was chosen for the analysis of vegetative and geological samples.

Environmental Investigation

The topography of the canyon for the first 90 m from the mouth of the waste outfall is relatively flat (Fig. 4). The stream bed, though relatively dry, contained small shallow (5-10 cm deep) pockets of standing water which supported some algal growth. These were situated within a 10 m distance, beginning 10 m from the mouth of the outfall. The soil and rocks located slightly down-slope from the stream bed and within the first 20 m from the mouth of the waste outfall were stained black. This discoloration is believed due to the presence of Ag_2O formed by the reaction of silver metal, Ag°, with ozone (34). These soils were sticky and plastic and did not support any vegetative growth. Vegetation samples within this area were therefore taken from the upslope region of the stream bed. The other area with sparse vegetation occurred downslope of the stream bed, 90 m from the mouth of the waste outfall, where the waste flow converges with Cañon de Valle. Because the stream bed was essentially dry, water samples were taken during a discharge operation. In general, the volume of waste discharged

during a single operation is insufficient to maintain surface flow much past 70 or 80 m down stream before infiltrating into the soils and underlying alluvium. The only other surface waters were situated at the confluence of a side canyon with Canon de Valle (Fig. 4). These pockets of water were deep (30-60 cm), shaded, and supported no algal growth. Because these waters were located 300 and 330 m from the mouth of the waste outfall, they are believed to be accumulations of runoff water from recent summer rains.

Spent fixing bath solutions contain silver thiosulfate ($Na_3Ag(S_2O_3)_2$), sodium thiosulfate or "hypo" ($Na_2S_2O_3$), sulfuric acid (H_2SO_4), and boric acid (H_3BO_3) (1). Eight months prior to this investigation, the Laboratory began to recover the silver from the spent fixing baths before discharging the waste into the canyon. A silver recovery column, available from Kodak Chemical Company (Rochester, New York), was employed for this purpose. In this procedure, spent fixing bath solution is passed through a column containing steel wool. As the silver precipitates onto the metal, a reductive exchange or metallic replacement is effected which results in the release of iron ions into solution (1). In this manner, approximately 95% of the silver may be removed from solution. The silver content of the canyon water samples were therefore quite low, generally less than 2 ppb (Fig. 5). The sample taken at 60 m was somewhat higher, however, with a silver content of 6.7 ppb (Fig. 5). Measurements of the pH of these waters indicate that the sample taken at 60 m is much more acidic than those upstream (Table 2). This may lend support to the fact that silver

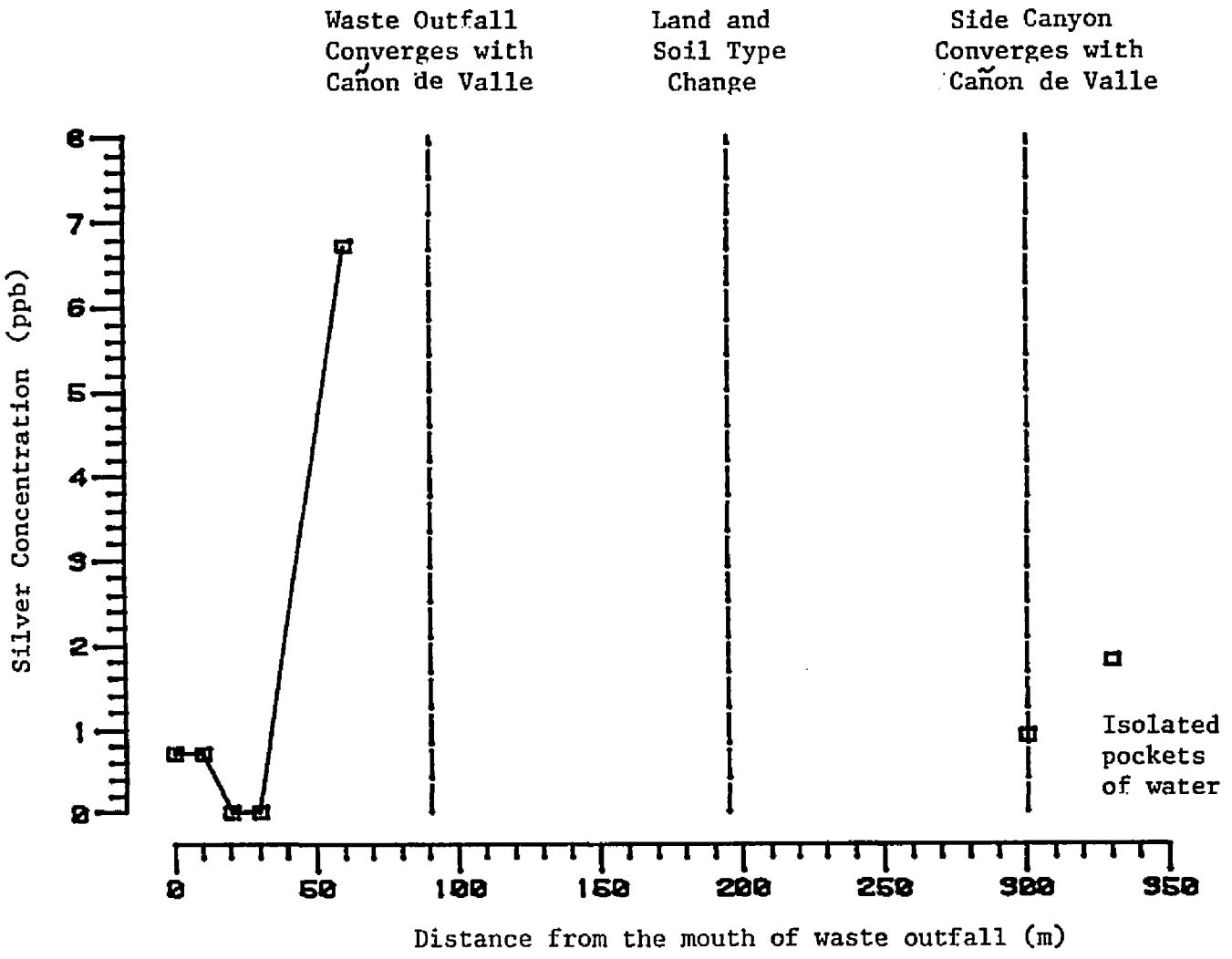


Figure 5. Silver content of water samples. -- Control is -0±0.5 ppb silver. Data points and standard deviations found in Table 2.

Table 2. Silver content and pH of water.

Location from outfall (m)	Silver Content (ppb)	pH
Control	-0 ± 0.5	6.8
0	0.7 ± 0.5	7.4
10	0.7 ± 0.5	7.3
20	-0 ± 0.5	7.0
30	-0 ± 0.5	6.6
60	6.7 ± 0.5	4.8
***300	0.9 ± 0.5	5.8
330	1.8 ± 0.5	6.4

*** Side canyon converges with Cañon de Valle at approximately 300 m.

compounds in general are more soluble and therefore more mobile in an acidic environment (34). Of note, however, is the apparently rapid drop in pH of these waters as they coursed down the canyon (Table 2). This is of particular interest considering the fact that all of the water samples within the first 60 m had been collected within an hour from a flowing stream. These solutions, exposed to increased oxygen and ultraviolet light, may have undergone a chemical or photo-oxidation which resulted in the release of H^+ into solution. However, since the complete chemical composition of the fixing bath solution is unknown (patented), what was actually occurring is only conjecture.

The silver content of the sediments and the soils decreased with increasing distance from the mouth of the waste outfall (Fig. 6 and Fig. 7). The sediments, in particular, showed marked decreases in silver content at the confluence of two stream channels. These occurred at 90 m where the waste outfall converges with Cañon de Valle, and at 300 m where a side canyon converges with Cañon de Valle (Fig. 6). These sharp decreases may reflect a diluting and/or leaching action of fresh waters that entered at these confluences during spring runoff or after summer rains when the canyon stream flows. The change in land and soil type that occurred at 195 m appeared to have little direct effect on the silver content of the sediments (Fig. 6). The drop in silver content of the soils followed a much more erratic pattern and did not appear to correlate with either the points of confluence nor with the change in land and soil type (Fig. 7). Although the decrease in silver content of the sediments and soils matched fairly closely (Fig. 8), one curious

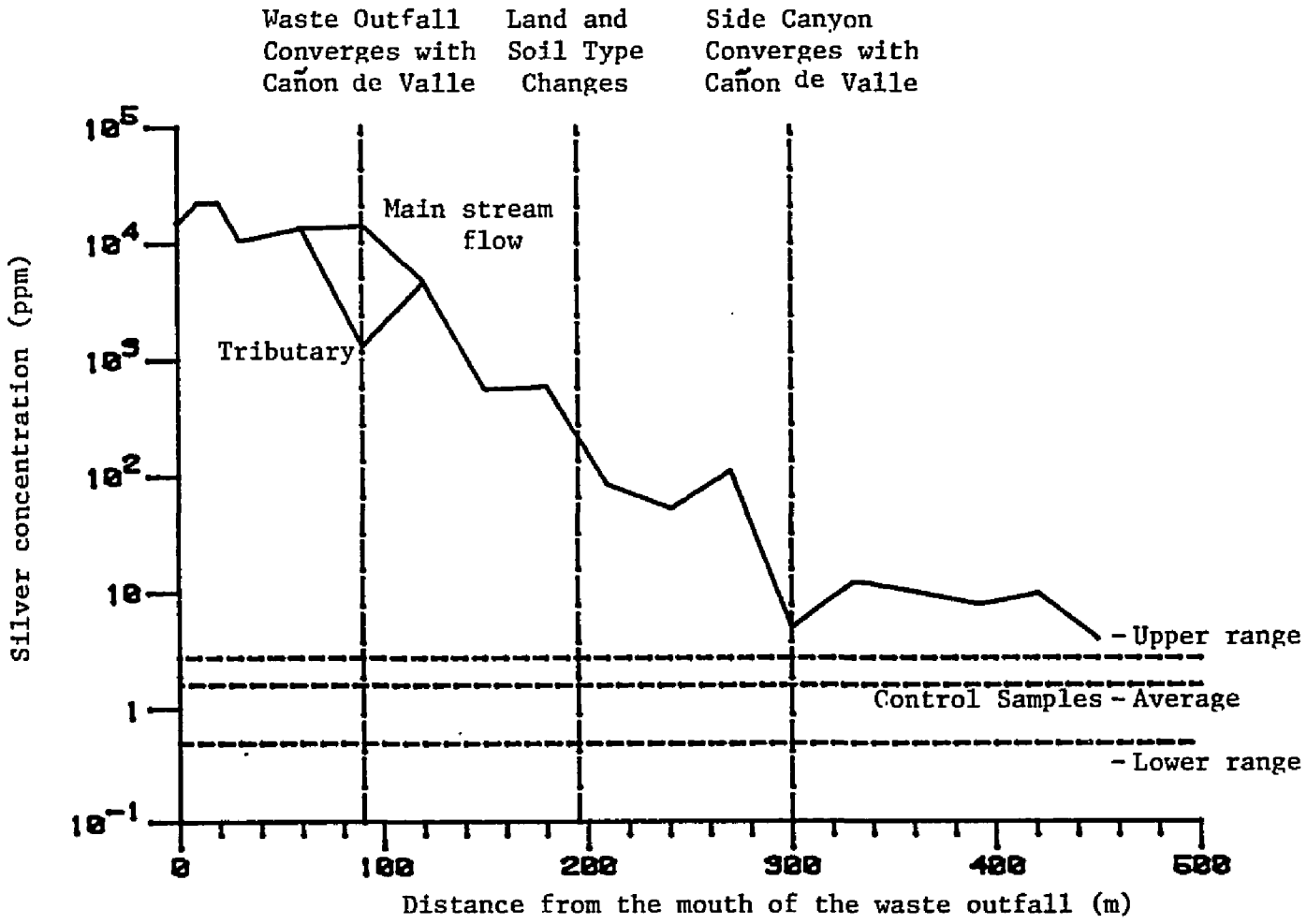


Figure 6. Silver content of sediment. -- Data points and standard deviations found in Table C.1.

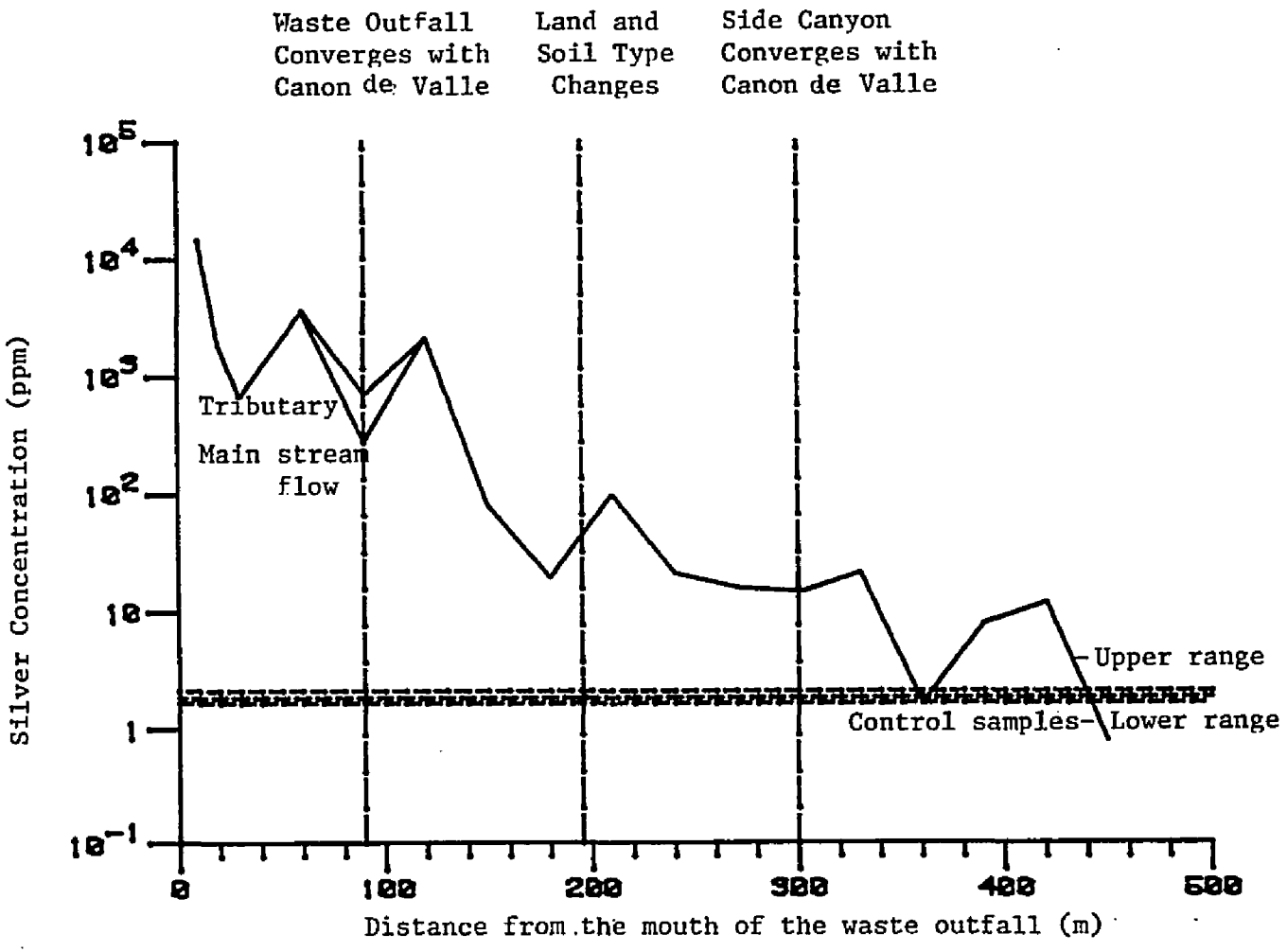


Figure 7. Silver content of soil. -- Data points and standard deviations found in Table C.1.

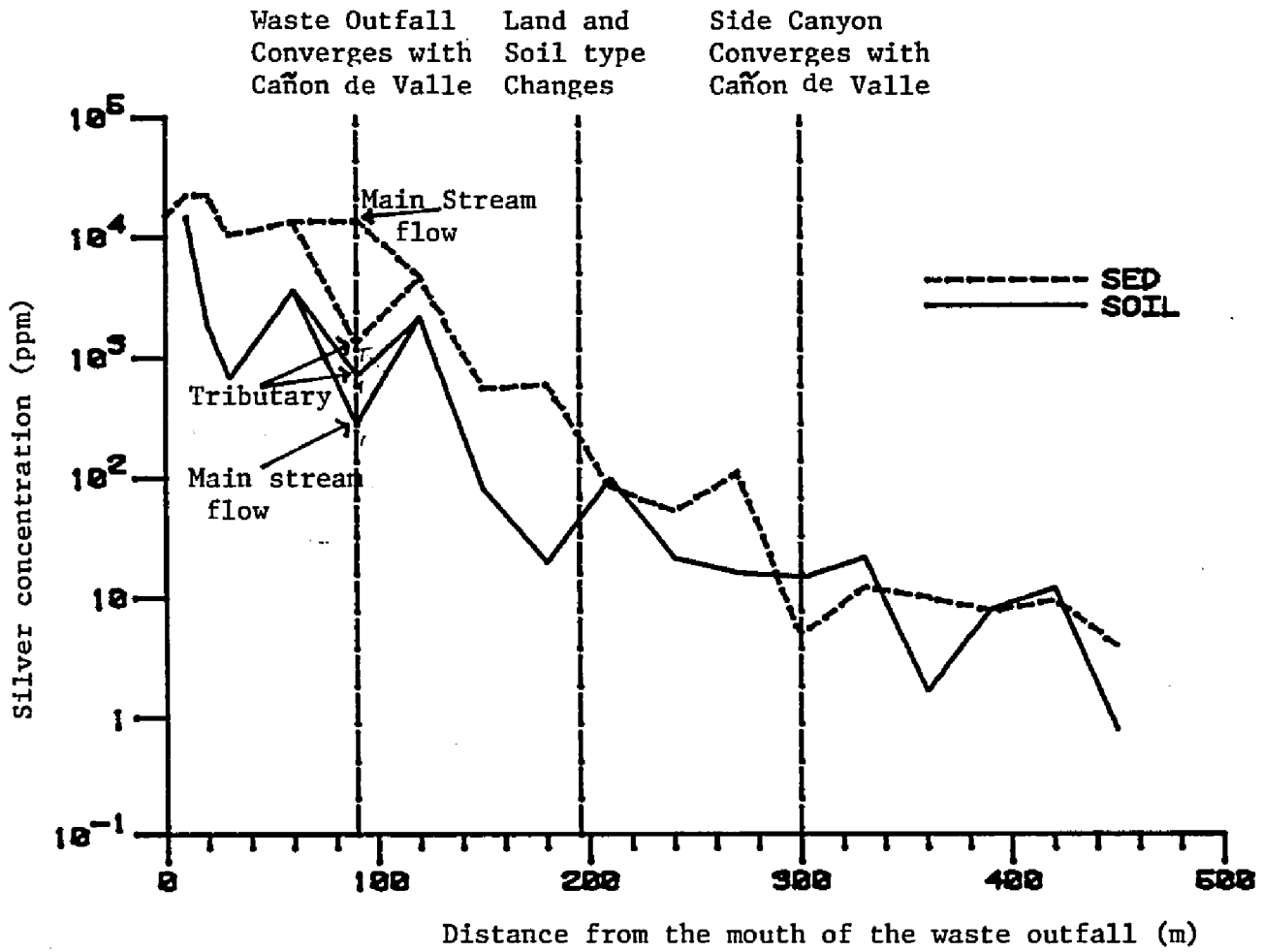


Figure 8. Comparison of silver content of sediments and soils. -- Data points and standard deviations found in Table C.1.

anomaly was observed in the samples taken 90 m from the mouth of the waste outfall. At this location, there are two stream channels, the main and the tributary. The main stream channel is well defined and appears to be older. However, the stream flow in this channel has been obstructed by a fallen tree branch and has begun to fill with soil. The tributary, on the other hand, is less well defined and appears to be of a more recent origin. While the sediments of the main stream flow have higher silver concentrations than those of the tributary, the soils around the stream channels exhibit just the opposite, with the soils around the main stream flow having lower silver content than the soils around the tributary (Fig. 8). An explanation may lie in the fact that the tributary was established slightly downslope from the main stream flow. Since the land is quite flat in this area, the waters may have been diverted down-slope when the tree branch fell across the main stream channel. Until a new stream channel had been cut, these soils were blanketed by the silver rich wastewaters. This resulted in the increased silver content of the soils around the tributary. The sediments of the tributary, however, had been exposed to less silver-bearing wastewater than had the sediments of the main stream flow which was formed when the laboratory was developing x-rays 24 hours a day. These tributary sediments had also since been exposed to the silver "clean" wastewaters and fresh runoff waters, whereas the main stream flow sediments had not. These "clean" waters may have further served to leach the silver from the tributary sediments. A vertical profile of the silver content of the soils shows the silver content decreasing with

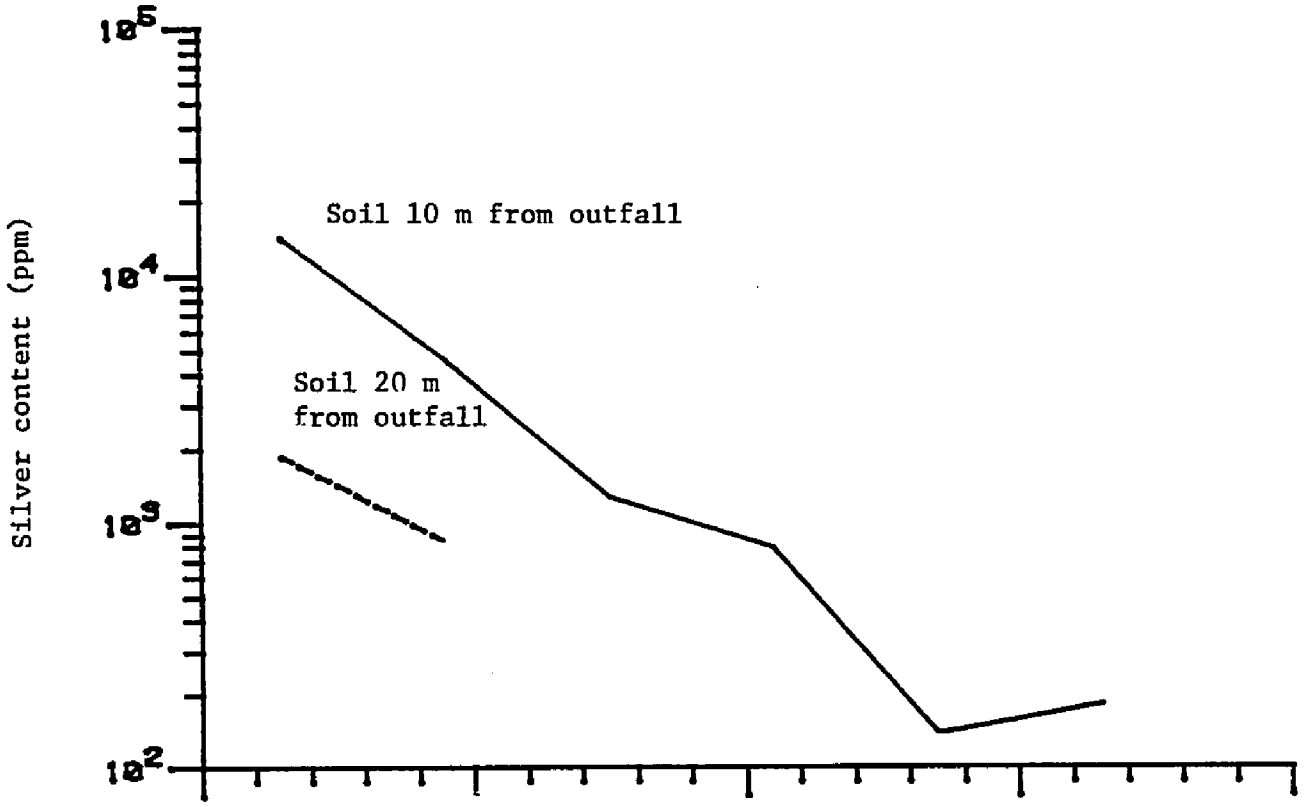
increasing depth from the soil surface (Fig. 9). At 30 to 36 inches, however, the soils exhibit a slight rise in silver concentration.

The three representative plant types examined for silver content were: grass, an annual; shrub oak, a woody perennial; and ponderosa pine, an evergreen. The foliage from all three plant types showed a decrease in silver content with increasing distance from the mouth of the waste outfall (Fig. 10, Fig. 11, and Fig. 12). At approximately 330 m, the silver content of the foliage approached background levels. Although a direct correlation between the silver content of the soils and that of the foliage was not apparent at all sampling locations, i.e. 60 m (Fig. 13, Fig. 14, and Fig. 15), a general trend was evident. Of all three plant types, the shrub oak most closely mimicked the silver content of the soils (Fig. 14).

Migration of Silver in Soil

The soils used in this investigation were clayey-skeletal Typic Eutroboralfs. They are comprised principally of clays and have significant quantities of fine black iron and manganese concretions (88). The columns were packed with a homogenous mixture of all the soil horizons and as such did not mimic conditions in the natural setting. Therefore, direct extrapolation to field conditions can not be made. Despite this, comparative data on silver mobility was gathered and possible mechanisms of silver attenuation were determined.

In the initial experiment, breakthrough (effluent silver concentration $\geq$ 1% influent concentration of silver for two to three consecutive sample volumes) occurred after 50 mg of silver had been



Depth from surface (in)	0-6	6-12	12-18	18-24	24-30	30-36
Depth from surface (cm)	0-15	15-30	15-46	46-61	61-76	76-91
Soil horizon	A1	A/B	B1t	B2t	B2t	B2t

Figure 9. Silver content of vertical profile of soil. -- Data points and standard deviations found in Table C.1.

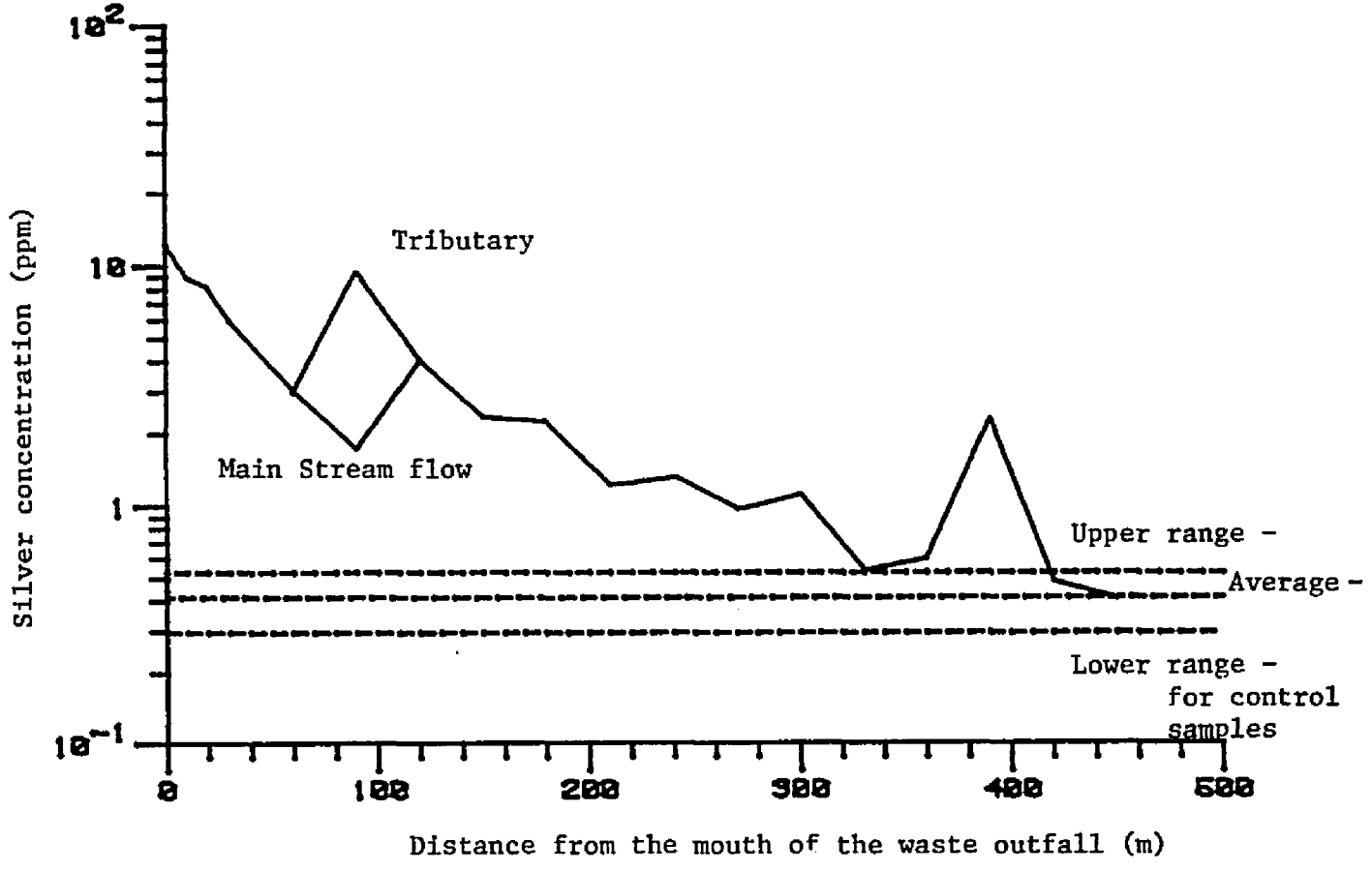


Figure 10. Silver content of grass. -- Data points and standard deviations found in Table C.1.

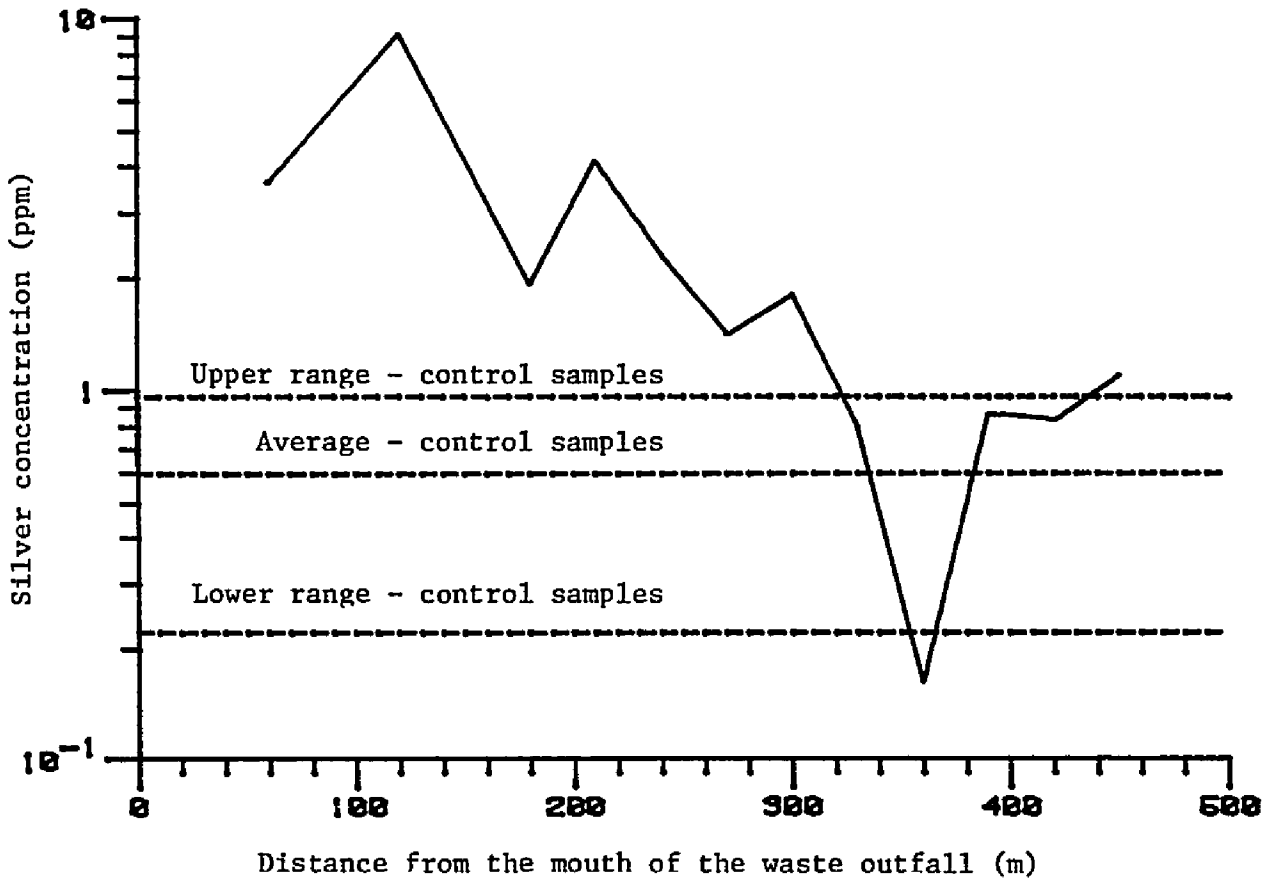


Figure 11. Silver content of shrub oak. -- Data points and standard deviations found in Table C.1.

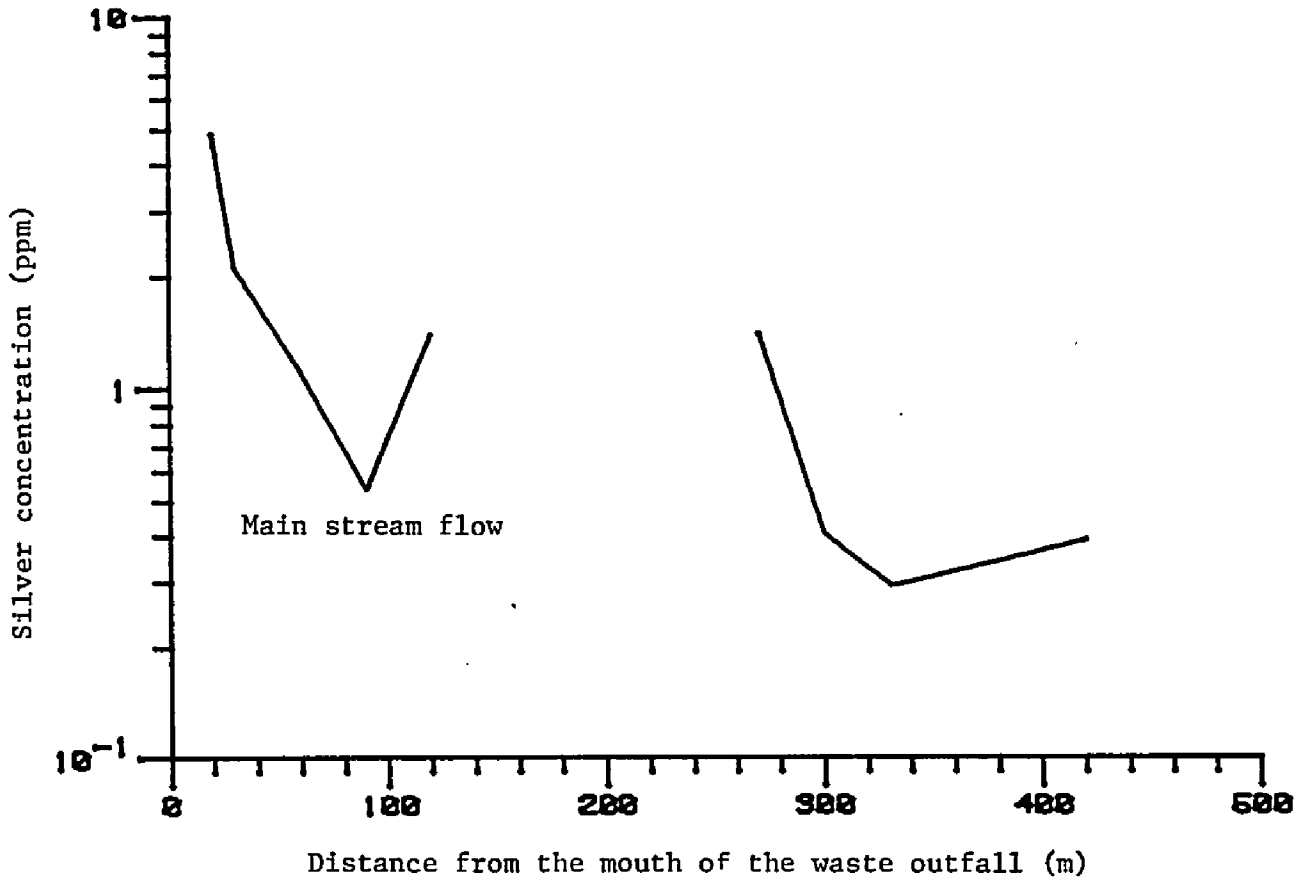


Figure 12. Silver content of ponderosa pine. -- Data points and standard deviations found in Table C.1.

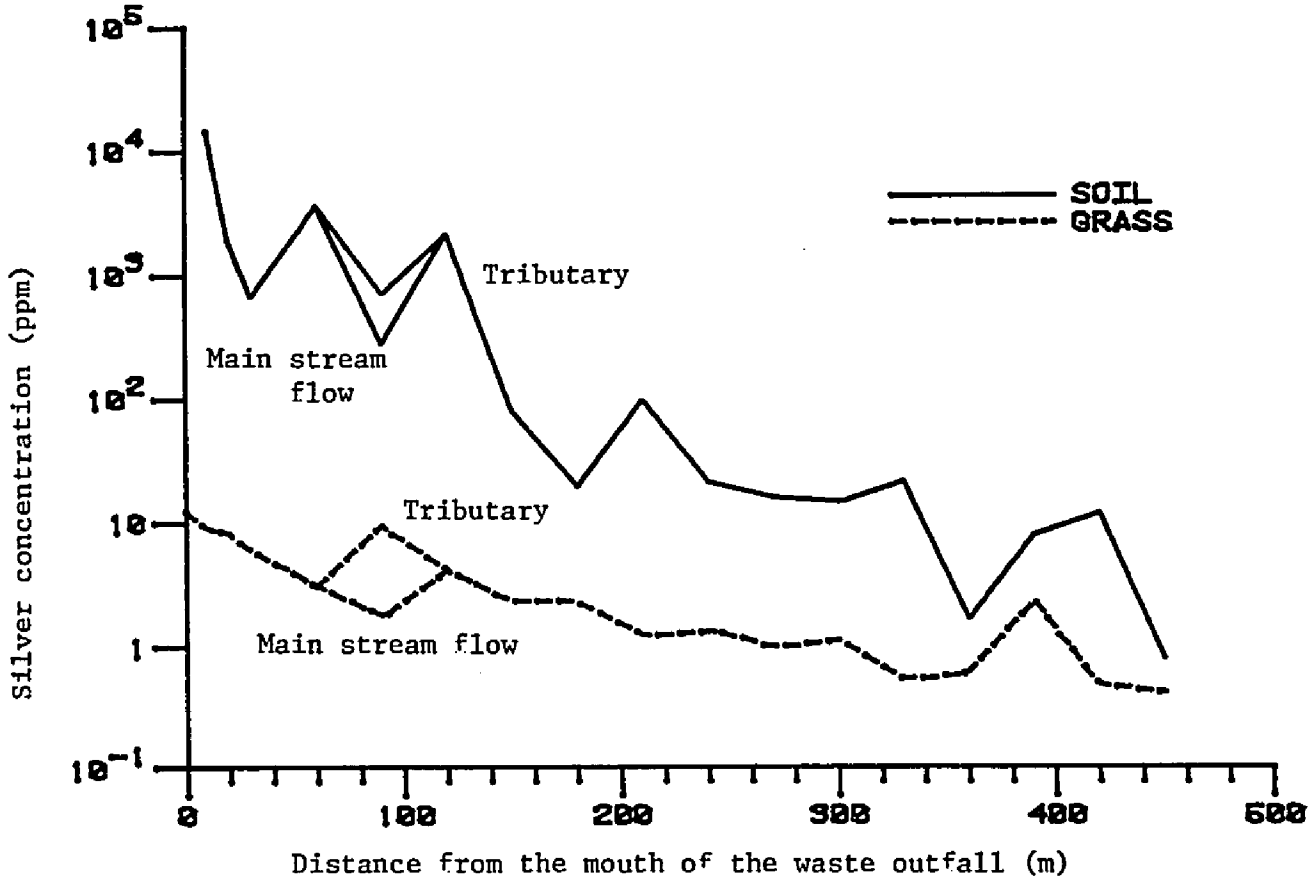


Figure 13. Comparison of silver content of soil and grass. -- Data points and standard deviations found in Table C.1.

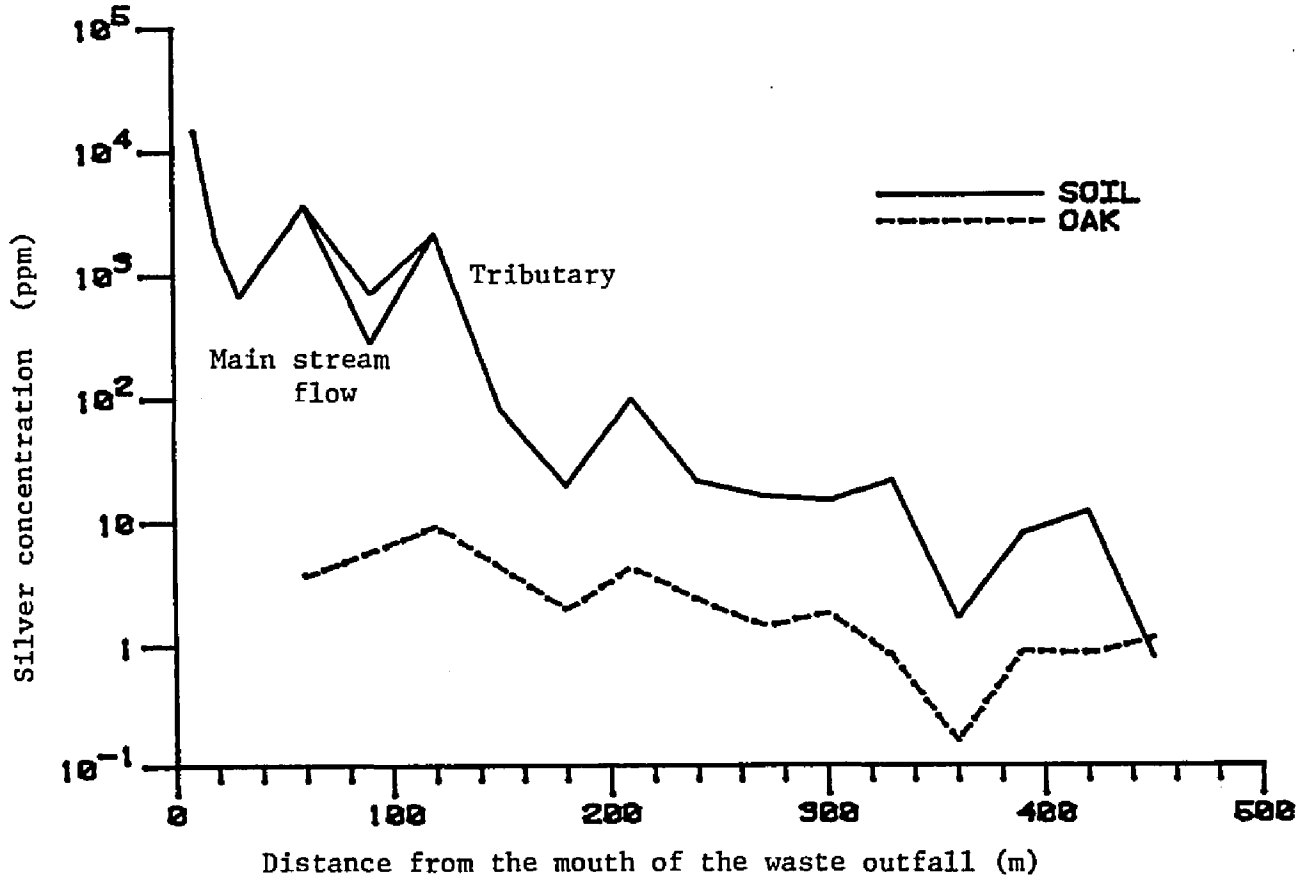


Figure 14. Comparison of silver content of soil and shrub oak. -- Data points and standard deviations found in Table C.1.

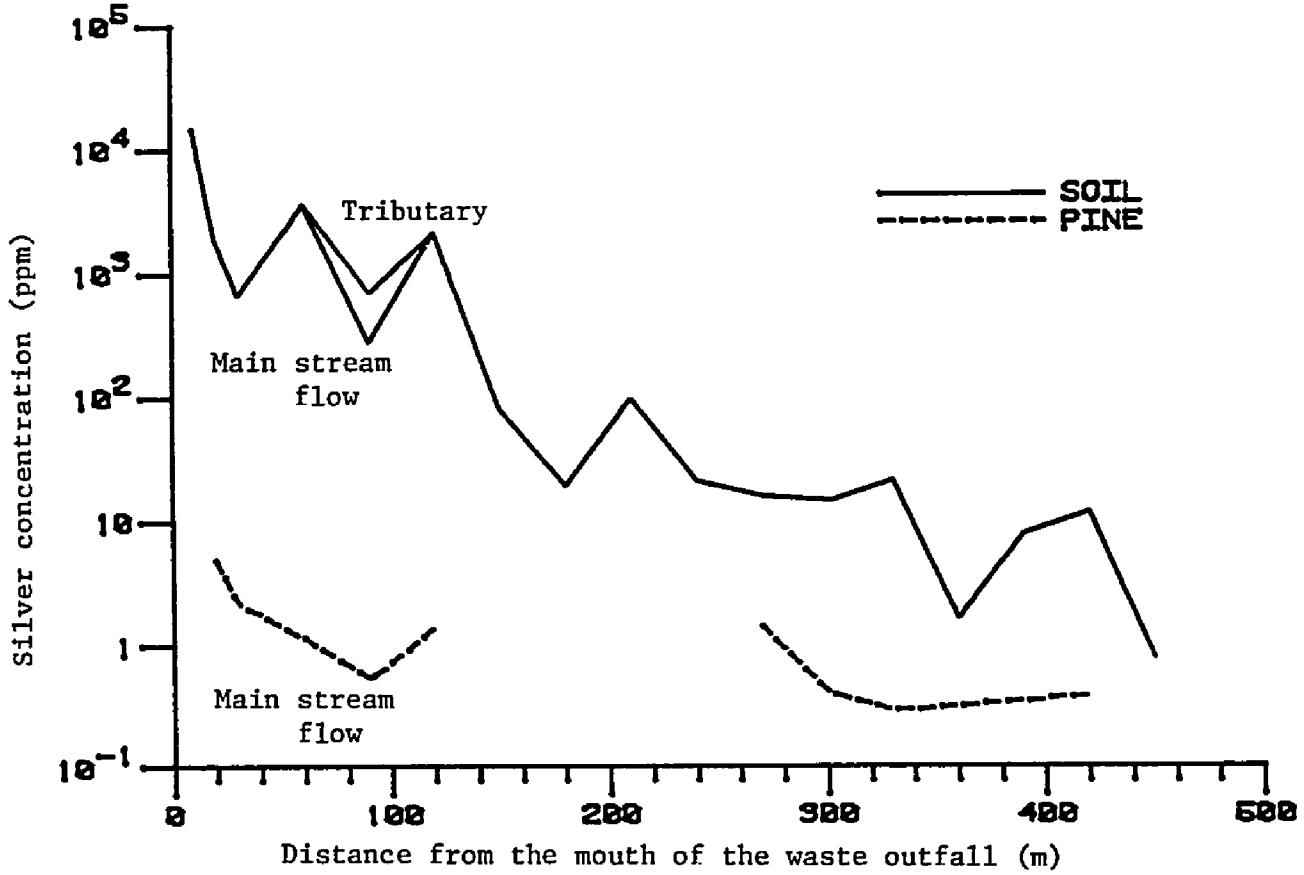


Figure 15. Comparison of silver content of soil and Ponderosa pine. -- Data points and standard deviations found in Table C.1.

introduced onto the soil as silver thiosulfate in fixing bath solution. However, silver remained undetected in the effluent of those columns receiving either silver nitrate or silver sulfate solutions following additions of 70 mg silver or 140 mg silver, respectively. Analysis of the soils shows that the concentration of silver was distributed fairly evenly throughout the vertical distance of the columns receiving silver thiosulfate solution. In contrast, the majority of silver in the columns receiving either silver nitrate or silver sulfate solution was concentrated within the first two inches of soil from the surface (Fig. 16).

In the second experiment, the silver thiosulfate solutions were prepared from an "improved" Kodak Rapid Fixer. The silver in these solutions exhibited none of the attenuation characteristics of the silver thiosulfate solution in the initial experiment. Approximately 95 to 97% of the silver introduced into the columns as silver thiosulfate prepared with the "improved" Kodak Rapid Fixer eluted from the columns in the first sample volume (Table 3). The focus of this study was, therefore, directed toward determining the amount of silver lost from the approximately 77 ml of solution that remained on the column after each sample volume had eluted. In order to detect a small decrease in silver content in this relatively small volume of solution, smaller sample volumes of solution were applied to the columns. In general, the average amount of silver retained by the soils increased with an increase in the duration of time the solution remained in contact with the soil (Table 3). A concomitant increase in silver attenuation

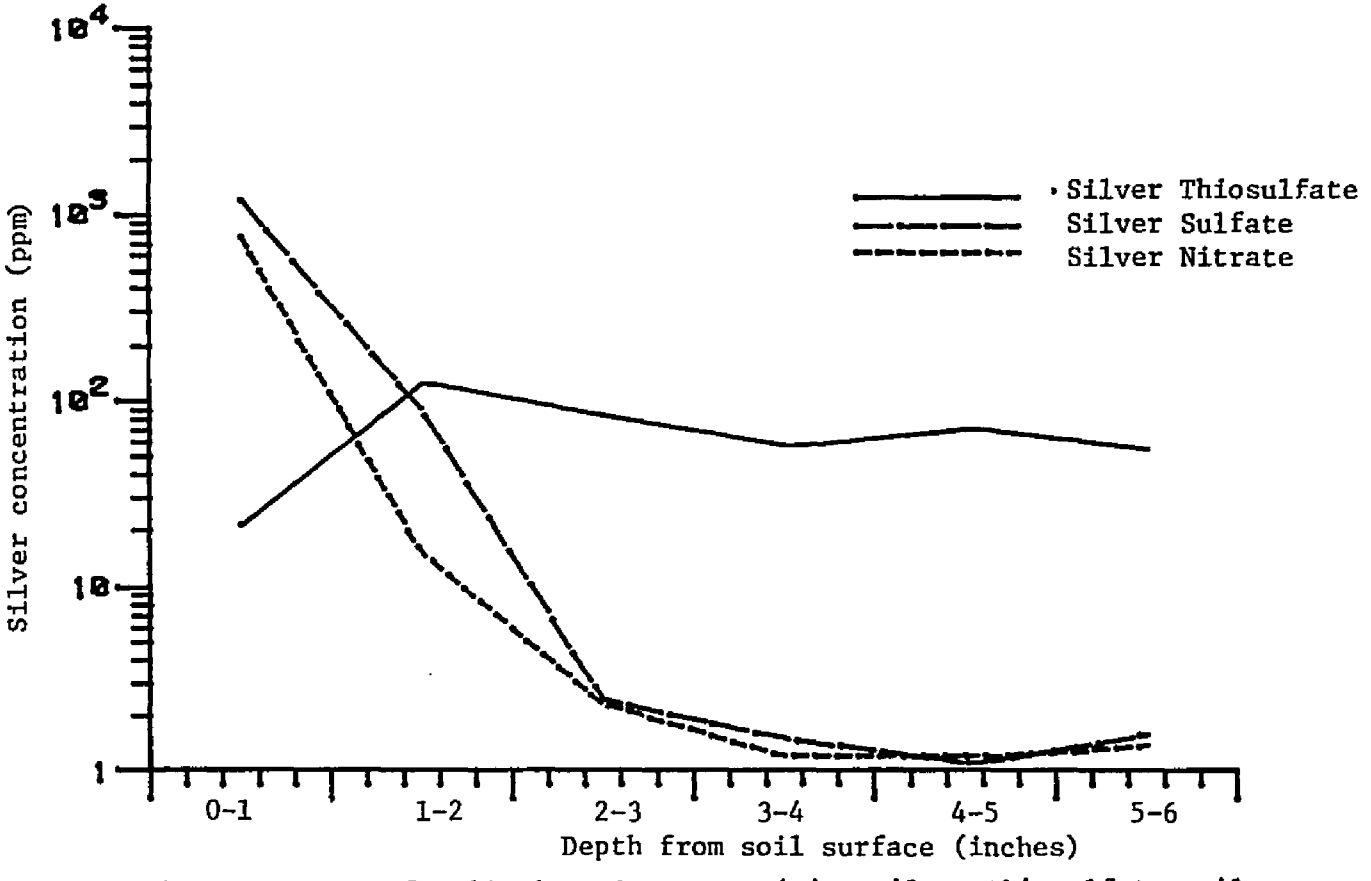


Figure 16. Average silver content of soils in columns receiving silver thiosulfate, silver nitrate, or silver sulfate. -- Silver thiosulfate columns received 10 volumes of 500 milliliters of 10 ppm silver or 50 mg Ag; silver sulfate columns received 14 volumes of 500 milliliters of 20 ppm silver or 140 mg Ag; silver nitrate columns received 14 volumes of 500 milliliters of 10 ppm silver or 70 mg Ag. Data points and standard deviations found in Table D.1.

Table 3. pH and average silver loss from silver thiosulfate solution remaining on columns. -- pH of silver thiosulfate solutions prior to elution: pH 4.3. Approximately 77 ml of solution remained on each column after sample volumes had eluted. Averages are taken from data in Table E.1.

Conc. Ag Applied to column (ppm)	Day Solution Applied to Column	pH of Effluent	Volume of Solution Applied to column (ml)	Avg. Conc. Ag Lost from solution on column (ppm)	Avg. % Ag lost from solution on column
10	1	5.9	500	0.5 ± 0.1	5 ± 1
	2	-	278	4.5 ± 0.3	45 ± 3
	12	7.0	200	7.6 ± 2.4	76 ± 24
50	1	5.9	500	1.7 ± 0.4	3 ± 1
	2	-	278	3.2 ± 1.7	6 ± 3
	12	7.0	200	14.1 ± 2.2	28 ± 5
100	1	5.9	500	5.0 ± 0.6	5 ± 1
	2	-	278	0	0
	12	7.0	200	15.6 ± 2.8	16 ± 3

also accompanied the increase in silver concentration of solutions applied to the soils (Table 3). However, the average percent silver loss from solution decreased as the concentration of silver applied to the soils increased (Table 3). After remaining on the soil for ten days, 76% of the silver from the 10 ppm silver thiosulfate solution had been lost from solution. Yet, only 28% of the silver from the 50 ppm silver solution and 16% of the silver from the 100 ppm silver solution had been retained by the soils within the same period of time.

The data from these investigations suggest that two separate mechanisms of silver attenuation are in effect. One set of soil/chemical reactions is believed to govern the removal of silver from silver nitrate and silver sulfate solutions. A second set of reactions is believed to function in the retention of silver from silver thiosulfate complexes present in spent fixing bath solutions.

The attenuation of silver from silver nitrate and from silver sulfate solutions took place rapidly. The majority of silver was retained by the soil in the relatively short time it took for the solutions to migrate through the first two inches of soil. The pH of the solutions applied to the soil were neutral to slightly acidic and are believed to have changed little within the short time they were exposed to the surface soils. Since atmospheric oxygen is abundant at the soil surface, the mechanism of silver attenuation for both silver nitrate and silver sulfate solutions operated under a high oxidation potential.

The silver in both silver nitrate and silver sulfate solutions is in ionized form. As the Ag^{+} ion, the silver is readily available to

participate in numerous soil/chemical reactions. Some of the silver may have been removed from solution by ferric oxide hydrates, $FeO(OH)\cdot nH_2O$. Although the hydrated colloid bears a positive charge, elements such as PO_4^{3-}, AsO_4^{3-}, hydrated MnO_2, silica, and humic colloids, when present in the soil, are attracted to the hydrate, giving the combined colloidal complex a negative charge. These combined complexes may then adsorb and coprecipitate Ag^+ (34). In a very weakly acidic or neutral soil/chemical environment, the silver may also be precipitated by the manganous ion according to the reaction:

$$2\ Ag^+ + Mn^{2+} + 4\ OH^- = 2\ Ag + MnO_2 \cdot H_2O + H_2O$$

Under alkaline conditions, however, the oxidation potential developed by the oxygen couple would be sufficient to oxidize Mn^{2+} to MnO_2, thereby mobilizing the silver (34,92). Hydrated manganese oxides would also precipitate in a weakly acidic environment. Bearing a negative charge, these colloids could then adsorb and coprecipitate Ag^+ (34). Anions such as PO_4^{3-}, Cl^-, Br^-, I^-, CrO_4^{3-}, and AsO_4^{3-} could also react with the Ag^+ to precipitate insoluble compounds and reduce the mobility of silver. Organic matter would serve to immobilize silver by possible forming chelated complexes with the metal. However, under a high oxidation potential, the silver may be liberated as the humic complexes are oxidized to CO_2 and H_2O, etc. (34). The principal mechanism of silver attenuation is believed to be cation exchange. The clayey-skeletal Typic Eutroboralf soils are comprised primarily of clays. The silver ion (Ag^+), because of its similarity in ionic structure and adsorption

characteristics, may effectively replace the Na^+ and/or K^+ in the clay structure and in so doing be removed from solution (34).

Because the majority of silver was removed from the silver nitrate and silver sulfate solutions under a high oxidation potential, certain reactions have been ruled out. The acid reaction:

$$Fe^{2+} + Ag^+ \rightleftharpoons Ag + Fe^{3+}$$

would only serve to mobilize the silver. Iron, if present in the ferrous state (Fe^{2+}) would be rapidly oxidized to the ferric state (Fe^{3+}). This would cause a shift in the Fe^{2+}/Fe^{3+} ratio resulting in the mobilization of silver (34). Silver would also not precipitate as the sulfide (Ag_2S) since the S^{2-} in the reaction:

$$2\ Ag^+ + S^{2-} = Ag_2S$$

would be oxidized on to sulfur (92) or in neutral to alkaline solutions to thiosulfate $(S_2O_3)^{2-}$ or sulfate $(SO_4)^{2-}$ (93):

$$S^{2-} \longrightarrow (S_2O_3)^{2-} \longrightarrow (SO_3)^{2-} \longrightarrow (S_nO_6)^{2-} \longrightarrow (SO_4)^{2-};$$

(n = 2-6).

In an alkaline environment, $(FeOH)_2$ effectively reduces Ag^+ to the metal. However, under the high oxidation potential in the soil surface, it would be oxidized to $Fe(OH)_3$ and essentially removed from the oxidation-reduction reactions with Ag^+ (34).

The silver attenuation characteristics for silver thiosulfate complexes ($Na_3Ag(S_2O_3)_2$) in spent fixing bath solution differ from those exhibited by both silver nitrate and silver sulfate solutions (Fig. 16).

The fact that the average percent of silver lost from silver thiosulfate solution decreased as the concentration of silver applied to the soils increased (Table 3), suggests there is a maximum concentration of silver that may be lost to the soil within a given amount of time. Therefore, the soil/chemical reactions involved in the attenuation of silver from spent fixing bath solution are believed to be readily saturated. The amount of silver lost to the soil would thus be governed by the rate of these reactions.

The silver in spent fixing bath solution is present as a silver complex of the type $[Ag(S_2O_3)_2]^{3-}$ (1). In neutral or alkaline conditions this silver thiosulfate ion is extremely stable and mobile and dissociates with the formation of S and Ag_2S only when there is an increase in acidity or when the solution comes in contact with reducing substances such as carbonaceous matter. As shown in Table 3, the pH of the silver thiosulfate solutions increased as they passed through the soil. This is believed due to the reaction of carbonates in the soil with the sulfuric acid present in the fixing bath solution (1). This would result in the formation of bicarbonate ion (HCO_3^-) or in the formation of carbonate sulfates according to the reaction:

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2$$

The pH of the solutions were also found to increase with increased contact with the soil (Table 3). Since pH is not additive, the actual pH of the approximately 77 ml of solution which remained in contact with the soil can not be determined. However, since the pH of the effluent

200 ml of solution, which includes the 77 ml, is pH 7.0, and the pH of the solution after passing through the column once is 5.9 (Table 3), the pH of the 77 ml which remained on the column is believed to be much higher than pH 7.0. Therefore, since there is a decrease in the acidity of the solutions, the dissociation of the silver thiosulfate complex to Ag_2S could only result from contact with reducing substances, such as carbonaceous matter, in the soil. The silver sulfide (Ag_2S) so formed could then precipitate out of solution or react with any sulfuric acid remaining in the fixing bath solution to form silver sulfate (34):

$$Ag_2S + H_2SO_4 = Ag_2SO_4 + H_2S$$

As long as H_2S is present, the above reaction does not proceed far (34). However, under a high oxidation potential, this constituent may be oxidized on to sulfur and/or sulfate (34). The silver sulfate formed when the silver sulfide reacts with the sulfuric acid could then participate in the numerous soil/chemical reactions described previously.

Thus, under a high oxidation potential, the ultimate sink for the silver removed from spent fixing bath solution may be a constituent of the clay fraction in the soils. However, in the first experiment, the silver concentration in the first inch of soil, where the oxidation potential is high, was lower than that of the rest of the column (Fig. 6). Furthermore, as solutions remain in contact with the soil, oxygen is consumed and the oxidation potential gradually decreases (34). Yet, more silver was attenuated from the solutions which remained in contact with the soil for the greater length of time (Table 3).

Although the two spent fixing bath solutions differed in attenuation characteristics, they were somewhat similar in chemical character. The reaction:

$$Ag_2S + H_2SO_4 = Ag_2SO_4 + H_2S$$

proceeds with greater facility under a high oxidation potential. However, the reduction of the silver thiosulfate complex in spent fixing bath solution to Ag_2S, under the same condition, may be inhibited. The limiting reaction is thus believed to be the reduction of the silver thiosulfate complex $[Ag(S_2O_3)_2]^{3-}$ to sulfur (S) and silver sulfide (Ag_2S). The limiting factors determining the amount of silver attenuated by the soils are, therefore, the amount of reducing substances present in the soil and the amount of oxygen present.

Phytotoxicity of Silver

When silver solutions are applied to plants in a study such as this, it is difficult to separate the effects of the silver ion (Ag^+) from the effects of the anion with which it is associated. The anion may be beneficial and even essential to the plants, as in the case of the NO_3^- anion in silver nitrate and the SO_4^- anion in silver sulfate solutions (49), or the anion may exert its own toxic effect.

For the first 20 days of this investigation, the rates of germination appeared to differ little among the various groups. The exception to this was the group receiving silver sulfate solution. This group appeared to exhibit an initially faster rate of germination (Fig. 17). Groups receiving either sodium thiosulfate (fixing bath

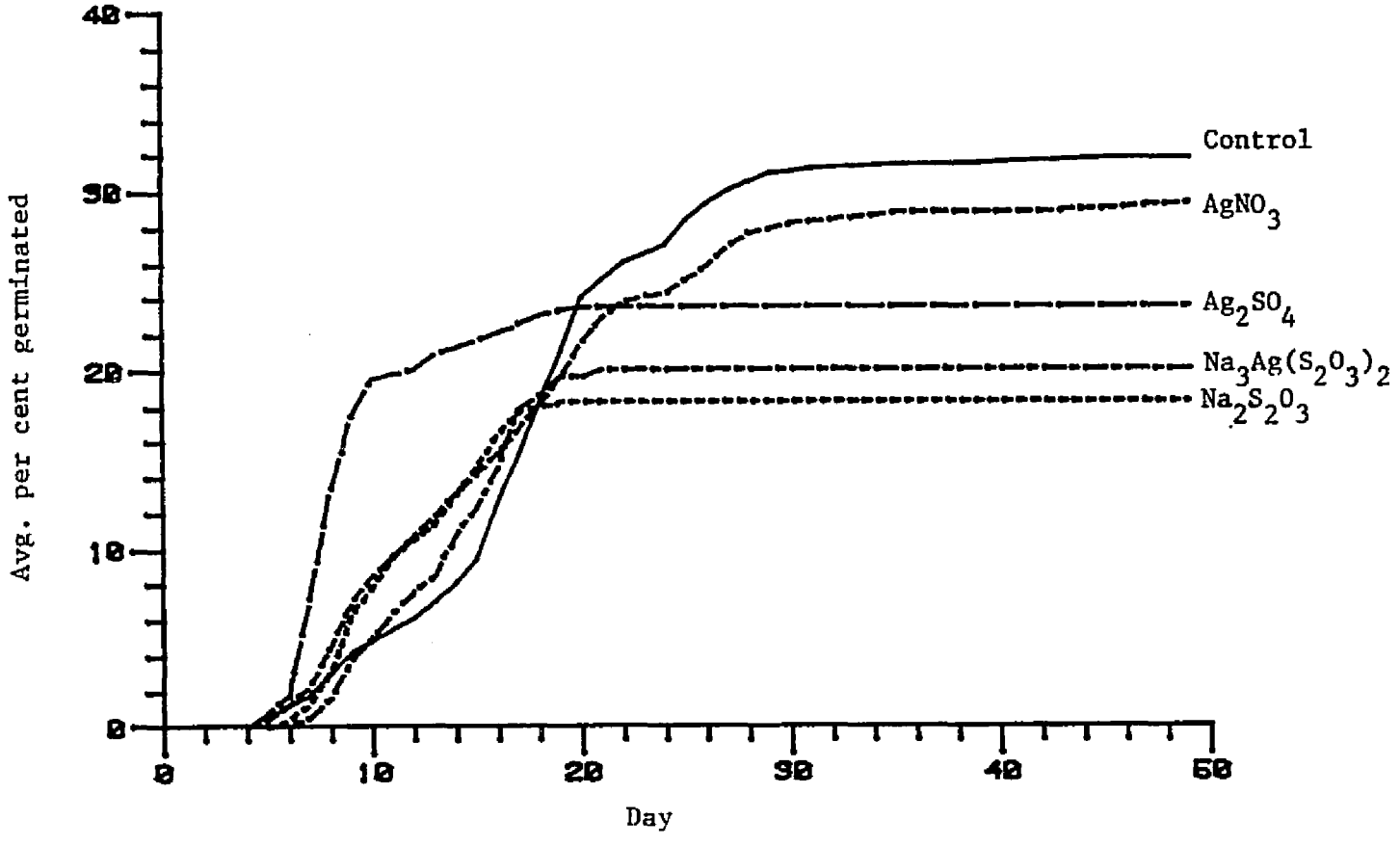


Figure 17. Comparison of average per cent sprouts germinated. -- Data points and standard deviations found in Table F.1.

solution), 10 ppm Ag as silver thiosulfate in spent fixing bath solution or 20 ppm Ag as silver sulfate fell statistically below that of the controls. The group receiving 10 ppm Ag as silver nitrate solution, however, was within the statistical variation of the control (Table 4). The germination rates of $Na_2S_2O_3$ were statistically lower than all other groups.

The only groups that had significant numbers of deaths were those plants that had received either the fixing bath solution or the spent fixing bath solution. The only difference between the two solutions is the concentration of silver. Although the silver thiosulfate solution exhibited a slightly higher rate of deaths (Fig. 18), the difference between the two rates is statistically insignificant.

In the determination of potential gross productivity, the groups receiving both silver nitrate and silver sulfate solutions for the duration of the study were statistically lower than that of the control. In contrast, however, all of the groups receiving solutions after the first 24 days of the study exhibited statistically higher rates of potential gross productivity than that of the control (Table 5). Both post silver nitrate and post silver sulfate solutions exhibited statistically higher rates of potential gross productivity than their counterparts in the germination group. The post silver thiosulfate group also exhibited statistically slightly higher rates of gross productivity than did the post group which received sodium thiosulfate (Table 5).

Table 4. Germination. -- Statistical evaluation using Student's t at 95% confidence $\bar{x} \pm (s/\sqrt{n})(t_{n-1;\ 0.975})$.

Sample	n	s	$\bar{x}$	95% confidence limits
Control	18	7.07	31.84	28.32-35.36
Sodium Thiosulfate	18	6.82	18.22	16.61-19.83
Silver Thiosulfate	18	6.25	20.00	18.53-21.47
Silver Nitrate	18	4.18	29.43	28.44-30.42
Silver Sulfate	18	4.63	23.67	22.58-24.76

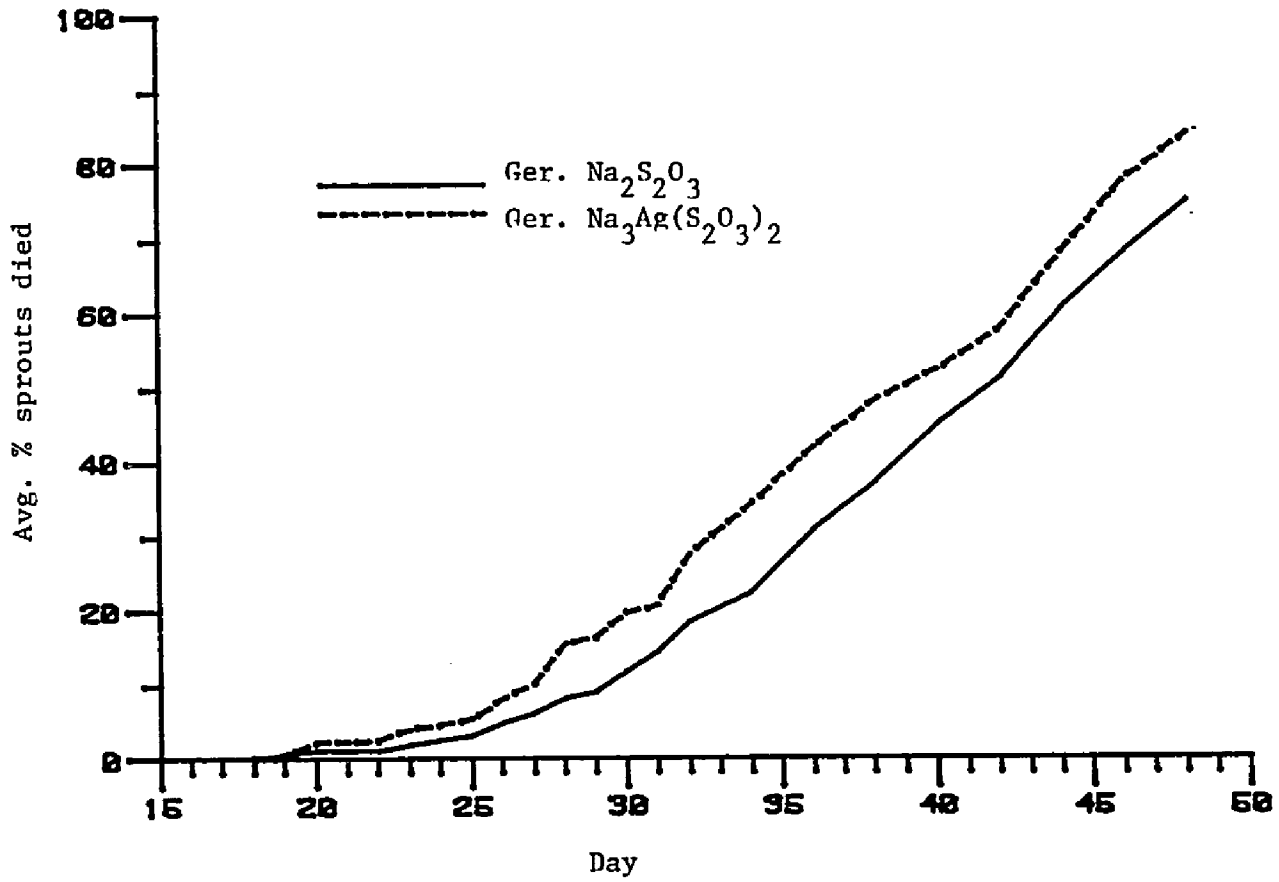


Figure 18. Comparison of average per cent sprouts died. -- Data points and standard deviations found in Table G.1.

Table 5. Gross potential productivity (chlorophyll content). -- Statistical evaluation using Student's t at 95% confidence $\bar{x} \pm (s/n)(t_{n-1;0.975})$.

Sample	n	s	$\bar{x}$	95% confidence limits (g/chlor/l)
Control	15	1.26	18.47	18.14-18.79
Sodium Thiosulfate	Too few plants to determine			
Silver Thiosulfate	Too few plants to determine			
Silver Nitrate	18	1.95	17.10	16.64-17.56
Silver Sulfate	18	1.68	16.94	16.54-17.34
Post Sodium Thiosulfate	14	1.83	19.51	19.02-20.00
Post Silver Thiosulfate	14	2.24	20.63	20.03-21.23
Post Silver Nitrate	14	2.72	18.78	18.05-19.51
Post Silver Sulfate	14	2.15	19.45	18.88-20.02

The net productivity of the controls was statistically higher than that of the groups receiving either sodium or silver thiosulfate solutions (Table 6). Those groups receiving either silver nitrate or silver sulfate solutions exhibited statistically higher rates of net productivity. The sodium or the silver thiosulfate groups in the post germination groups also exhibited statistically higher rates of net productivity than their coutnerparts in the germination group (Table 6).

However, in order to determine the health of the plants, the measure of the ratio of net productivity/potential gross productivity is more significant. Net productivity determines growth. It is the measure of the energy stored by photosynthetic activity (49). Gross productivity is the measure of the total rate of photosynthesis including the organic matter used in respiration (49). Therefore, if a plant exhibits a high rate of potential gross productivity, yet a low rate of net productivity, its energies are directed more towards sustaining its life than towards energy storage and growth. The ratios displayed in Table 7 suggest that those groups receiving the silver nitrate solutions are better off than the controls. The post silver sulfate groups appeared to do as well as the controls. However, those groups receiving the thiosulfate solutions did poorly in comparison.

While silver may at first be thought to be responsible, examination of the silver content of the plants shows otherwise. The post silver sulfate group, which was comparatively as healthy as the controls, had an extremely high concentration of silver, similar to the group receiving silver thiosulfate solution for the entire duration of the experiment (Table 7, Table 8). In contrast, the groups receiving

Table 6. Net productivity. -- Statistical evaluation using Student's t at 95% confidence $\bar{x} \pm (s/\sqrt{n})(t_{n-1;0.975})$.

Sample	n	s	$\bar{x}$	95% confidence limits (gm/plant)
Control	15	.0012	.0078	.0075-.0081
Sodium Thiosulfate	18	.0030	.0048	.0041-.0055
Silver Thiosulfate	18	.0027	.0048	.0042-.0054
Silver Nitrate	18	.0018	.0093	.0089-.0097
Silver Sulfate	18	-	-	-
Post Sodium Thiosulfate	14	.0012	.0065	.0062-.0068
Post Silver Thiosulfate	14	.0007	.0058	.0056-.0060
Post Silver Nitrate	14	.0012	.0091	.0088-.0094
Post Silver Sulfate	14	.0013	.0082	.0079-.0085

Table 7. Ratio: net productivity (g/plant)/gross productivity (g chlor/l).

Control	4.2×10^{-4}
Sodium Thiosulfate	Too few plants to determine
Silver Thiosulfate	Too few plants to determine
Silver Nitrate	5.4×10^{-4}
Silver Sulfate	-
Post Sodium Thiosulfate	3.3×10^{-4}
Post Silver Thiosulfate	2.8×10^{-4}
Post Silver Nitrate	4.8×10^{-4}
Post Silver Sulfate	4.2×10^{-4}

Table 8. Silver level (ppm).

Sample	1st Faction	2nd Faction	Avg ($\bar{x}$)	s
Control	6.5 ± 0.6	5.8 ± 0.6	6.15	0.49
Sodium Thiosulfate	8.8 ± 0.9	-	8.8	0.90
Silver Thiosulfate	161 ± 8.0	-	161	8.00
Silver Nitrate	106 ± 5	92 ± 5	99	9.90
Silver Sulfate	145 ± 7	162 ± 8	153.5	12.02
Post Sodium Thiosulfate	9.4 ± 0.8	5.8 ± 0.6	7.6	2.55
Post Silver Thiosulfate	37 ± 4	47 ± 3	42	7.06
Post Silver Nitrate	94 ± 5	99 ± 5	96	3.54
Post Silver Sulfate	145 ± 7	161 ± 8	153	11.31

sodium thiosulfate exhibited silver levels close to those of the control. A curious anomaly was also observed between the germination groups and the post germination groups. The silver concentrations of the silver nitrate and silver sulfate germination groups were similar to the concentrations of silver found in their counterparts within the post germination groups (Table 8). The silver content of the post silver thiosulfate group was significantly lower than that of its counterpart in the germination group. The amount of silver applied as silver thiosulfate solution was at the same concentration as that of the silver nitrate solutions. However, more silver was taken up by the plants receiving silver thiosulfate solution as compared to with those plants receiving silver nitrate in the germination group. The reverse was observed in the post germination groups. The plants receiving silver nitrate solution exhibited a greater silver content than those receiving silver thiosulfate solution. These data may suggest that there is a maximum quantity of silver that may be incorporated into the plants from soils receiving either silver nitrate or silver sulfate solutions. In contrast, silver appears to be incorporated into the plant at a much slower or gradual rate from soils receiving silver thiosulfate in spent fixing bath solution. The silver concentration in these plants appears to vary with the concentration of silver in the solution applied.

Since silver can not be labeled as being responsible for the toxicity in these investigations perhaps sodium can. During the course of this investigation, several curious anomolies were observed. When the solutions were applied to the soil, most penetrated through soon

after hitting the soil surface. The surface appearance of these soils also remained unchanged. However, the soil in those cups receiving $Na_2S_2O_3$ in fixing bath solution and $Na_3Ag(S_2O_3)_2$ in spent fixing bath solution behaved differently. The first thing noticed was the general appearance of the surface. After several daily applications of these solutions, the soils appeared darker in color and seemed to be cracked and dry. As the experiment progressed, the solutions did not readily penetrate the soil surface. They remained in a small pool on the surface of the soil before very gradually gravitating downward. Despite the appearance of the surface layer of soil, the soils in these groups probably were not drying out as rapidly as those in the other groups. This was confirmed on the 28th day from the initiation of the experiment when the fixing bath and spent fixing bath solutions eluted from the bottoms of their cups. Thereafter, these solutions eluted from the cups after every application. This did not occur in any of the other groups. Sodium, present in significant quantity in fixing bath solution, is believed to be responsible.

The main cause of salination in agricultural soils is the adsorption of sodium on particles of clay. When this occurs the clay particles swell and the space between the particles is reduced (82). Because the soils are relatively impermeable, water tends to remain at the surface (83). Acharya et al. (83) showed that increased sodium content of such soils also leads to a decrease in the hydralic conductivity of the soil. The upward water flux to replenish the loss occurring at the surface is therefore reduced. This results in a

desiccation of the surface zone under a high evaporative demand. Water below the surface layer is trapped. The water saturated soil is not well aerated and anaerobic conditions may result. The reduced atmosphere limits the ability of the plant to handle excess sodium present in its environment. Since the sodium-potassium pump derives its energy from the hydrolysis of adenosine triphosphate (ATP) (68), a root hair cell will consume oxygen as fast as needed to regenerate ATP (85). In the absence of molecular oxygen the activity of the pump gradually declines as the cell must rely on the energy liberated from the food stores by glycolysis. Thus, net productivity is reduced. The majority of the plants energy is directed toward removing excess sodium from its cells. However, as oxygen is depleted, high concentrations of sodium may readily saturate the pump resulting in a net influx of Na^+ into the cell until osmotic equilibrium is established. Since high external concentrations of sodium also depolarize the cell, the resulting loss in electrical current flow combined with the maintained osmotic equilibrium effects a loss in net water movement into the cell (68). Therefore, a plant's ability to absorb water from soils containing high levels of sodium is greatly reduced.

Unfortunately, the reduced water content of a plant may have dramatic effects on the values received for the measurements of both the net productivity and the potential gross productivity. In the determination of net productivity the plants are weighed and counted shortly after harvesting. Drier plants weigh lighter and the net productivity may appear to be lower. The same is true for those plants weighed for

chlorophyll determinations. Since the plants are direr the ratio of plant mass/weight will be increased. More plant mass and less water will be weighed for analysis. The spectrophotometric readings may also differ (51). Those with higher water content would have more diluted solutions and read lower than those with less water content. Therefore, the actual productivity measurements taken for the plants receiving fixing bath solution or spent fixing bath solution may be erroneous. However, the plants in these groups were visibly smaller and less well developed. They were dark green in color and appeared to be dry and stiff. Those plants in the other groups were much larger and better developed. They were lighter green in color and were flexible. Thus, the rationale of plant health stated earlier still applies. This determination, however, is based on qualitative and not quantitative data for those plants receiving the fixing bath solution and the spent fixing bath solutions.

SUMMARY

Although the laboratory data may not be extrapolated directly to field conditions, the results of this investigation give some indication of what may have occurred in the natural setting of Cañon de Valle. The silver thiosulfate complex in the spent fixing bath solution was probably reduced to silver sulfide in the soils. However, as demonstrated previously, the attenuation characteristics of two similar solutions may differ markedly. The attenuation characteristics and chemical behavior of all of the various spent fixing bath solutions eluted into the canyon over a period of 20 years can not be determined. The only relevant data that may be gained from the environmental investigation is the status of the canyon at the time it was sampled.

There was a general decrease in silver content of the sediments, soils, and vegetation as the distance from the mouth of the waste outfall increased. At approximately 300 m distance, the silver levels of the vegetation approached those of the background. The silver content of the sediments and the soils however remained significantly higher than the background for 420 m.

The sodium present in the spent fixing bath solution may have reacted with the clays in the clayey-skeletal Typic Eutroboralf soils resducing the downward mobility of the solutions in the canyon. This would have increased runoff and have helped to transport the silver solutions further from the mouth of the waste outfall. The reduced

downward mobility may also account to some degree for the increased levels of silver in the oxidation zone of the soil in the canyon. Each time effluent was released from the facility, very little of it would penetrate very far beneath the surface. The solution near the surface could then dry out, precipitating the silver. This would lead to an enrichment of the surface layers not observed under controlled laboratory conditions.

The phytotoxicity of the spent fixing bath solution is believed to be due primarily to the presence of excess sodium in the solutions. The impact of sodium on plants in a natural setting may also reach further than that observed in the laboratory. In field conditions plants derive some mineral nutrients from microbial activity. Sodium, as well as silver, may cause a reduction in the level of microorganisms essential for organic matter turnover rate (75,76,77,79). This would then result in a reduction of available nitrogen (78) that is essential to plants (49).

ENVIRONMENTAL ASSESSMENT AND RECOMMENDATIONS FOR FURTHER WORK

Present

For a periód of 20 years, Cañon de Valle received significant quantities of silver, ≤12 g/l (1), as silver thiosulfate complexes in untreated spent fixing baths. Although the concentration of silver in the canyon decreases with increasing distance from the mouth of the waste outfall, the silver content of the vegetation and that of the sediments and soils remains significantly higher than background levels for 300 m and 420 m, respectively.

The sediments contain the highest quantity of silver with 45,000 ppm silver, or approximately 45 µg silver/g sediment, at the mouth of the waste outfall (Fig. 6). After the waste outfall converges with Cañon de Valle at 90 m, the silver content drops by a factor of 10. At 150 m from the mouth of the waste outfall the silver content drops by another factor of 10. Here the sediments contain 542 ppm silver or approximately 542 ng silver/g sediment. Another 10% drop in silver content occurs at 330 m, shortly after a side canyon converges with Canon de Valle. At 450 m the silver content of the sediments approaches that of background levels with 3.8 ppm silver or approximately 3.8 ng silver/g sediment. The drop in silver content of the soils follows a much more erratic pattern (Fig. 7), but matches that of the sediments fairly closely (Fig. 8). The drop in silver content of the vegetation follows a similar trend (Fig. 10, Fig. 11, Fig. 12). The silver content

of the grass at the mouth of the waste outfall is 12 ppm silver or approximately 12 ng silver/g grass. At 300 m the silver content approaches that of background levels with 1.1 ppm silver, or approximately 1.1 ng silver/g grass.

Insects, birds, squirrels, deer, and elk are typical foragers within this area. Because deer and elk generally have rather large grazing ranges, the small increases in the amount of silver they ingest when feeding in the contaminated area is believed to offer little likelihood of health risk to these populations. Squirrels and birds may be at higher risk, however, because they tend to feed on seeds and nuts which have greater concentrationsof silver than the foliage of a plant.

Future

A vertical profile of the soils shows the silver content decreasing with increasing depth from the soil surface (Fig. 9). Although all silver compounds are slightly soluble and are removed from the various soil horizons with time, the drainage condition of a soil will determine its relative silver content. Excess sodium present in the fixing bath solution may have a marked effect on soil drainage. The clayey-skeletal Typic Eutroboralf soils in the canyon contain a high percentage of clays (88) which adsorb sodium. The clay particles subsequently swell, the space between the pores is reduced, and the permeability of the soil is decreased. Although the silver is now recovered from the spent fixing bath solutions before being discharged into the canyon, the sodium is still present in solution. Therefore, as long as sodium is continually introduced into the canyon the

mobility of silver through the soil horizons should be limited. The silver may eventually migrate through the soil into the underlying alluvium. However, because the alluvium generally overlies the less permeable volcanic tuff and sediments, the downward movement of solutions is impeded. At this juncture, a shallow alluvial ground water body may then form and more downgradient in the alluvium at a rate of 1 to 20 m/day (3-60 ft/day)(88). This perched water is then depleted by evapotranspiration and infiltration into the underlying tuff. The main aquifer in the Los Alamos area is situated within the Tesuque Formation beneath the entire plateau and the Rio Grande Valley. Because perched water has not been found in the tuff, volcanic sediments, or basalts above this aquifer in either the western or central portions of the plateau, there is virtually no potential for alluvial waters in waste discharge areas to infiltrate to the deep aquifers used for human consumption.

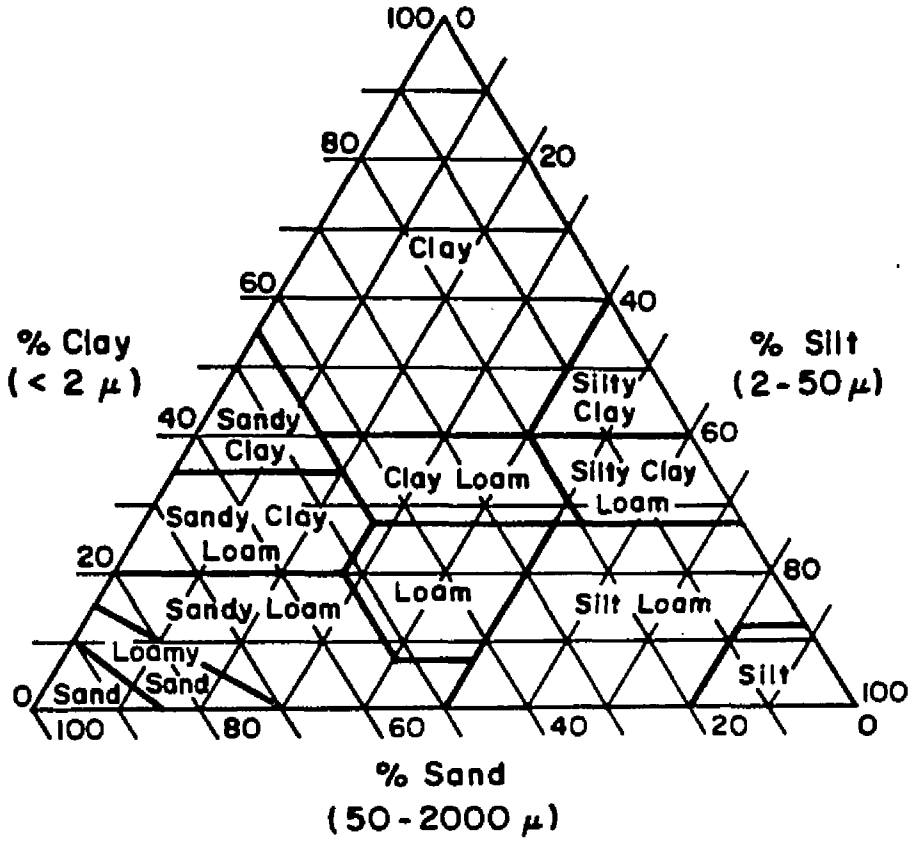
Further Research

A more detailed assessment of the extent of silver pollution in the canyon is recommended. Estimates of the volume of contaminated soil may be attained by measuring the silver content of several strategically placed 3 ft vertical soil profile samples. Because the stream bed received and exhibits the greatest silver concentrations, 3 ft vertical soil profiles should be taken at 60 m and 90 m from the mouth of the waste outfall. The erratic pattern of decreasing silver content of the soils was believed due to the fact that no notice was taken of whether the samples were taken upstream or downstream of the stream bed.

Therefore, when assessing the soils of the area notice should be made of the slope of the land in relation to the stream bed. Three foot vertical soil profiles should also be taken at 30 m, 60 m, and 90 m from the mouth of the waste outfall at 2 m upslope and 2 m and 4 m downslope of the stream bed.

APPENDIX A

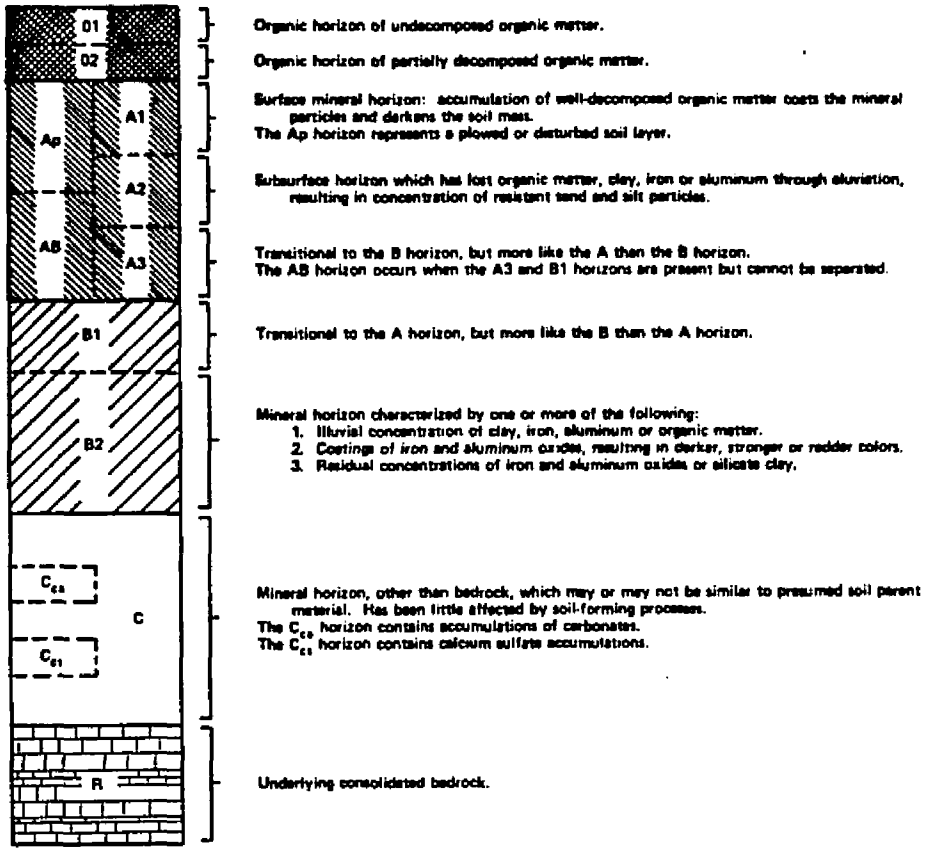
THE SOIL TEXTURE TRIANGLE



(ref. 88)

APPENDIX B

HYPOTHETICAL SOIL PROFILE SHOWING PRINCIPAL HORIZON



(ref. 88)

APPENDIX C

SILVER CONTENT OF SAMPLES COLLECTED IN CAÑON DE VALLE AND CONTROL CANYON

All data represent one sample. Blanks indicate that sample material was not present at sample location. Numbers in parenthesis represent distance (m) that samples were collected from the center of the stream channel. Numbers in parenthesis for water samples indicate pH.

Table C.1. Silver content of samples collected in Canon de Valle and control canyon.

Location from outfall (m)	Water (ppb)	Sediment (ppm)	Soil (ppm)	Grass (ppm)
Control	-0 ± 0.5 (6.8)	0.48 ± 0.29	1.60 ± 0.40	0.29 ± 0.11
		2.60 ± 0.70	2.00 ± 1.00	0.52 ± 0.08
0	0.7 ± 0.5 (7.4)	14500 ± 1100		12 ± 1 (1.0)
10	0.7 ± 0.5 (7.3)	22300 ± 1800	14000 ± 1100 (0.8)	8.80 ± 0.85 (2.0)
20	-0 ± 0.5 (7.0)	22400 ± 1800	1860 ± 150 (1.2)	8.00 ± 0.90 (2.4)
30	-0 ± 0.5 (6.6)	10500 ± 800	654 ± 52 (1.6)	5.80 ± 0.60 (1.7)
60	6.7 ± 0.5 (4.8)	13700 ± 1100	3520 ± 280 (0.6)	3.00 ± 0.30 (1.9)
* main 90		14100 ± 1100	278 ± 23 (0.7)	1.70 ± 0.30 (1.2)
trib 90		1280 ± 100	686 ± 56 (0.7)	9.40 ± 0.80 (1.3)
120		4660 ± 380	2160 ± 170 (0.4)	4.00 ± 0.40 (0.1)
150		542 ± 44	78 ± 6 (0.6)	2.30 ± 0.30 (0.5)
180		600 ± 48	19 ± 2 (0.8)	2.20 ± 0.20 (0.6)
** 210		81 ± 7	97 ± 8 (1.0)	1.20 ± 0.10 (0.4)
240		51 ± 4	20 ± 2 (0.6)	1.30 ± 0.10 (0.4)
270		109 ± 9	15 ± 1 (1.2)	0.95 ± 0.09 (0.2)
*** 300	0.9 ± 0.5 (5.8)	4.80 ± 0.90	14 ± 1 (1.6)	1.10 ± 0.10 (1.7)
330	1.8 ± 0.5 (6.4)	12 ± 1	21 ± 2 (1.2)	0.53 ± 0.10 (0.9)
360		9.60 ± 1.10	1.60 ± 0.70 (0.1)	0.60 ± 0.15 (1.4)
390		7.60 ± 0.90	8.00 ± 0.90 (0.7)	2.30 ± 0.20 (0.5)
420		9.70 ± 1.10	12 ± 2 (0.9)	0.47 ± 0.15 (0.9)
450		3.80 ± 0.80	0.76 ± 0.38 (0.7)	0.40 ± 0.15 (1.5)

Table C.1. Silver content--Continued.

Location outfall (m)	Shrub Oak (ppm)		Ponderosa Pine (ppm)		Douglas-fir (ppm)	
Control	0.22 ± 0.13					
	0.96 ± 0.09					
0						
10						
20			4.80 ± 0.50	(3.9)		
30			2.10 ± 0.20	(3.1)		
60	3.60 ± 0.40	(5.4)	1.10 ± 0.20	(5.4)		
*main 90			0.53 ± 0.18	(3.2)		
trib 90						
120	9.10 ± 0.80	(1.9)	1.40 ± 0.20	(1.8)		
150						
** 180	1.90 ± 0.30	(1.1)				
210	4.10 ± 0.40	(1.1)				
240	2.30 ± 0.30	(0.8)				
270	1.40 ± 0.20	(2.9)	1.40 ± 0.10	(3.1)		
*** 300	1.80 ± 0.40	(2.9)	0.40 ± 0.15	(1.5)		
330	0.79 ± 0.10	(2.3)	0.29 ± 0.11	(2.8)	0.46 ± 0.15	(2.0)
360	0.16 ± 0.08	(1.7)			0.24 ± 0.11	(1.4)
390	0.86 ± 0.09	(2.4)			0.38 ± 0.11	(0.6)
420	0.82 ± 0.08	(1.7)	0.39 ± 0.11	(2.8)		
450	1.10 ± 0.10	(2.1)				

* Waste outflow converges with main stream channel of Cañon de Valle at approximately 90 m.

** Land and soil type changes at approximately 195 m

*** Side canyon converges with Cañon de Valle at approximately 300 m.

Table C.1. Silver content--continued.

Depth from Surface (in)	Soil 10 m from outfall (ppm)	Soil 20 m from outfall (ppm)
0- 6	14000 ± 1100 (0.8)	1860 ± 150 (1.2)
6-12	4480 ± 285	824 ± 66
12-18	1250 ± 75	
18-24	770 ± 50	
24-30	138 ± 9	
30-36	182 ± 12	

APPENDIX D

SILVER CONTENT OF SOILS IN COLUMNS RECEIVING SILVER THIOSULFATE, SILVER NITRATE, OR SILVER SULFATE

All data represent one sample. Total ppm Ag recovered includes the amount of silver found on the soil and that recovered in the effluent. Although the gram weight of soil in the columns was not measured, the ppm Ag recovered per mg Ag added provides a means of comparing silver recovery in columns receiving varying quantities of silver. The variation between these ratios is statistically insignificant.

Table D.1. Silver content of soils in columns receiving silver thiosulfate, silver nitrate or silver sulfate.

Inch of soil from top of column	$Na_3Ag(S_2O_3)_2$* (ppm Ag)			$AgNO_3$ ** (ppm Ag)		
	Column 1	Column 2	Average	Column 1	Column 2	Average
0-1	15 ± 2	27 ± 3	21 ± 8	750 ± 35	775 ± 35	762 ± 18
1-2	104 ± 5	146 ± 8	125 ± 30	7.2 ± 1.1	24 ± 2	15 ± 12
2-3	123 ± 6	40 ± 4	82 ± 59	2.2 ± 1.0	2.4 ± 0.8	2.3 ± 0.1
3-4	62 ± 6	49 ± 5	56 ± 9	0.9 ± 0.7	1.4 ± 0.7	1.2 ± 0.4
4-5	84 ± 8	58 ± 6	71 ± 18	0.6 ± 0.3	1.8 ± 0.6	1.2 ± 0.8
5-6	45 ± 4	62 ± 6	54 ± 12	1.6 ± 0.6	1.2 ± 0.6	1.4 ± 0.3
Sample Volume #						
7		0.1	0.1 ± 0.1			
8		2.9	1.4 ± 2.1			
9	1.7	3.5	2.6 ± 1.3			
10	3.7	5.7	4.7 ± 1.4			
Total ppm Ag recovered	438.4	394.2	409.0	762.5	805.8	783.1
ppm ag recovered / mg Ag added	8.8	7.8	8.3 ± 0.7	10.9	11.5	11.2 ± 0.4

Table D.1. Silver content of soils in columns--Continued.

Inch of soil from top of column	Ag_2SO_4 *** (ppm Ag) Column 1	Column 2	Average
0-1	1240 ± 50	1150 ± 60	1195 ± 64
1-2	123 ± 6	52 ± 5	88 ± 50
2-3	3.3 ± 0.7	1.6 ± 0.7	2.4 ± 1.2
3-4	2.1 ± 0.6	0.9 ± 0.9	1.5 ± 0.8
4-5	1.1 ± 0.5	1.0 ± 0.6	1.1 ± 0.1
5-6	1.1 ± 0.7	2.0 ± 0.8	1.6 ± 0.6
Sample Volume #			
7			
8			
9			
10			
Total ppm Ag recovered	1370.6	1207.5	1289.6
ppm Ag recovered / mg Ag added	9.8	8.6	9.2 ± 0.9

* 10 sample volumes of 500ml of 10ppm Ag added = 5 1(10 ng/µl) = 50 mg silver applied to soil

** 14 sample volumes of 500ml of 10ppm Ag added = 7 1 (10 ng/µl) = 70 mg silver applied to soil

*** 14 sample voulmes of 500ml of 20ppm Ag added = 7 1 (20 ng/µl) = 140 mg silver applied to soil

APPENDIX E

SILVER LOSS FROM SILVER THIOSULFATE SOLUTION REMAINING ON COLUMNS

All data represent one sample. Explanation of the table with sample calculations follows.

Table E.1. Silver loss from silver thiosulfate solution remaining on columns. -- ∿77 ml of solution remained on each column after each sample volume had eluted.

Column	Conc. Ag Applied to Column (ppm)	Day Solution Applied to Column	Volume of Solution Applied to column (ml)	Concentration Ag Recovered in Effluent (ppm)	Conc. Ag in Solution on Column (ppm)	Conc. Ag Lost from Solution on Column (ppm)	% Ag Lost from Solution on Column
1	10	1	500	9.4	9.4	0.6	6
		2	278	8.3	5.4	4.6	46
		12	200	6.1	0.8	9.2	92
2	10	1	500	9.6	9.6	0.4	4
		2	278	8.4	5.3	4.7	47
		12	200	6.4	1.3	8.7	87
3	10	1	500	9.4	9.4	0.6	6
		2	278	8.4	5.8	4.2	42
		12	200	7.8	5.2	4.8	48
4	50	1	500	48.6	48.6	1.4	3
		2	278	47.6	45.0	5.0	10
		12	200	43.4	35.1	14.9	30
5	50	1	500	47.8	47.8	2.2	4
		2	278	47.6	47.1	2.9	6
		12	200	44.2	38.5	11.6	23
6	50	1	500	48.4	48.4	1.6	3
		2	278	48.4	48.4	1.6	3
		12	200	42.4	34.1	15.9	32
7	100	1	500	95.6	95.6	4.4	4
		2	278	97.6	102.8	0	0
		12	200	90.5	82.4	17.6	18

Table E.1. Silver loss--continued.

Column	Conc. Ag Applied to Column (ppm)	Day Solution Applied to Column	Volume of Solution Applied to Column (ml)	Concentration Ag Recovered in Effluent (ppm)	Conc. Ag in Solution on Column (ppm)	Conc. Ag Lost from Solution on Column (ppm)	% Ag Lost from Solution on Column
8	100	1	500	94.4	94.4	5.6	6
		2	278	98.4	108.8	0	0
		12	200	91.8	87.6	12.4	12
9	100	1	500	95.0	95.0	5.0	5
		2	278	100.0	113.0	0	0
		12	200	90.5	83.3	16.7	17

Explanation of Table E.1. with Sample Calculations.

Concentration Ag Recovered in Effluent (ppm):
The silver content of the solution in the beaker after the entire sample volume had eluted.
Note: Entire sample volume = volume of solution introduced into column minus 77 ml of solution which remained on the column.

Concentration Ag in Solution on Column (ppm):
The calculated silver content of the 77 ml of solution which remained on the column after the previous sample volume had eluted.
Calculation:

$$\frac{\left[\begin{array}{l}(\text{Vol. soln. applied to column} - 77\text{ml})(\text{ppm Ag in soln. after passing through soil once}) \\ + (77\text{ ml soln. which remained on column})(x\text{ ppm Ag of 77 ml})\end{array}\right]}{\text{Volume of solution applied to column}}$$

= Concentration Silver Recovered in Effluent (ppm)

Sample Calculation for Column 1, Day 2:
Vol. soln. applied to column: 278 ml
ppm Ag in soln. after passing thru soil once: 9.4 ppm
Conc. Ag recovered in effluent: 8.3 ppm

$$\frac{(278 - 77)(9.4) + (77)(x)}{278} = 8.3$$

$$x = \frac{(8.3)(278) - (278 - 77)(9.4)}{77}$$

$x = 5.4$ ppm Ag

The silver content of the solution which had remained on the column following the previous elution is 5.4 ppm.

Concentration Ag Lost from Solution on Column (ppm):
Concentration of silver applied to column minus concentration of silver in solution on the column.
Sample Calculation for Column 1, Day 2:
Conc. Ag applied to column: 10 ppm
Conc. Ag in solution on column: 5.4 ppm
10 - 5.4 = 4.6 ppm
The concentration of silver lost from the solution which had remained on the column is 4.6 ppm.

% Ag Lost from Solution on Column:

$$\frac{\text{Conc. Ag lost from solution on column}}{\text{Conc. Ag Applied to Column}} \times 100$$

Sample calculation for Column 1, Day 2:

Conc. Ag lost from solution on column: 0.6 ppm

Conc. Ag applied to column: 10 ppm

(0.6/10)(100) = 6%.

6% of the silver from the solution which had remained on the column was lost to the soil.

APPENDIX F

AVERAGE PER CENT SPROUTS GERMINATED

All data represent the added percentage of plants that germinated per cup divided by the number of cups within the group. The total ml represent the total volume of solution which had been applied by that day. The total Ag (mg) represents the total amount of silver that had been applied to the soils by that day.

The control and $Na_2S_2O_3$ received no silver. The $Na_3Ag(S_2O_3)_2$ and $AgNO_3$ received volumes of 10 ppm Ag. The Ag_2SO_4 group received volumes of 20 ppm Ag.

Table F.1. Average per cent sprouts germinated.

Day	Total ml	Control Total Ag(mg)	Control Avg. % Ger.	$Na_2S_2O_3$ Total Ag(mg)	$Na_2S_2O_3$ Avg. % Ger.
5	65	--	0.54±0.46	--	0 ±0
6	75	--	1.24±0.71	--	0.44±1.10
7	85	--	1.84±0.80	--	1.33±2.17
8	95	--	3.05±1.30	--	3.11±3.08
9	105	--	4.22±2.40	--	6.44±4.63
10	115	--	4.96±2.63	--	7.89±5.42
11	125	--	5.56±3.05	--	9.67±5.63
12	140	--	6.19±3.16	--	10.56±6.24
13	155	--	7.08±3.43	--	11.44±6.01
14	170	--	8.16±3.60	--	13.00±6.33
15	185	--	9.49±3.71	--	14.56±6.43
16	200	--	12.69±4.24	--	16.33±6.48
17	215	--	15.24±4.56	--	17.67±6.70
18	230	--	18.18±3.92	--	18.00±6.78
19	245	--	21.11±3.86	--	18.22±6.82
20	260	--	24.06±3.38	--	"
21	275	--	25.14±3.59	--	"
22	290	--	26.10±4.20	--	"
23	305	--	26.47±5.13	--	"
24	320	--	27.08±4.61	--	"
25	335	--	28.45±4.91	--	"
26	350	--	29.37±5.47	--	"
27	365	--	30.03±5.95	--	"
28	380	--	30.54±6.12	--	"
29	395	--	31.05±6.86	--	"
20	410	--	31.17±6.79	--	"
31	425	--	31.30±6.76	--	"
33	455	--	31.46±6.90	--	"
35	485	--	31.49±6.93	--	"
37	520	--	31.52±6.92	--	"
39	560	--	31.56±6.90	--	"
41	600	--	"	--	"
43	640	--	"	--	"
45	680	--	31.84±7.07	--	"
47	720	--	"	--	"
49	760	--	"	--	"

Table F.1. Average per cent sprouts germinated--Continued.

Day	Total ml	$Na_3Ag(S_2O_3)_2$ Total Ag(mg)	$Na_3Ag(S_2O_3)_2$ Avg. % Ger.	$AgNO_3$ Total Ag(mg)	$AgNO_3$ Avg. % Ger.
5	65	0.65	0 ±0	0.65	0.51±0.58
6	75	0.75	0.22±0.65	0.75	1.30±0.94
7	85	0.85	0.56±0.92	0.85	2.32±1.15
8	95	0.95	1.67±2.59	0.95	4.57±2.27
9	105	1.05	3.89±3.53	1.05	7.05±3.62
10	115	1.15	5.06±3.54	1.15	8.48±4.22
11	125	1.25	6.44±4.15	1.25	9.65±4.43
12	140	1.40	7.67±4.24	1.40	10.70±4.54
13	155	1.55	8.56±4.69	1.55	11.88±4.68
14	170	1.70	10.78±5.54	1.70	13.18±4.41
15	185	1.85	12.33±5.05	1.85	14.29±4.18
16	200	2.00	14.44±5.02	2.00	15.36±4.40
17	215	2.15	17.78±4.70	2.15	16.73±4.29
18	230	2.30	18.56±4.86	2.30	18.06±4.26
19	245	2.45	19.67±54.6	2.45	19.61±3.54
20	260	2.60	19.67±6.03	2.60	21.61±3.66
21	275	2.75	20.00±6.25	2.75	22.99±3.12
22	290	2.90	"	2.90	23.84±3.29
23	305	3.05	"	3.05	24.19±3.23
24	320	3.20	"	3.20	24.38±3.30
25	335	3.35	"	3.35	25.11±3.59
26	350	3.50	"	3.50	25.90±4.03
27	365	3.60	"	3.60	26.95±4.16
28	380	3.80	"	3.80	27.71±4.16
29	395	3.95	"	3.95	27.94±4.18
30	410	4.10	"	4.10	28.22±4.17
31	425	4.25	"	4.25	28.41±4.21
33	455	4.55	"	4.55	28.60±4.24
35	485	4.85	"	4.85	28.86±4.34
37	520	5.20	"	5.20	28.89±4.31
39	560	5.60	"	5.60	"
41	600	6.00	"	6.00	"
43	640	6.40	"	6.40	28.98±4.27
45	680	6.80	"	6.80	29.08±4.28
47	720	7.20	"	7.20	29.27±4.38
59	760	7.60	"	7.60	29.43±4.18

Table F.1. Average percent sprouts germinated--Continued.

		Ag_2SO_4	
Day	Total ml	Total Ag(mg)	Avg. % Ger.
5	65	1.30	8.89±1.41
6	75	1.50	1.78±1.80
7	85	1.70	7.00±3.51
8	95	1.90	13.11±4.71
9	105	2.10	17.44±4.27
10	115	2.30	19.56±4.58
11	125	2.50	19.89±4.31
12	140	2.80	20.11±4.36
13	155	3.10	21.00±4.86
14	170	3.40	21.33±4.90
15	185	3.70	21.78±4.60
16	200	4.00	22.22±4.75
17	215	4.30	22.67±4.55
18	230	4.60	23.11±4.71
19	245	4.90	23.44±4.22
20	260	5.20	23.56±4.37
21	275	5.50	"
22	290	5.80	"
23	305	6.10	"
24	320	6.40	"
25	335	6.70	"
26	350	7.00	"
27	365	7.20	"
28	380	7.60	"
29	395	7.90	"
30	410	8.20	"
31	425	8.50	"
33	455	9.10	"
35	485	9.70	"
37	520	10.40	"
39	560	11.20	"
41	600	12.00	"
43	640	12.80	"
45	680	13.60	"
47	720	14.40	"
49	760	15.20	23.67±4.63

APPENDIX G

AVERAGE PER CENT SPROUTS DIED

All data represent the added percentage of plants that died per dup divided by the number of cups within the group. On days 1-24 the post groups had received only deionized water. On day 25 they began receiving aliquots of either sodium or silver thiosulfate solution.

Table G.1. Average per cent sprouts died.

Day	Total ml	$Na_2S_2O_3$ Total Ag(mg)	$Na_2S_2O_3$ Avg. % Died	$Na_3Ag(S_2O_3)_2$ Total Ag(mg)	$Na_3Ag(S_2O_3)_2$ Avg. % Died	Post $Na_2S_2O_3$ Total Ag(mg)	Post $Na_2S_2O_3$ Avg. % Died	Post $Na_3Ag(S_2O_3)_2$ Total Ag(mg)	Post $Na_3Ag(S_2O_3)_2$ Avg. % Died
19	245	-	0.79±3.37	2.45	0.62±2.62	-	-	-	-
20	260	-	1.19±3.68	2.60	2.41±6.00	-	-	-	-
21	275	-	1.19±3.68	2.75	2.41±6.00	-	-	-	-
22	290	-	1.19±3.68	2.90	2.83±6.10	-	-	-	-
23	305	-	2.12±5.16	3.05	4.09±6.64	-	-	-	-
24	320	-	2.73±5.54	3.20	4.92±6.54	-	-	-	-
25	335	-	3.35±6.96	3.35	5.54±7.60	-	-	0.15	-
26	350	-	5.05±9.00	3.50	8.27±9.17	-	-	0.30	-
27	365	-	6.30±8.73	3.60	10.24±9.11	-	-	0.45	-
28	380	-	8.42±9.28	3.80	15.57±11.47	-	-	0.60	-
29	395	-	9.15±9.37	3.95	16.53±12.04	-	-	0.75	-
30	410	-	11.84±13.05	4.10	19.89±11.55	-	-	0.90	-
31	425	-	14.59±13.10	4.25	20.93±12.22	-	-	1.05	-
32	455	-	18.56±14.87	4.55	27.53±10.45	-	-	1.35	-
34	485	-	22.48±17.69	4.85	34.46±13.71	-	-	1.65	-
36	520	-	30.89±20.61	5.20	42.04±14.29	-	-	2.00	-
38	560	-	37.32±19.77	5.60	48.52±16.55	-	-	2.40	-
40	600	-	45.27±17.53	6.00	52.70±18.78	-	0.36±1.34	2.80	0.36±1.34
42	640	-	51.50±17.65	.6.40	58.17±20.75	-	1.79±3.17	3.20	1.79±3.17
44	680	-	60.93±19.43	6.80	68.39±19.03	-	2.14±3.78	3.60	3.93±4.01
46	720	-	68.27±18.40	7.20	77.85±18.24	-	3.21±4.21	4.00	6.43±6.91
48	760	-	75.21±19.66	7.60	84.12±14.70	-	4.64±4.99	4.40	9.64±8.20

APPENDIX H

CHLOROPHYLL CONTENT

Each sample number represents the plants in one cup. A649 and A665 represent the spectrophotometric readings at 649 and 665 mu, respectively. The total chlorophyll content was calculated from the equation (47):

$$\text{total chlorophyll (mg/liter)} = 6.45(A665) + 17.72(A649)$$

Table H.1. Chlorophyll content.

	Control			Silver Nitrate			Silver Sulfate			Post Sodium Thiosulfate		
Sample	A649	A665	Total	A649	A665	Total	A649	A665	Total	A649	A665	Total
1	.62	1.2	18.73	.58	1.1	17.37	.45	1.4	17.00	.62	1.3	19.38
2	.55	1.2	17.49	.53	.98	15.71	.32	1.1	12.77	.57	1.2	17.84
3	.66	1.4	20.73	.48	.92	14.44	.45	1.4	17.00	.62	1.2	18.73
4	.54	1.1	16.66	.55	1.1	16.84	.40	1.3	15.47	.64	1.2	18.73
5	.56	1.1	17.02	.50	.83	14.21	.45	1.4	17.00	.64	1.3	19.73
6	.58	1.2	18.02	.60	1.2	18.37	.43	1.4	16.65	.68	1.4	21.08
7	.61	1.2	18.55	.62	1.2	18.73	.47	1.5	18.00	.68	1.4	21.08
8	.62	1.2	18.73	.60	1.2	18.37	.52	1.6	19.53	.51	1.0	15.49
9	.62	1.2	18.73	.61	1.2	18.55	.45	1.4	17.00	.74	1.5	22.79
10	.65	1.3	19.90	.47	.87	13.94	.47	1.5	18.00	.72	1.4	21.79
11	.58	1.2	18.02	.57	1.1	17.20	.50	1.5	18.54	.64	1.3	19.73
12	.58	1.2	18.02	.62	1.2	18.73	.41	1.4	16.30	.64	1.2	19.08
13	.61	1.2	18.55	.54	1.0	16.02	.36	1.3	14.76	.58	1.2	18.02
14	.67	1.4	20.90	.68	1.4	21.08	.49	1.5	18.36	.64	1.3	19.73
15	.56	1.1	17.02	.60	1.2	18.37	.45	1.4	17.00			
16				.51	.95	15.16	.47	1.4	17.36			
17				.54	1.0	16.02	.41	1.4	16.20			
18				.62	1.2	18.73	.52	1.7	20.00			
	Average = 18.47			Average = 17.10			Average = 16.94			Average = 19.51		
	s = 1.26			s = 1.95			s = 1.68			s = 1.83		

Table H.1. Chlorophyll content--Continued.

	Post Silver Thiosulfate			Post Silver Nitrate			Post Silver Sulfate		
Sample	A649	A665	Total	A649	A665	Total	A649	A665	Total
1	.62	1.2	18.73	.57	1.0	16.55	.62	1.2	18.73
2	.71	1.4	21.61	.57	1.0	16.55	.52	.98	15.54
3	.64	1.3	19.72	.68	1.3	20.44	.56	1.1	17.02
4	.74	1.4	22.14	.54	1.0	16.02	.68	1.4	21.08
5	.64	1.2	19.08	.64	1.2	19.08	.67	1.3	20.26
6	.73	1.4	21.97	.68	1.3	20.44	.54	1.0	16.02
7	.70	1.4	21.43	.57	1.0	16.55	.68	1.3	20.44
8	.73	1.4	21.97	.47	.85	13.81	.68	1.4	21.08
9	.60	1.2	18.37	.83	1.6	20.64	.67	1.3	20.26
10	.63	1.2	18.90	.60	1.2	18.37	.61	1.2	18.55
11	.71	1.4	21.61	.64	1.2	19.08	.65	1.3	19.91
12	.70	1.4	21.43	.68	1.3	20.44	.61	1.2	18.55
13	.66	1.2	25.46	.67	1.3	20.26	.76	1.4	22.50
14	.56	1.0	16.37	.81	1.6	24.67	.71	1.4	21.61
	Average = 20.63			Average = 18.78			Average = 19.45		
	s = 2.24			s = 2.72			s = 2.15		

APPENDIX I

NET PRODUCTIVITY

Each sample represents one cup. The no. represents the no. of plants per cup. The wt. represents the combined weight of all of the plants per cup.

Table I.1. Net productivity.

	Control			Silver Nitrate			Silver Sulfate			Sodium Thiosulfate		
Sample	No.	Wt.	Avg Wt (gm)	No.	Wt.	Avg Wt (gm)	No.	Wt.	Avg Wt (gm)	No.	Wt.	Avg Wt (gm)
1	17	.1051	.0062	15	.0928	.0062	-	.127	-	1	.0016	.0016
2	17	.1331	.0078	15	.1653	.0110	-	.057	-	3	.0209	.0070
3	16	.1474	.0092	18	.2214	.0123	-	.120	-	2	.0043	.0022
4	13	.1160	.0089	15	.0972	.0065	-	.158	-	1	.0016	.0016
5	14	.0760	.0054	15	.1271	.0085	-	.117	-	2	.0065	.0033
6	16	.1355	.0085	15	.1589	.0106	-	.130	-	3	.0074	.0025
7	14	.1062	.0076	15	.1459	.0097	-	.055	-	2	.0142	.0071
8	15	.1270	.0085	16	.1887	.0118	-	.161	-	-	--	--
9	17	.1180	.0069	15	.1048	.0070	-	.129	-	3	.0202	.0067
10	15	.1238	.0083	18	.1519	.0084	-	.140	-	-	--	--
11	10	.1024	.0102	16	.1699	.0106	-	.114	-	3	.0216	.0072
12	13	.0920	.0071	17	.1910	.0112	-	.156	-	2	.0230	.0115
13	15	.1047	.0070	15	.1532	.0102	-	.094	-	1	.0033	.0033
14	14	.1111	.0079	17	.1312	.0077	-	.130	-	2	.0032	.0016
15	15	.1134	.0076	17	.1574	.0093	-	.105	-		--	--
16				15	.1237	.0082	-	.988	-	1	.0074	.0074
17				16	.1446	.0090	-	.122	-	1	.0035	.0035
18				15	.1500	.0100	-	.100	-	-	--	--
	Average = .0078			Average = .0093						Average = .0048		
	s = .0012			s = .0018						s = .0030		

Table I.1. Net productivity--Continued.

Sample	Silver Thiosulfate			Post Silver Nitrate			Post Silver Sulfate			Post Sodium Thiosulfate		
	No.	Wt.	Avg Wt (gm)	No.	Wt.	Avg Wt (gm)	No.	Wt.	Avg Wt (gm)	No.	Wt.	Avg Wt (gm)
1	2	.0071	.0036	17	.1467	.0086	16	.1055	.0066	3	.0201	.0067
2	2	.0066	.0033	17	.1623	.0095	14	.1319	.0094	12	.0786	.0066
3	-	-	-	15	.1570	.0105	16	.1453	.0091	13	.0653	.0050
4	-	-	-	15	.1296	.0086	14	.0899	.0064	7	.0564	.0081
5	4	.0334	.0084	14	.1053	.0075	14	.0895	.0064	13	.0701	.0054
6	2	.0200	.0100	14	.1642	.0117	12	.0727	.0061	14	.0998	.0071
7	-	-	-	14	.1412	.0101	14	.1150	.0082	12	.0693	.0058
8	4	.0114	.0029	16	.1101	.0069	16	.1565	.0098	13	.0890	.0068
9	2	.0088	.0044	17	.1625	.0096	15	.1371	.0091	11	.0749	.0068
10	2	.0080	.0040	12	.1099	.0092	16	.1457	.0091	10	.0433	.0043
11	1	.0034	.0034	14	.1245	.0089	16	.1493	.0093	11	.0801	.0073
12	1	.0026	.0026	16	.1424	.0089	15	.1300	.0087	9	.0656	.0073
13	1	.0063	.0063	15	.1377	.0092	16	.1272	.0080	10	.0573	.0057
14	-	-	-	11	.0859	.0078	14	.1150	.0082	11	.0931	.0085
15	-	-	-									
16	-	-	-									
17	1	.0077	.0077									
18	2	.0026	.0013									
	Average = .0048 s = .0027			Average = .0091 s = .0012			Average = .0082 s = .0013			Average = .0065 s = .0012		

Table I.1. Net productivity--Continued.

	Post Silver Thiosulfate		
Sample	No.	Wt.	Avg Wt (gm)
1	12	.0739	.0062
2	6	.0394	.0066
3	8	.0427	.0053
4	4	.0271	.0068
5	14	.0618	.0044
6	8	.0508	.0064
7	10	.0570	.0057
8	13	.0800	.0062
9	14	.0907	.0065
10	14	.0822	.0059
11	8	.0363	.0045
12	10	.0557	.0056
13	15	.0900	.0060
14	11	.0621	.0056
15			
16			
17			
18			
	Average = .0058		
	s = .0007		

APPENDIX J

GLOSSARY OF TERMS (44,87,88,94,95)

Alfisol - A soil order, one of the broadest category of soil classification. These soils have a clayey subsoil horizon and a moderate to high base (cation) saturation. Alfisols are generally higher in hydroxy-oxides than most soils. They are usually moist, yet may become dry during the warm season.

Alluvium - Clay, sand, silt, gravel, or similar deitral material deposited by running water.

Annual - A plant which completes its entire life cycle, from seed germination to seed production, followed by death, within a single season.

Attenuation - Mass of element adsorbed per gram of soil per milliliter of added eluent.

Basalt - A dark colored, fine grained, heavy, crystalline volcanic rock rich in iron and magnesium compounds; poorest of all volcanic rock in silica.

Clay - Individual mineral particles in the soil which are less than 0.002 mm in diameter. A soil textural class which contains 40% or more clay, less than 45% sand, and less than 40% silt. See Appendix A.

Clay film - A morphological characteristic of soil described by recording the frequency of occurence and thickness of film of clay in a soil mass.

Thin - Very fine sand grains are readily apparent in the clay film and/or sand grains are only thinly coated and are held together by weak bridges.

Cobble (cobblestone) - A rounded or partly rounded rock fragment which is 7.6 to 25 cm in diameter.

Concretion - Masses formed by deposition of material about a nucleus.

Confluence - The place of meeting of two streams.

Evapotranspiration - The loss of water from the soil both by evaporation from the surface and by transpiration from the plants growing therein.

Evergreen - A plant which retains its folliage throughout the year.

Foliage - The leaves of a plant.

Forb - An herb other than grass.

Frigid - A land type found on gently sloping to steep mesa tops and edges consisting of about 65% tuff rock outcrop.

Gravel - Course rock or mineral fragments, 0.2 cm to 7.6 cm in diameter.

Horizon boundary, soil - The lower boundary of a soil. The distinctness of a horizon boundary is classified relative to the thickness of the transition zone. See Appendix B.

Loam - A soil textural class which contains 75 to 95% silt, 25 to 55% sand, and 5 to 25% clay. See Appendix A.

Mesa - Usually isolated hill having a level top and steeply sloping sides.

Mesic - Pertaining to a soil or rock's water relationships intermediate between dry (xeric) and wet (hydric). A land type found on moderately sloping to steep meas tops and edges consisting of about 65% tuff rock outcrop.

Overstory - The trees and/or layer of foliage in a forest canopy.

Pebbles - A round or partly rounded rock or mineral fragment, 4 to 64 mm in diamter.

Perched Alluvial Water - Unconfined ground water which is separated from the underlying main aquifer by an unsaturated zone.

Perennial, woody - A plant which loses its leaves at the end of the season, yet retains permanent woody stems above ground which act as starting points for next years growth (stems and foliage).

Permeability - The rate at which water penetrates or passes through a soil mass or soil horizon.

Pores, soil - Space between soil particles or coarse fragments in a bulk volume of soil.

Sand - Individual mineral or rock fragments that range in diameter from 0.05 to 2.0 mm. Sand grains may be of any mineral composition, but most consist of quartz. A textural class name of a soil that contains 85% or more sand and not more than 10% clay. See Appendix A.

Sediments, stream - Rock or mineral fragments deposited by running water.

Silt - Individual soil mineral particles that range in diameter from the upper limit of clay (0.002 mm) to the lower limit of a very fine sand (0.05 mm). A textural class of soil containing 80% or more silt and less than 12% clay. See Appendix A.

Silt Loam - A soil textural class which contains 70% or more silt, less than 50% sand, and less than 30% clay. See Appendix A.

Tuff - Rock composed of fine particles of volcanic ash and volcanic dust. The pores in the tuff are not all interconnected and the natural moisture content is generally less than 5% by volume.

Understory - A layer of foliage in a forest below the level of the trees or main canopy.

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