RHS Consulting

Final Report

# 2006 Mokelumne Watershed Lake and Sediment Study

by

Richard H. Stone

Prepared for the
Pacific Gas and Electric Company
3400 Crow Canyon Rd.
San Ramon, CA 94583
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## Introduction

Pacific Gas and Electric Company (PG&E) has conducted cloud seeding operations targeting the Mokelumne watershed under various permits from the U.S. Forest Service (USFS) since 1953. To continue operations PG&E had to renew its permit with the USFS Stanislaus National Forest in the fall of 1993, however the action was appealed by the Central Sierra Environmental Resource Center (CSERC). An agreement was reached with the understanding that PG&E would prepare an Environmental Assessment (EA) that would address the potential impacts of continued cloud seeding operations by the end of 1996. In the interim, PG&E was permitted to continue its cloud seeding operations during the winters of 1994-1995 and 1995-1996.

The draft EA was circulated for public review and comment for a period of 30 days in October and November, 1995 and was sent directly to 18 agencies, individuals and organizations that submitted responses to a scoping letter sent out by PG&E and the USFS at the onset of the preparation of the EA.

The final EA was prepared and other minor changes to the draft EA text which did not affect any of the analyses or conclusions contained in the draft EA. Given these minor changes the draft EA text did not need to be reissued with significant text changes as part of the final EA.

The only mitigation recommended as part of the final EA was monitoring of silver levels in water samples collected from Lower Blue Lake and Salt Springs Reservoir every ten years at the time of permit renewal. PG&E would perform the monitoring to assure that silver levels in the water samples from the target watershed continue to remain well below the "no effect" threshold established in the EA. Other than this water quality monitoring program, no mitigation was required for the project beyond the suspension criteria and other measures already incorporated into project operations that were summarized in the draft EA project description.

An initial lake and sediment survey was conducted as part of the 1995 Mokelumne EA. The study found the following conclusions:

1. No evidence of silver iodide released from the operational program over a 40 year period could be detected above the natural silver background levels from samples collected from Lower Blue Lake and Salt Springs Reservoir. Silver concentrations in the samples averaged $6.7 \times 10^{-12}$ g Ag/ml;

2. Silver was detectable in the lake sediment samples and highly variable ranging from 0.035 mgAg/kg from Lower Blue Lake up to 0.107 mgAg/kg (parts per million) from Salt Springs Reservoir; and

3. Most importantly, no detectable bio-available silver could be measured in the leachates of the lake sediment samples processed at pH 5 (using Toxicity Characteristic Leaching Procedures, EPA Method 1311), indicating that the silver contained in the sediment samples was highly insoluble and very tightly bound to the sediments preventing any detectable silver from entering the lake water environment.

The current study was conducted to fulfill the mitigation requirements of the final 1995 EA and is part of the continuing project permit renewal process. Although the final 1995 EA did not specifically require the analysis of any lake sediment samples, they were included in the current scope of work for the sake of continuity and too allow comparison with the previous 1995 study.

The remainder of this report is divided into four sections including a description of the scope of work; sampling methods and analytical techniques; discussion of the results; and summary conclusions and recommendations. Appendix A contains additional information regarding the environmental toxicity of silver and silver iodide. Appendix B includes a copy of the Material Safety Data Sheet (MSDS) for Silver Iodide.

## Scope of Work

The following tasks were conducted in this study:

- Hygienically clean trace chemistry sampling equipment was prepared and 20 lake water sample and sediment samples were collected from two locations in the Mokelumne watershed. PG&E provided equipment to collect the sediment samples and furnished helicopter support to allow access to sampling sites located in the target area.
- Sample sets were split into two groups at the time of collection to provide for a duplicate sample set in the event any concerns developed regarding the chemical measurements or other unforeseen problems. This also allowed for the possibility that additional analysis of the samples for other elements could be conducted at a future date.
- An ultra trace chemical laboratory was selected to conduct the chemical analysis of the lake water samples. The samples were analyzed using high resolution inductively coupled plasma mass spectroscopy (HiRes-ICPMS) during January 2006. The sediment samples were submitted to the same laboratory for determination of total dissolved silver (TDS) and environmentally free "bio-available" silver. Several other metals were also measured. The free metal contents of the sediment samples were determined by extracting available metals from the sediments using modified Toxicity Characteristic Leaching Procedures (TCLP, Method 1311) followed by chemical analysis of the leachate using standard inductively coupled plasma atomic emission spectroscopy (ICP-AES). The second duplicate sets of lake water and sediment samples were stored frozen in the event problems were encountered with the analysis of the

first two sets or if it was determined that additional analyses were desirable at a later date.

- The three sets of chemical analysis results were analyzed and compared with measurements made previously at the same sampling locations and other nearby locations. These analyses were reviewed and form the basis of the conclusions and recommendations found in this study.

## Methodology

### *Operational Seeding Program*

Pacific Gas and Electric (PG&E) operates a cloud seeding program on the North Fork of the Mokelumne River targeting the higher elevations of the watershed to augment snow water for subsequent runoff. PG&E has operated the Mokelumne cloud seeding program since 1953. The size of the target area is approximately 200 square miles. Elevations range from about 1200 m at Salt Spring Reservoir to over 3100 m along the Sierra Nevada crest line located on the eastern side of the target.

The program uses surface-based ground generators to disperse silver iodide type seeding materials which are released into the winter storm clouds as they cross over the watershed. The target area also includes portions of the Bear River drainages. Figure 1 gives a map of the target area.

**Figure 1. Mokelumne cloud seeding target area and sampling locations. The red dots in the figure give the lake water and sediment sampling locations and the target area boundary is shown in black.**

### *Sampling*

To gather physical evidence of the distribution of aluminum (Al), cesium (Cs), chromium (Cr), copper (Cu), indium (In), iron (Fe), manganese (Mn), rubidium (Rb), silver (Ag) and vanadium (V) in the lake waters and sediments, a field expedition was conducted on November 15, 2005 to collect samples. Silver was selected to provide evidence of seeding effects. Al, Cs, Fe, Mn and Rb can be used for finger printing the sources of local (granitic) soils. Cr, Cu, In and V can provide evidence of contamination from anthropogenic sources other than cloud seeding such as fuels additives from road construction or snowmobile activities. Indicators of unusual sample composition can be developed by forming characteristic ratios or calculating enrichment factors of these elements relative to the average crustal values.

The sampling sites selected were Lower Blue Lake (LBL) and the upper end of Salt Springs Reservoir (SSR). LBL is located on the upper north east side of the cloud seeding target area. Winds are often favorable for the transport of ice nucleating seeding aerosols from the ground-based generators to the high elevation terrain surrounding LBL. Temperatures are frequently cold enough for the submicron sized aerosols to function as efficient ice nuclei which create new seeded precipitation that fall within the target area. If these materials were to become mobile in the environment, subsequent transport from the higher elevations above LBL could lead to higher concentrations in LBL or one of the surrounding lakes. LBL was selected on this basis and also ease of access.

SSR is located at the upper end of Salt Springs Reservoir just west of the Mokelumne Wilderness area boundary. The majority of surface runoff from the target area flows past this location and therefore SSR provides an ideal location for measuring any elevated metals concentrations or silver above natural background levels in water or sediment samples. These two locations were identical to those used in a similar study conducted during the 1995 season and allowed direct comparison of results obtained from the current study with those obtained in the earlier study. Figure 1 shows the locations of the two sampling sites.

A total of 40 samples were collected for chemical analysis, 10 lake samples and 10 sediment samples from each location. Helicopter transport to the sampling sites was provided by PG&E. Each 200ml lake sample was stored in a clean linear polyethylene container and preserved with 1% lot certified ultra trace level $HNO_3$ (Tamapure AA-10). Sediment samples were collected using a dredge and stored in clean linear polyethylene bags. The samples were returned to Reno for preparation and chemical analysis following collection. A detailed sampling summary is provided in Table 1.

| Sample ID | Location | Type | | Latitude | | Longitude | |
|---|---|---|---|---|---|---|---|
| LBW05001 | Lower Blue Lake | Water | | 38 | 36.625 | 119 | 55.7 |
| LBW05003 | Lower Blue Lake | Water | | 38 | 36.625 | 119 | 55.7 |
| LBW05004 | Lower Blue Lake | Water | | 38 | 36.625 | 119 | 55.7 |
| LBW05005 | Lower Blue Lake | Water | | 38 | 36.625 | 119 | 55.7 |
| LBW05010 | Lower Blue Lake | Water | | 38 | 36.625 | 119 | 55.7 |
| SSW05001 | Salt Springs Resevoir | Water | | 38 | 29.665 | 120 | 9.445 |
| SSW05005 | Salt Springs Resevoir | Water | | 38 | 29.665 | 120 | 9.445 |
| SSW05006 | Salt Springs Resevoir | Water | | 38 | 29.665 | 120 | 9.445 |
| SSW05007 | Salt Springs Resevoir | Water | | 38 | 29.665 | 120 | 9.445 |
| SSW05009 | Salt Springs Resevoir | Water | | 38 | 29.665 | 120 | 9.445 |
| LBS05001 | Lower Blue Lake | Sediment | Fine | 38 | 36.625 | 119 | 55.7 |
| LBS05002 | Lower Blue Lake | Sediment | Gravel | 38 | 36.625 | 119 | 55.7 |
| LBS05003 | Lower Blue Lake | Sediment | Fines w/Gravel | 38 | 36.625 | 119 | 55.7 |
| LBS05004 | Lower Blue Lake | Sediment | Fine | 38 | 36.625 | 119 | 55.7 |
| LBS05007 | Lower Blue Lake | Sediment | Fine | 38 | 36.625 | 119 | 55.7 |
| SSS05004 | Salt Springs Resevoir | Sediment | Fine/Gold | 38 | 29.665 | 120 | 9.445 |
| SSS05006 | Salt Springs Resevoir | Sediment | Fine/Gold | 38 | 29.662 | 120 | 9.475 |
| SSS05007 | Salt Springs Resevoir | Sediment | Large Grain | 38 | 29.659 | 120 | 9.48 |
| SSS05008 | Salt Springs Resevoir | Sediment | Fine/Organic | 38 | 29.669 | 120 | 9.491 |
| SSW05009 | Salt Springs Resevoir | Sediment | Fine | 38 | 29.669 | 120 | 9.491 |

**Table 1. Sampling Summary**

### *Analytical Techniques*

All samples were submitted to the Balazs Analytical Laboratory, Freemont, CA. Ten (10) lake samples were analyzed using a high resolution Finnegan 2 sector field inductively coupled mass spectrometer (HR-ICPMS). This unit and all related apparatus were housed in a Class 10 clean room. Each sample was melted, acidified with ultra pure 1% $HNO_3$ and then analyzed four times. These analyses were compared with a standard calibration curve so that the mean concentration and relative standard deviation could be reported for each sample. Distilled-deionized blanks were also analyzed and subtracted from the instrument responses. Reporting limits for Ag, Cr, Cs, Cu, In, Rb, V, were all one part per trillion (ppt, $1 \times 10^{-12}$g/ml). The ICPMS reporting limits and calibration curves for the more common elements were higher bracketing the natural range of concentrations encountered in the samples. The reporting limit for Al was 100 parts per trillion and 1 part per billion (ppb, $1000 \times 10^{-12}$ g/ml).

Sediment samples were prepared for the same elemental analyses using two different procedures. In the first procedure 5-10g of each sample was digested in concentrated nitric acid and hydrogen peroxide and the remaining extract was analyzed for total metal contents. No hydrochloric (HCL) was used in the digestion procedure and this could have lead to an underestimate of the total dissolved solid concentrations.

In the second procedure, each sample was prepared using modified TCLP extraction procedures (EPA 1311) and then the extract from each sample was analyzed using ICP-AES. This procedure is designed to simulate the mobility of organic and in organic analytes present in liquid, solid or multiphasic samples. In this study it is used to determine the amount of free “bio-available” silver and other metals that can be leached from the lake sediment samples with pH=5.2 solutions during an eight hour period. Each leachate sample is then analyzed for its silver and other metal contents. pH 5.2 solutions are used in the preparation process because this is the lowest pH value that snowmelt water reaches during spring runoff. Snowfall becomes slightly acidic because of its extremely low buffering capacity and exposure to atmospheric $CO_2$. All leachate analysis results have been reported as leachate concentration and not corrected back to dry soil sample weight. This was done to provide an estimate of actual lake sample elemental concentrations that would develop over time when exposed to the individual soils. The details of these methods are covered in EPA standard analysis method 1311 procedures (http://www.epa.gov/sw-846/pdfs/1311.pdf) and will not be discussed in more detail in this report.

## Results and Discussion

Tables 4-6 list the results for each of the ten elements and three sample analysis methods for each of the two sites. Table 4 displays a listing of the measured lake water concentrations; Table 5 a listing of the leachate extraction concentrations and Table 6 provides a listing of the total dissolved sediment sample analyses. The next few sections will discuss these results by type beginning with the lake water sample analyses. For convenience a reference units table is listed below; note that m=milli, µ=micro, n=nano and p=pico.

| Unit | Abbreviation | Mass/L | Mass/ml | Scientific-Liquid | Scientific-Soil |
|---|---|---|---|---|---|
| Parts per million | ppm | mg/L | µg/ml | x $10^{-6}$ g/ml | x 10-6 g/g |
| Parts per billion | ppb | µg/L | Ng/ml | x $10^{-9}$ g/ml | x 10-9 g/g |
| Parts per trillion | ppt | ng/L | pg/ml | x $10^{-12}$ g/ml | x $10^{-12}$ g/g |

***Lake Water Samples***

Figures 3 and 4 give graphical displays of the frequency distributions of the lake water sample measurements from Lower Blue Lake (LBL) and Upper Salt Springs Reservoir (SSR) respectively; Table 2 gives the range of element concentrations measured at LBL and Table 3 displays the ranges of values from SSR.

At LBL aluminum ranged between 6.1 to 8.8 ng/ml (ppb), copper between 110 and 130 pg/ml (ppt), iron between 73 to 97 ng/ml (ppb), manganese from 38 to 51 ng/ml, rubidium from 410 to 530 pg/ml (ppt), silver from less than detection to 0.2 pg/ml and vanadium from 79 to 110 pg/ml (ppt). Elemental concentrations in the current sample sets are generally in good agreement with measurements reported by others and within a factor of three of values reported in the literature by others.

Al, Fe and Mn are common crustal elements and the higher values ranging between a few parts per billion up to about 100 parts per billion are well with observations collected by others in the region. For example aluminum concentrations (6.1 to 8.8 ppb) were slightly lower than those observed by others. Bradford, 1992 found aluminum values ranging as high as 39 ppb from lake water samples surveys conducted in central and southern Sierra lakes. Stone, 1986 found aluminum concentrations reaching peak values of 27-54 ppb in a survey of 124 central and southern Sierra lakes. Conversely, iron and manganese concentrations in the LBL samples were slightly higher that values from the literature. The LBL set ranged between 73 to 97 ppb iron and 38 to 51 ppb manganese. Stone, 1986 found iron ranged as high 26.7 and manganese as high as 16.8 ppb, a factor of three lower than the values measured in the current sample set.

| Element | Minimum Conc. | Average Conc. | Maximum Conc. |
|---|---|---|---|
| Aluminum (pg/ml) | 6100 | 7280 | 8800 |
| Chromium (pg/ml) | - | - | <1 |
| Cesium (pg/ml) | - | - | <1 |
| Copper (pg/ml) | 110 | 114 | 130 |
| Indium (pg/ml) | - | - | <1 |
| Iron (pg/ml) | 73000 | 85400 | 97000 |
| Manganese (pg/ml) | 38000 | 45000 | 51000 |

| | | | |
|---|---|---|---|
| Rubidium (pg/ml) | 410 | 460 | 530 |
| **Silver (pg/ml)** | **-** | **0.04** | **0.2** |
| Vanadium (pg/ml) | 79 | 95.4 | 110 |

**Table 2. Element concentration ranges from LBL water samples.**

Rubidium and copper are common trace element components of Sierra granite and other soils; the values measured in this study are consistent with those observed by Stone and others in similar studies. The lake water measurements from this study are also consistent with the background concentration levels of silver in snow which has been measured in several watersheds located in the Sierra Nevada, the western U. S. and other regions of the world. Assuming a normal distribution, it can be stated as $[Ag]_{bkg} = 1.88 \times 10^{-12}$ $gAgml^{-1}$ ($\sigma \pm 1.11 \times 10^{-12}$ $gAgml^{-1}$). The background of cesium has also been measured in several of these same areas and is estimated to be $[Cs]_{bkg} \sim 1 \times 10^{-12}$ g/ml. The background level for rubidium is about fifty times higher than silver in snow due to its presence in granites. Local weathering of these rocks acts to increase rubidium's natural background level in snow. It has been measured and found to be approximately $[Rb]_{bkg} \sim 50 \times 10^{-12}$ g/ml ± 100%. Similarly, the natural background for copper in snow is also found at higher levels. It has been measured as part of cloud seeding tracer programs and estimated to be $[Cu]_{bkg} \sim 200 \times 10^{-12}$ g/ml ±50%. Chromium, Indium and Vanadium were not detectable above the reporting limit of one part per trillion, a surprising result given the low lake water level and amount of recent construction activity taking place at LBL with the extension of paved surface road from CA highway 88 through to LBL. All of these elements are additives to engine component alloys and fuels; any fuel spills, emissions from heavy equipment or snow mobiles that may have collected in LBL would have concentrated of these elements to higher values.

Table 3 give the range of elemental lake water concentrations observed at SSR. As in the case of LBL all of the lake water sample measurements collected from SSR are well within the range of those observed in the local region and in good agreement with those previously observed at the same or nearby locations. Aluminum, rubidium and vanadium values were slightly higher than the concentrations observed at LBL, while copper, iron and were observed at levels slightly below those measured at LBL. Cesium, chromium, and indium were not detectable as in the case of LBL. These results are reasonable given the extremely high levels of natural variability in mineral composition of the rocks and soil that occur as surface flows pass through the Mokelumne watershed on route to Salt Springs Reservoir.

| Element | Minimum Conc. | Average Conc. | Maximum Conc. |
|---|---|---|---|
| Aluminum (pg/ml) | 7900 | 10780 | 13000 |
| Chromium (pg/ml) | - | - | <1 |
| Cesium (pg/ml) | - | - | <1 |
| Copper (pg/ml) | 81 | 97 | 110 |
| Indium (pg/ml) | - | - | <1 |
| Iron (pg/ml) | 26000 | 30200 | 33000 |
| Manganese | 3700 | 4180 | 4500 |

| | | | |
|---|---|---|---|
| (pg/ml) | | | |
| Rubidium (pg/ml) | 890 | 1038 | 1100 |
| **Silver (pg/ml)** | **-** | **<0.5** | **0.9** |
| Vanadium (pg/ml) | 110 | 128 | 140 |

**Table 3. Elemental concentration ranges from SSR water samples.**

In summary, the range of concentrations of the measured metals all suggest that the samples were characteristic and very representative of Mokelumne watershed lake and stream chemistry and that no significant sources of contamination exist in the samples set.

The silver contents of the samples will be discussed in the next section as they relate to cloud seeding activities will be discussed in the next section.

### *Lake Samples – Silver Concentrations*

At LBL detectable silver was found in only one sample. The average silver concentration observed at LBL in this study was $[Ag]<0.04\times10^{-12}$ gAg/ml with a peak value of $[Ag]=2.0\times10^{-12}$ gAg/ml. In contrast the average silver content for all samples observed in the 1995 study was $\mu_{[Ag]}=6.7\times10^{-12}$ gAg/ml or an order of magnitude higher than the measurements obtained from the current study. The silver contents of lake water samples collected during the 1995 study were measured using graphite furnace flameless atomic absorption methods as compared with the HR-ICPMS methods used in this study. Both studies were conducted in clean room facilities although the DRI clean room was only equipped with Class 100 working surfaces as compared with the Balazs clean room which is certified as a Class 10 room. It is not known whether changes in analytical methods and facilities, reduced seeding levels or seasonal sampling differences were responsible for the lower observed silver levels. However, all of these observations remain well within the natural silver background concentrations measured in the region in both surface waters and precipitation.

Results from SSR were very similar to those observed at LBL although silver was present at slightly higher levels and detectable in four of the five samples. The average silver concentration observed at SSR was $\mu=<0.5\times10^{-12}$ gAg/ml and a maximum concentration of $[Ag]=0.9\times10^{-12}$ gAg/ml, which was about twice the maximum concentration observed at LBL but still well below the natural silver background found in snow in the watershed and lake and water samples collected previously from the Carson, Mokelumne and Walker catchments. These results were again roughly ten times lower than those observed in the 1995 study.

Figure 4 shows the distribution of silver from samples collected from the Carson and Walker river watersheds located immediately downwind of the Mokelumne watershed. All of the samples measured in the current and 1995 studies fall within the range of values observed between 1977 through 1995. The results displayed in Figure 4 are for stream and lake samples collected during periods when no seeding activities were taking place and therefore represent the best available estimate of the natural silver background level for surface waters in the area.

Figure 4 also shows the "no effect" silver iodide concentration for silver iodide-sodium iodide toxicity tests of green rainbow trout eggs. Silver iodide was solublized by complexing it with sodium iodide in these tests. The "no-effect" level measured by Davies, et. al., was found to be between 30.0 and 60.0x$10^{-12}$ gAg/ml after 13 months of exposure, which is approximately 50 to 100 times higher than the silver concentrations measured in this study. Similar tests using fish show that the "no effect" toxicity level was between 180 to 400x$10^{-12}$ gAg/ml. These concentration levels should be considered extremely high for silver resulting from cloud seeding activities. These concentration levels and are rarely observed (1-2%) of precipitation samples collected from cloud seeding target areas (e.g., Stone and Warburton (1989), Warburton, et. al., (1996)). Davies, et. al. also found high mortality rates in the sodium iodide control tanks where a 100% mortality rate made it evident that the iodide ion contributed significantly to the deaths of both eggs and fish regardless of the level of silver iodide present in the tanks. Additional long term tests using only silver iodide at much lower concentrations (because of its extremely low solubility) failed to show any differences in the growth rates of fish exposed to silver iodide compared with the controls.

There is some evidence that an annual silver cycle occurs in high alpine lakes and streams and therefore sampling during the winter or early spring when a deep snowpack and frozen lake surfaces are present can lead to slightly higher silver measurements. Studies conducted as part of the State of Nevada cloud seeding monitoring program and in a high alpine Colorado lake by Freeman (1975) observed seasonal trends in silver concentrations with peaks occurring at the end of the plant growth season and the spring thaw. Boyle (1968) postulated that plant die-offs occurring at the end of the season released additional silver into the groundwater and near the surface. As winter approaches and the lakes freeze and the amount of water in the lakes is reduced which leads to higher silver levels than those observed following the spring melt. With the onset of the spring thaw dilution occurs and silver levels can recede and then rise again following the thaw when biological activity reinitiates the cycle.

A detailed summary of the natural silver background concentrations observed in precipitation from several areas of the western U. S collected during period's minimal or no seeding activity was taking place is provided in Appendix A. These observations show that only a very minor difference in the background of silver level occurs in the pristine high elevations of the far western U. S., an observation that has not been widely publicized. The extremely low solubility of silver iodide and its strong affinity to bind with soils has not lead to a wide spread detectable increase in the natural silver background in the western U. S. Given the consistency of the low silver background in precipitation and surface water of the observations from the two sample sets collected from LBL and SSR, it is reasonable to conclude that there is no detectable evidence that seeding activities are having an impact on the water chemistry of either Lower Blue Lake or Salt Springs Reservoir.

| Sample ID | Aluminum (Al) | Chromium (Cr) | Cesium (Cs) | Copper (Cu) | Iron (Fe) | Indium (In) | Manganese (Mn) | Rubidium (Rb) | Silver (Ag) | Vanadium (V) |
|---|---|---|---|---|---|---|---|---|---|---|
| | ppt (pg/g) | ppt (pg/g) | ppt (pg/g) | ppt (pg/g) | ppt (pg/g) | ppt (pg/g) | ppt (pg/g) | ppt (pg/g) | ppt (pg/g) | ppt (pg/g) |
| LBW05001 | 7700 | <1 | <1 | 130 | 95000 | <1 | 50000 | 510 | <1 | 110 |
| RSD | 2.84% | 13.31% | 107.00% | 3.41% | 6.76% | 5.71% | 4.92% | 6.97% | 2.39% | 5.29% |
| LBW05003 | 8800 | <1 | <1 | 130 | 97000 | <1 | 51000 | 530 | <1 | 110 |
| RSD | 3.90% | 15.67% | 141.86% | 5.32% | 1.72% | 2.95% | 3.22% | 2.18% | 3.33% | 1.83% |
| LBW05004 | 6800 | <1 | <1 | 110 | 87000 | <1 | 46000 | 440 | <1 | 92 |
| RSD | 5.91% | 14.57% | 19.16% | 9.71% | 2.20% | 3.24% | 1.77% | 2.93% | 4.12% | 5.44% |
| LBW05005 | 6100 | <1 | <1 | 100 | 73000 | <1 | 38000 | 410 | <1 | 79 |
| RSD | 5.89% | 12.86% | 20.25% | 8.07% | 3.38% | 4.87% | 5.77% | 4.75% | 5.50% | 4.07% |
| LBW05010 | 7000 | <1 | <1 | 100 | 75000 | <1 | 40000 | 410 | 0.2 | 86 |
| RSD | 3.84% | 27.12% | 15.65% | 10.33% | 3.69% | 2.14% | 1.01% | 6.91% | 5.97% | 6.03% |
| SSW05001 | 11000 | <1 | 120 | 100 | 30000 | <1 | 4200 | 1100 | 0.5 | 130 |
| RSD | 7.67% | 21.32% | 2.88% | 7.28% | 6.12% | 2.82% | 8.53% | 4.54% | 2.26% | 6.30% |
| SSW05005 | 7900 | <1 | 97 | 81 | 26000 | <1 | 3700 | 890 | <1 | 110 |
| RSD | 6.20% | 10.43% | 6.21% | 2.67% | 4.81% | 2.78% | 4.95% | 4.04% | 7.50% | 6.07% |
| SSW05006 | 12000 | <1 | 100 | 94 | 31000 | <1 | 4500 | 1000 | 0.6 | 130 |
| RSD | 4.13% | 16.16% | 5.18% | 3.56% | 6.69% | 3.10% | 3.09% | 1.80% | 6.53% | 10.33% |
| SSW05007 | 13000 | <1 | 120 | 110 | 33000 | <1 | 4300 | 1100 | 0.9 | 140 |
| RSD | 4.01% | 13.77% | 2.75% | 7.25% | 3.17% | 2.60% | 3.43% | 3.65% | 4.77% | 6.41% |
| SSW05009 | 10000 | <1 | 110 | 100 | 31000 | <1 | 4200 | 1100 | 0.5 | 130 |
| RSD | 5.73% | 26.41% | 6.24% | 5.79% | 6.98% | 3.26% | 7.78% | 5.21% | 2.52% | 10.31% |

**Table 4. Trace element concentrations in lake water samples from the Mokelumne watershed. The * symbol represents an element not measured. A less than value (<) indicates the concentration was below the minimum detectable concentration listed in the table.**

| Sample ID | Aluminum (Al) | Chromium (Cr) | Cesium (Cs) | Copper (Cu) | Iron (Fe) | Indium (In) | Manganese (Mn) | Rubidium (Rb) | Silver (Ag) | Vanadium (V) |
|---|---|---|---|---|---|---|---|---|---|---|
| | Ppb (ug/Kg) | Ppb (ug/Kg) | ppb (ug/Kg) | ppb (ug/Kg) | ppb (ug/Kg) | ppb (ug/Kg) | ppb (ug/Kg) | ppb (ug/Kg) | ppb (ug/Kg) | ppb (ug/Kg) |
| LBS05001 | 1.10E+07 | <100 | * | 4000 | 1.40E+07 | <100 | 220000 | * | <50 | 26000 |
| RSD | 1.34% | 1.46% | | 2.57% | 0.42% | 6.85% | 0.32% | | 6.33% | 3.17% |
| LBS05002 | 5900000 | <100 | * | 2000 | 1.10E+07 | <100 | 160000 | * | <50 | 16000 |
| RSD | 0.81% | 1.47% | | 1.75% | 1.05% | 6.43% | 0.31% | | 5.79% | 2.13% |
| LBS05003 | 8400000 | <100 | * | 3500 | 1.10E+07 | <100 | 190000 | * | <50 | 18000 |
| RSD | 0.88% | 1.60% | | 1.57% | 0.74% | 4.49% | 0.52% | | 8.43% | 2.90% |
| LBS05004 | 1.20E+07 | <100 | * | 2200 | 1.30E+07 | <100 | 240000 | * | <50 | 27000 |
| RSD | 1.58% | 1.09% | | 2.74% | 0.64% | 6.13% | 0.50% | | 8.61% | 4.64% |
| LBS05007 | 5600000 | <100 | * | 2100 | 6400000 | <100 | 160000 | * | <50 | 12000 |
| RSD | 1.46% | 0.49% | | 4.90% | 0.24% | 5.12% | 0.34% | | 11.46% | 3.84% |
| SSS05004 | 6800000 | <100 | * | 2300 | 9900000 | <100 | 150000 | * | <50 | 20000 |
| RSD | 1.52% | 1.37% | | 1.43% | 0.46% | 6.65% | 0.50% | | 5.76% | 3.59% |
| SSS05006 | 6400000 | <100 | * | 2400 | 9800000 | <100 | 150000 | * | <50 | 20000 |
| RSD | 0.91% | 0.95% | | 5.44% | 0.75% | 3.48% | 0.22% | | 1.89% | 1.96% |
| SSS05007 | 4300000 | <100 | * | 2200 | 7200000 | <100 | 110000 | * | <50 | 13000 |
| RSD | 1.35% | 2.79% | | 2.65% | 1.45% | 10.66% | 0.80% | | 7.38% | 3.92% |
| SSS05008 | 9800000 | <100 | * | 2100 | 1.30E+07 | <100 | 220000 | * | <50 | 26000 |
| RSD | 0.57% | 0.60% | | 4.36% | 1.30% | 2.07% | 0.27% | | 0.81% | 1.76% |
| SSS05009 | 9500000 | <100 | * | 2000 | 1.10E+07 | <100 | 160000 | * | <50 | 23000 |
| RSD | 1.52% | 1.90% | | 3.97% | 1.33% | 10.49% | 0.90% | | 0.99% | 3.26% |

**Table 5. Total Dissolved Metal Concentrations in Sediment Samples. The * symbol represents and element not measured. A less than value (<) indicates the concentration was below the minimum detectable concentration listed in the table.**

| Sample ID | Aluminum (Al) | Chromium (Cr) | Cesium (Cs) | Copper (Cu) | Iron (Fe) | Indium (In) | Manganese (Mn) | Rubidium (Rb) | Silver (Ag) | Vanadium (V) |
|---|---|---|---|---|---|---|---|---|---|---|
| | ppb (ug/Kg) | ppb (ug/Kg) | ppb (ug/Kg) | ppb (ug/Kg) | ppb (ug/Kg) | ppb (ug/Kg) | ppb (ug/Kg) | ppb (ug/Kg) | ppb (ug/Kg) | ppb (ug/Kg) |
| LBS05001 | 45.6 | <0.6 | * | <0.1 | 85.5 | <1.9 | 32.3 | * | <0.1 | <0.1 |
| RSD | 1.86% | 7.02% | | 0.93% | 0.42% | 17.91% | 0.86% | | 16.10% | 2.84% |
| LBS05002 | 30.4 | <0.6 | * | <0.1 | 18.2 | <1.9 | 5.7 | * | * | <50 |
| RSD | 0.84% | 4.40% | | 5.93% | 0.27% | 16.02% | 0.24% | | 54.55% | 3.37% |
| LBS05003 | 38 | <0.6 | * | <0.1 | 1.9 | <1.9 | 10.8 | * | <0.1 | <0.1 |
| RSD | 1.37% | 5.36% | | 5.99% | 0.84% | 8.17% | 0.35% | | 40.96% | 4.18% |
| LBS05004 | 24.7 | <0.6 | * | <0.1 | 32.3 | <1.9 | 11.2 | * | <0.1 | <0.1 |
| RSD | 2.32% | 4.74% | | 0.48% | 1.29% | 3.86% | 0.55% | | 11.36% | 6.35% |
| LBS05007 | 34.2 | <0.6 | * | <0.1 | 3.4 | <1.9 | 608 | * | <0.1 | <0.1 |
| RSD | 1.65% | 12.83% | | 11.18% | 0.71% | 36.01% | 1.29% | | 10.19% | 6.26% |
| SSS05004 | 22.8 | <0.6 | * | <0.1 | 17.9 | <1.9 | 7.8 | * | <0.1 | <0.1 |
| RSD | 2.19% | 11.60% | | 2.39% | 0.78% | 13.60% | 0.41% | | 111.10% | 6.01% |
| SSS05006 | 19 | <0.6 | * | <0.1 | 10.1 | <1.9 | 45.6 | * | <0.1 | <0.1 |
| RSD | 0.16% | 9.00% | | 4.09% | 0.16% | 2.25% | 0.19% | | 225.80% | 1.74% |
| SSS05007 | 24.7 | <0.6 | * | <0.1 | 19.3 | <1.9 | 3.8 | * | <0.1 | <0.1 |
| RSD | 0.44% | 1.62% | | 10.13% | 0.28% | 29.11% | 0.44% | | 39.47% | 1.46% |
| SSS05008 | 60.8 | <0.6 | * | <0.1 | 174.8 | <1.9 | 399 | * | <0.1 | <0.1 |
| RSD | 1.34% | 6.62% | | 41.98% | 0.24% | 6.49% | 0.53% | | 60.48% | 3.34% |
| SSS05009 | 28.5 | <0.6 | * | <0.1 | 45.6 | <1.9 | 7.4 | * | <0.1 | <0.1 |
| RSD | 0.51% | 8.13% | | 2.61% | 0.29% | 7.98% | 0.53% | | 160.00% | 0.80% |

**Table 6. TCLP Extraction Metal Concentrations in Sediment Samples. Note that the values listed in the table are the leachate concentrations not corrected to dry weight. The * symbol represents an element not measured. A less than value (<) indicates the concentration was below the minimum detectable concentration listed in the table.**

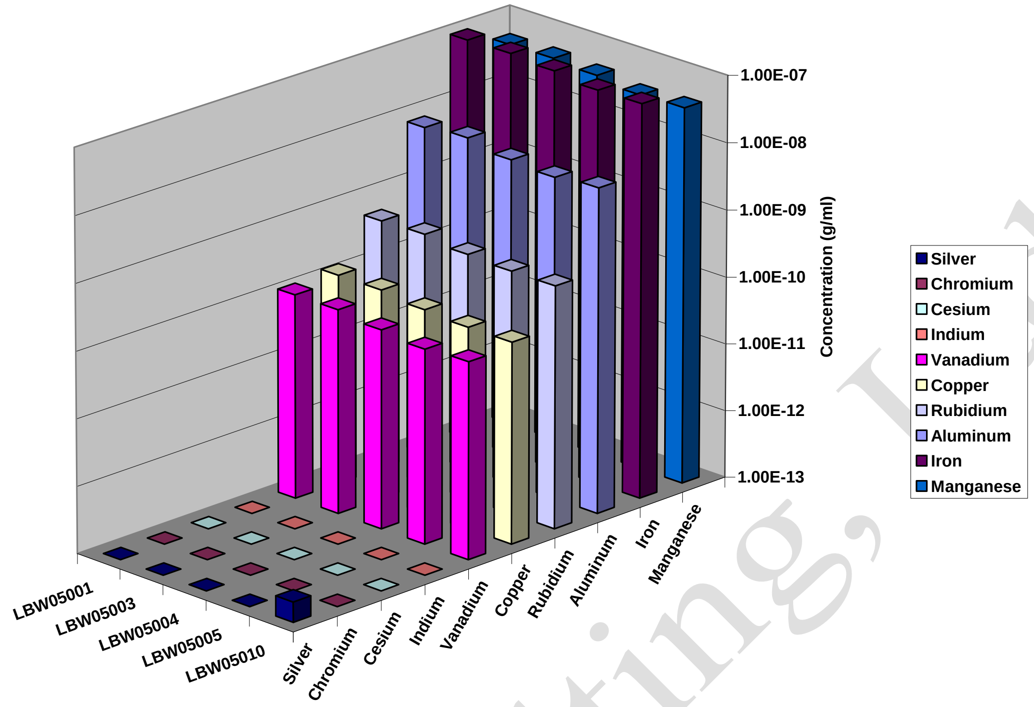

**Figure 2. Element Concentration Distributions measured in Lower Blue Lake water samples.**

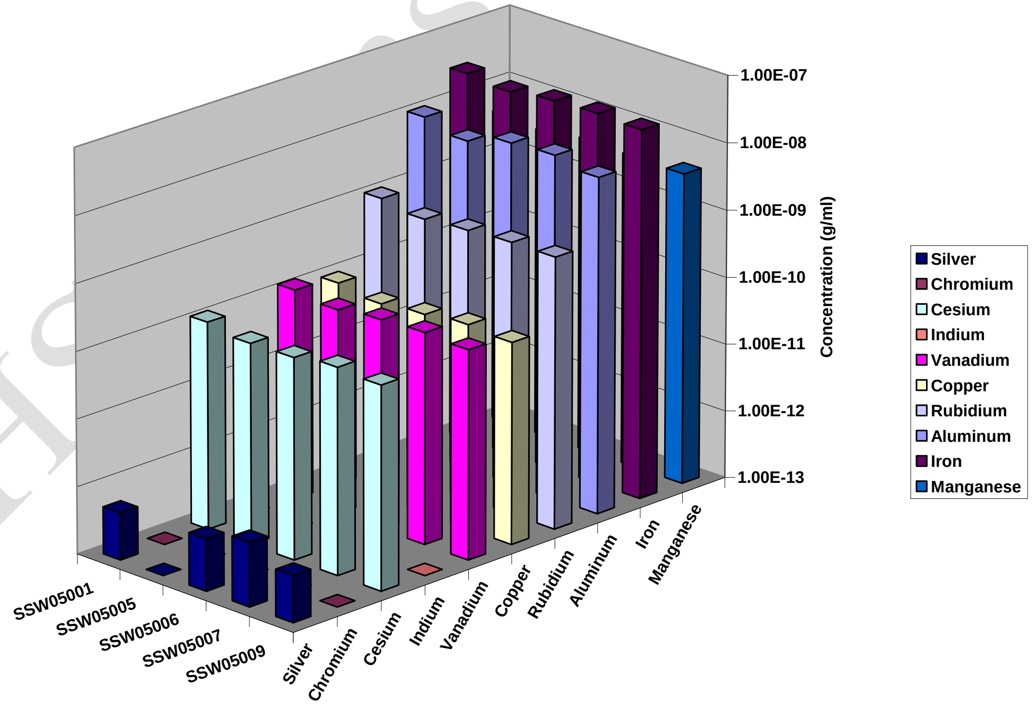

**Figure 3. Element Concentration Distributions measured in Salt Springs Reservoir water samples.**

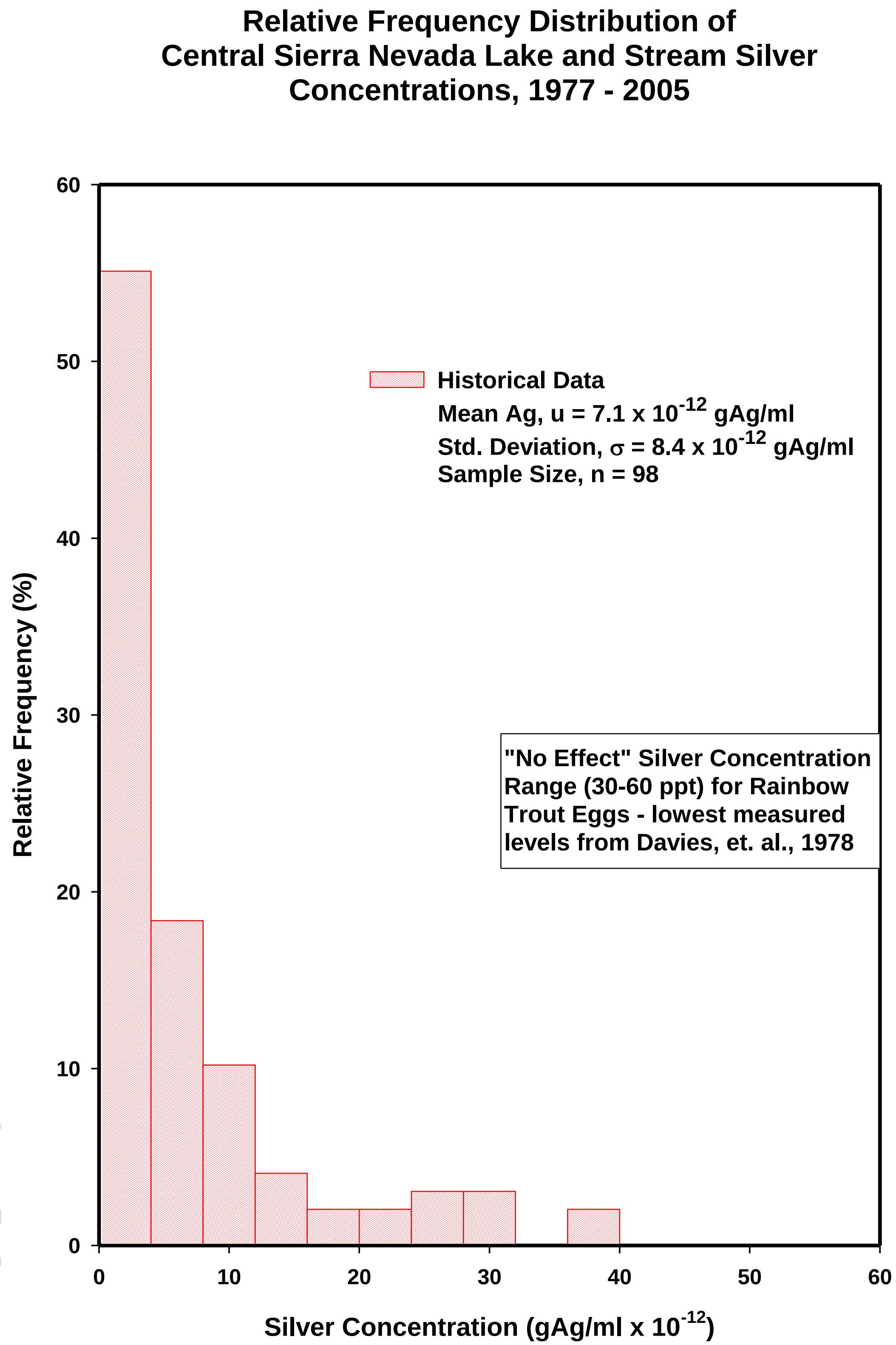

**Figure 4. Relative Frequency Distribution of Sierra Nevada Lake and Stream Silver Concentrations, 1977-2005**

### *Sediment Samples*

Table 5 gives the results of all elemental analyses of the dissolved lake sediment samples from both sampling sites. Average metal concentrations are in units of parts per million for each of the element. At LBL observed concentrations were as follows in descending order: Fe = 11.1x$10^3$ μg/ml, Al = 8.5x$10^3$, μg/ml, , Mn = 1.9x$10^2$ μg/ml, V = 6.8 μg/ml, Cu = 2.8 μg/ml, Cr < 0.1 μg/ml, In <0.1 μg/ml and Ag < 0.05 μg/ml. Cs and Rb were not reported. Comparison with the average crustal values for each of these elements as reported by DeMayo (65th CRC Handbook, F147) shows that the reported concentrations measured in the samples were lower than anticipated by a factor of 4.9 to 9.7 for Mn, Fe, Al and V.

Average dissolved metal concentrations at SSR were similar to those observed at LBL. Dissolved sediment metal concentrations in descending order were as follows: [Fe] = 10.2x$10^3$ μg/ml, [Al] = 7.4x$10^3$ μg/ml, [Mn] = 1.6x$10^2$ μg/ml, [V] = 20.4 μg/ml, [Cu] = 6.1 μg/ml, [Cr] < 0.1 μg/ml, [In] < 0.1 μg/ml and [Ag] < 0.05 μg/ml. Measurements of Cs and Rb were not reported. Comparison with average crustal values also indicated that these measurements were also low, ranging from a factor of 2.7 to 11.3 for V, Mn, Cu, Fe and Al.

Table 7 displays calculated enrichment factors with respect to iron for the average lake water and sediment samples collected at each of the sampling sites. The enrichment factor calculated in table 7 is defined as follows:

$$\mathbf{EF_{earth\ crust}\ (x/Fe) = ([metal\ x]/[Fe])_{lake\ or\ sediment}/([metal\ x]/[Fe])_{earth\ crust}}$$

Enrichment factors can be useful for identifying or revealing anthropogenic, contaminated or local sources of the elements in a sample relative to the average concentrations that occurs in the crust or ocean. If the local background value cannot be measured directly, crustal rock compositions are chosen for comparison because much of the inorganic input to environmental samples is derived from the weathering of crustal materials. Crustal values represent a global average which cannot take into account local variations in rock chemistry and therefore using these crustal enrichment factors can only lead to a rough estimate of potential outlier samples. Table 7 shows that the manganese is in very good agreement with reported crustal average values with enrichment factors near 1.0. Elements such as aluminum, copper and vanadium are all slightly depleted in the sediment samples; however, these differences should be considered relatively minor variations from typical crustal values. Rubidium, a significant trace chemical component of granite, is enriched by a factor of twenty, consistent with the composition of the local rocks. The concentrations measured in the individual samples are shown graphically in Figure 5. The upper panel of the figure shows the results from LBL and the lower panel from SSR. With the exception of LBS05003, which showed low aluminum levels, and SSS05009, which showed depressed iron values, all of the common elements from LBL and SSR show remarkable consistency by element and sample concentration. These results suggest that the sediment samples collected from LBL and SSR are quite representative of the local watershed geochemistry.

Based on the enrichment calculations shown in Table 7 it also becomes evident that some fraction of the total metal burden was not dissolved using the procedures followed in this study. It is recommended that future investigations include the use of both HCL and HF (to dissolve silica in the form of quartz) in the digestion procedures to ensure that all metals including oxides and chlorides are more completely digested so that better total recovery estimates and elemental concentrations can be made in the sediment samples.

Comparison of the average silver concentration of the sediment samples collected in the 1995 study from the same sites shows that the average sediment silver concentration from LBL and SSR ranged between 0.035 µg/ml to 0.107 µg/ml respectively, although some samples had silver contents less than 0.01 µg/ml at both sampling locations. All of the samples collected from the current study had extremely low silver contents [Ag] < 0.05 µg/ml. These results clearly demonstrate that silver is extremely immobile, insoluble and not readily bio-available to the environment from lake sediments of the Mokelumne watershed regardless of the source of silver. This suggests that it would be extremely difficult to detect any significant impacts or silver above the natural background released as a result of cloud seeding activities in the lakes and streams of the Mokelumne watershed.

| | Lake Water Concentration | | Sediment Concentration | | Average Crustal Concentration (mg/kg) | Enrichment Factor $EF_{crust}$ (x/Fe) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Lake Water | | Sediment | |
| Element (x) | LBL (pg/ml) | SSR (pg/ml) | LBS (µg/ml) | SSS (µg/ml) | | LBL | SSR | LBS | SSS |
| Ag | <0.04 | <0.5 | <0.05 | <0.05 | 7.00E-02 | BDL | BDL | BDL | BDL |
| Al | 7280.0 | 10780.0 | 8500.0 | 7400.0 | 8.32E+04 | 0.0577 | 0.2415 | 0.5229 | 0.4909 |
| Cr | BDL | BDL | <0.1 | <0.1 | 1.00E+02 | BDL | BDL | BDL | BDL |
| Cs | BDL | BDL | NM | NM | 1.00E+00 | BDL | BDL | NM | NM |
| Cu | 114.0 | 97.0 | 2.8 | 6.1 | 5.50E+01 | 1.3664 | 3.2878 | 0.2606 | 0.6122 |
| Fe | 85400.0 | 30200.0 | 11000.0 | 10200.0 | 5.63E+04 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| In | BDL | BDL | <0.1 | <0.1 | 1.00E-01 | BDL | BDL | BDL | BDL |
| Mn | 45000.0 | 4180.0 | 190.0 | 160.0 | 9.50E+02 | 31.2277 | 8.2026 | 1.0236 | 0.9296 |
| Rb | 460.0 | 1038.0 | NM | NM | 9.00E+01 | 3.3695 | 21.5009 | BDL | BDL |
| V | 95.4 | 128.0 | 6.8 | 20.4 | 1.35E+02 | 0.4659 | 1.7676 | 0.2578 | 0.8341 |

**Table 7. Lake water and sediment enrichment factors with respect to iron.**

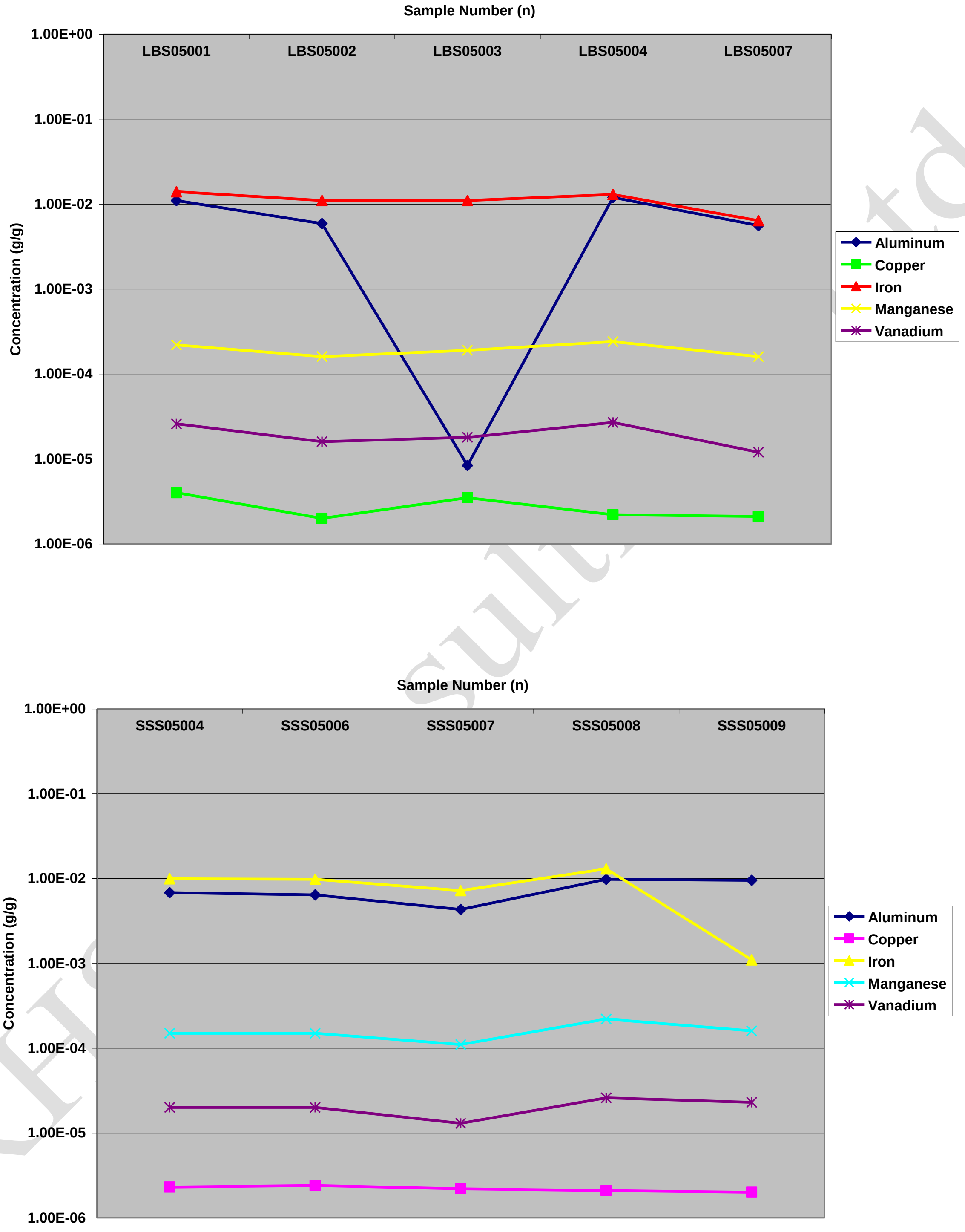

**Figure 5. Dissolved metals concentrations from LBL and SSR sediment samples.**

### *Extraction Samples*

Table 5 gives the results of all elemental analyses for the TCLP extraction (leachate) samples. Graphical displays of the extraction concentration results from the LBS and SSS samples are shown in Figures 6 and 7. Aluminum ranged from 19-60.8 ppb, chromium was less than 0.6 ppb, copper less than 0.1 ppb, iron from 1.9-174.8 ppb, manganese from 5.7-608 ppb, silver less than 0.1 ppb and vanadium less than 0.1 ppb. With the exception of manganese which included two high outliers, these values are all consistent and slightly higher than the concentrations measured in the lake samples, presumably because the lake water was not as acidic as the extraction leachate which limited peak concentrations. <u>No significant silver was detected in any of the samples.</u> Silver was found to be less than a detectable limit of 1.0x$10^{-10}$ g/ml in all of the samples collected in this study. Similar results were obtained in the 1995 study; silver was not detected at the same detectable limit of 1x$10^{-10}$ g/ml. Again the same conclusion is reached as with the lake water samples analysis. <u>No evidence of any bio-available silver could be detected in the extraction samples indicating that the impacts of cloud seeding activities are not significantly impacting the overall silver burden of the Mokelumne watershed in a detectable manner.</u>

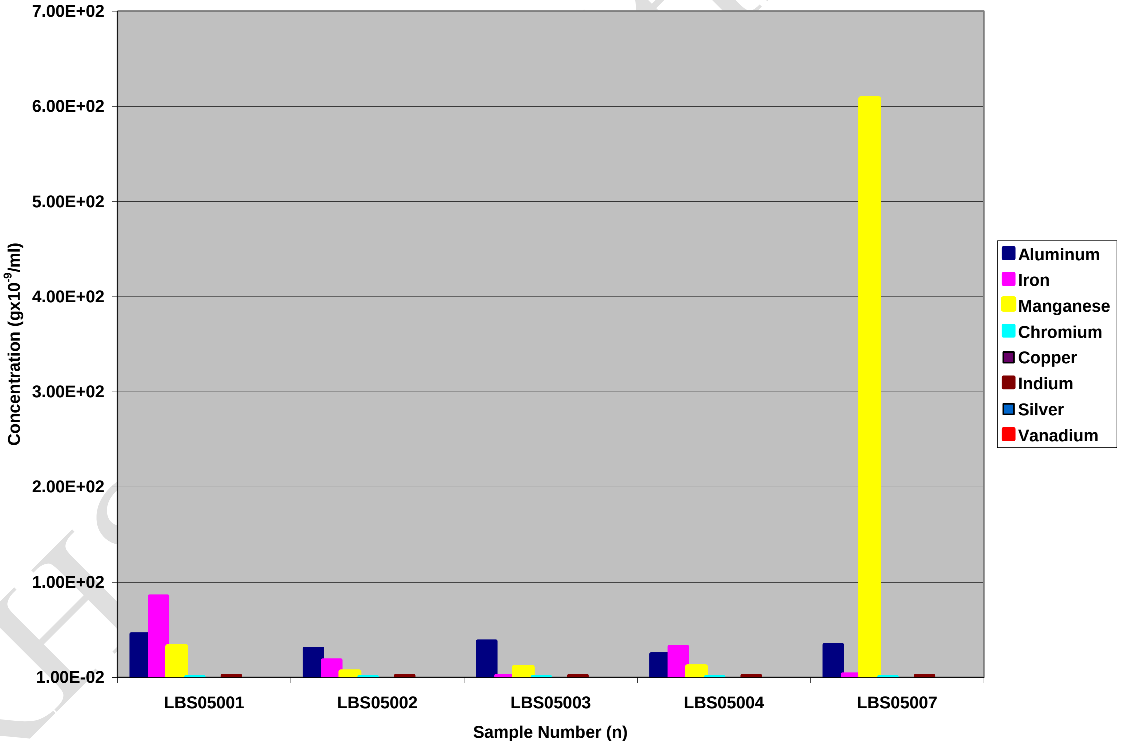

**Figure 6. Relative distribution of leachate elemental concentrations from Lower Blue Lake**

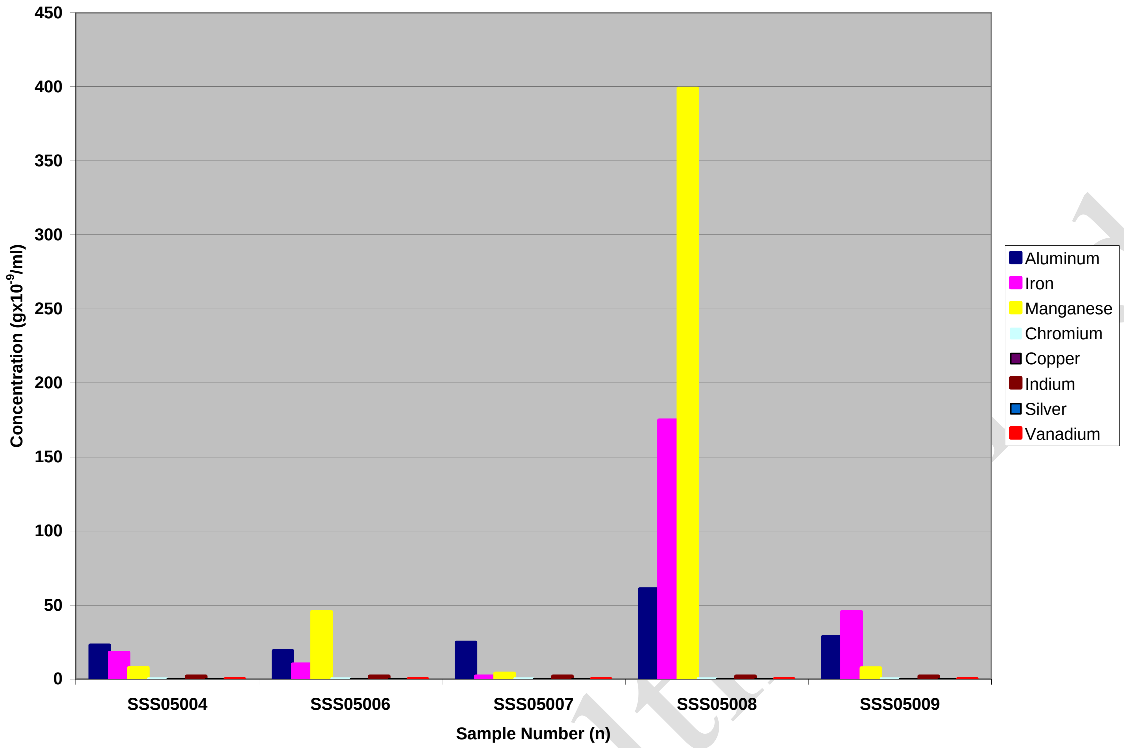

**Figure 7. Relative distribution of leachate elemental concentrations from Salt Springs Reservoir.**

## Conclusions

The expected environmental impact of cloud seeding activities on the Mokelumne watershed environment can be summarized as being insignificant for the reasons set out below:

- Silver iodide released from operational cloud seeding activities conducted by PG&E could not be detected above natural background levels from lake water samples collected at Lower Blue Lake or Salt Springs Reservoir. Silver concentrations from the current study averaged less than [Ag] < 0.5 x $10^{-12}$ gAg/ml as compared with an average value of [Ag] = 6.7 x 10-12 gAg/ml measured during the 1995 season. The silver contents of lake water samples collected during the 1995 study were measured using graphite furnace flameless atomic absorption methods as compared with the HR-ICPMS methods used in this study. Both studies were conducted in clean room facilities. It is not known whether changes in analytical methods, reduced levels of seeding or seasonal sampling differences were responsible for the lower observed silver levels. However, all of these observations remain well within the natural silver background concentrations measured in the region in both surface waters and precipitation.

- The silver concentrations measured during the 1995 study and the current study are less than the historical Eastern Sierra Nevada average of [Ag] = 7.0 x 10-12 gAg/ml. The historical sample set has a sample size of n=98 and is composed of samples collected from the East Carson River, West Walker River and the Mokelumne watershed.

- Aluminium, copper, iron, manganese, rubidium and vanadium were measured and found to be consistent with concentrations measured in other lake water studies conducted in the central and southern Sierra Nevada.

- Chromium, cesium, and indium were also measured and used as indicators of potential sample contamination from local or anthropogenic sources. Cesium and indium are also used as tracers of cloud seeding activities. None of these elements were detectable above a detection limit of 1.0 x 10-12 g/ml or one part per trillion indicating that the samples were not affected by any significant anthropogenic or local sources.

- Silver contents in the lake sediments samples were all less than [Ag]<50 x $10^{-9}$ gAg/ml indicating that silver is not present in the lake sediments at significant levels.

- No detectable bio-available silver could be measured from the lake sediment samples under going TCLP extractions.

- Both the 1995 and current study have shown that silver levels in lake water and sediment leachate samples are orders of magnitude lower than levels that can be considered toxic to the environment.

- Background levels of silver, cesium and indium occurring in snow in the Mokelumne are generally less than $2x10^{-12}$ g/L, while background levels of silver in stream runoff was below the detection limit of $1x10^{-12}$ g/L for silver, chromium, copper, indium and vanadium. These levels are several orders of magnitude below chronic toxicity levels for all of these elements.

No evidence has been found that the use of either silver iodide or silver chloroiodide seeding materials, at the levels currently released, has raised environmental levels significantly above background levels as measured in two different studies conducted ten years apart. This suggests that no detectable silver will be found in the future as a result of cloud seeding activities and that no acute or chronic toxic effects would be expected to occur as a result of the continuation of these activities in the future.

**The conclusion of this study is that the continuation of the PG&E cloud seeding program will not give rise to any unacceptable or significant impact on the environment of the Mokelumne Wilderness and surrounding areas of the central Sierra Nevada.**

## Appendix A - Environmental Toxicity of Silver Iodide

This section is intended to provide background information on the relevant issues concerning the environmental toxicity of silver and silver iodide. A review of the current world-wide published literature in terms of the toxicity of the silver, silver iodide and silver chloroiodide seeding materials currently used in the and relevant to the PG&E Mokelumne cloud seeding program is provided along with a discussion of related factors that have been demonstrated to ameliorate the bioavailability and hence toxicity of these materials. The bulk of the published work emanates from the research conducted in the U. S., but also includes several recent reports from European countries and Australia. Much of the material in this section was originally developed by Stone. et. al. (1995, 2003) and later significantly enhanced by Williams (2003) and included as part of an Expert Panel Cloud Seeding Report submitted to the Australian government. The current section includes an updated version of the material submitted to the Australian legislature in 2003. The section on natural silver background levels measured in the western U. S. has been expanded significantly. Not all of the information that appears in this Appendix is pertinent to the Mokelumne watershed, however it has been included in the discussion for the sake of completeness. One section that has not been included but may become of interest to the reader describes the anticipated impacts of episodic acidification of high elevation alpine lakes on silver and other metal concentrations. The interested reader should contact the author for additional information.

A Material Safety Data Sheet (MSDS) for silver iodide is included as Appendix B.

### *Environmental Concentrations of Silver Ions from Silver Iodide*

The element silver occurs naturally in the earth's crust at a concentration of $7 \times 10^{-2}$ mg/kg (CRC handbook) and is found in the free state as the metal and as ores such as the sulfide, arsenide and chloride (Cotton & Wilkinson, 1961). The metal is not soluble, but salts such as silver nitrate ($AgNO_3$) are very soluble. Other silver salts, such as silver sulfide ($Ag_2S$), silver chloride (AgCl) and silver iodide (AgI) are insoluble in water (Purcell and Peters, 1998).

Ratte (1999) has shown that insoluble or complexed silver compounds are much less toxic or virtually non-toxic to a range of terrestrial and aquatic vertebrates. For example, silver thiosulfate was found to be 15,000 times and AgCl 11,000 times less toxic than silver nitrate (Ratte, 1999), which is highly soluble. Particulate AgCl is described as virtually non-toxic by Bury *et al* 1999 and Rodgers *et al* 1996.

The silver cation ($Ag^+$) binds strongly with ligands found in natural waters. This means that in the event, seeding materials are broken down into their elemental components, toxicity will be reduced by the presence of substances with which they can associate or form covalent bonds. Some silver complexes and silver ions are readily adsorbed to particulate matter to the extent that only some 25% of total silver is estimated to be dissolved as either ion colloid or complex (Wen, 1997).

The free silver ion is fungicidal, algicidal and bactericidal at relatively low doses. Typically, bactericidal concentrations are of the order of 0.01–1.0 mg/L which are well below established human health hazard levels. Silver compounds have also used in medicine and for sterilizing potable water, in part due to the sensitivity of bacterial metabolism to $Ag^+$ inhibition of the thio functionality in enzymes.

### *Solubility of Silver Salts*

Over the past ten years most Sierra cloud seeding programs have switched from the use of pure silver iodide (AgI) to complexed silver chloroiodide (AgI-AgCl) or (AgI-Cl-xAlkI; where Alk= one of the alkali iodides) based seeding materials. The chlorination of standard silver iodide solutions produces more efficient ice nuclei with warmer activation temperatures. The AgI/AgCl ratio of these aerosols can range between 2.3:1 to 4:1 depending on the specific generator design and project. These newer seeding aerosols include an active ice nucleating component and often a hygroscopic component which controls the rates of ice formation. Many of the current programs use seeding aerosols specifically designed to function efficiently in the dominant clouds that pass over the target watersheds to improve the targeting effectiveness. One of the key cloud seeding properties of these compounds is their extremely low solubility in water, $K_{sp} \sim 8.3 \times 10^{-17}$ to $\sim 1.0 \times 10^{-12}$. This property prevents these seeding aerosols from dissolving in the clouds prior to the time that they can successfully nucleate new precipitation. This property also limits the degree to which they can become bioavailable in the environment.

Silver is a particular hazard in aquatic environments; however research over the last decade or more has shown that the toxicity is a function of silver speciation rather than total dissolved silver ion concentration. Nonetheless, where it is proposed to add a silver salt to the environment consideration of the salt's solubility is a useful starting point in a discussion of its likely bioavailability.

The solubility in water of some selected silver compounds is shown in Table 8.

| | **Solubility, in g/100 ml** | |
|---|---|---|
| | **Cold water** | **Hot water** |
| Silver nitrate $AgNO_3$ | 122 | 952 |
| Silver chloride AgCl | 0.000089 | 0.0021 |
| Silver iodide AgI | Insoluble | Insoluble |
| Silver sulfide $Ag_2S$ | Insoluble | Insoluble |

**Table 8. Solubility of Selected Silver Salts (CRC Handbook, 1984)**

In solution, the silver ion ($Ag^+$) has been shown to be toxic to aquatic plants and a range of animals (see Table 11), however the toxicity has been clearly demonstrated to be dependent on the chemical form and has been shown to correlate with free ionic silver ($Ag^+$).

For silver salts such as silver nitrate, which dissociate strongly, the concentration of silver ion equates to the concentration of the silver salt. As Ratte (1999) has noted *inter alia*, "…the perception of high silver toxicity has long been due to the fact that most laboratory toxicity trials used $AgNO_3$, which readily dissolves releasing the highly toxic free silver ion".

For silver salts that do not dissociate readily, such as silver iodide and silver chloroiodide, the concentration of silver ions derived from an either of these extremely insoluble salts that is augmented by the presence of additional salts or electrolytes such as silver chloride, sodium chloride or potassium iodide, which can furnish a common silver or chloride ions with the silver iodide ions, the effective solubility of the silver iodide will be decreased because the dissociation of silver iodide will be reduced, and the amount of AgI in solution decreased. The concentration of $Ag^+$ derived from the insoluble AgI salt will be determined by the dissociation constant $K_{SP}$ (see below) of the least soluble salt, which in this case will limit the concentration of silver ion to [Ag]~ $9x10^{-9}$ M. This means that the concentration of $Ag^+$ in a solution containing silver iodide can not be greater than this value. This is in contrast to the $Ag^+$ concentration derived from silver nitrate, which as Table 8 shows has a solubility constant many orders of magnitude greater than for silver iodide or silver chloroiodide.

It is important to note that, since water solubility generally controls bioavailability, silver compounds that are not readily soluble or insoluble are of less environmental concern, a point emphasized by Karen *et al* (1999).

For insoluble silver salts, the concentration of silver ion in equilibrium with the solid silver salt can be determined from the solubility constant in each case. The solubility product constants for the silver salts of interest to this project are shown in Table 9 along with the calculated silver ion concentrations that would exist in aqueous solution, at equilibrium.

| | Solubility product constant $K_{SP}$ at 25°C | Silver ion concentration (M) |
|---|---|---|
| Silver chromate<br>$Ag_2CrO_4$ | $2.40x10^{-12}$ | $1.7x10^{-4}$ |
| Silver chloride<br>AgCl | $1.77x10^{-10}$ | $1.33x10^{-5}$ |
| Silver Bromide<br>AgBr | $5.20x10^{-13}$ | $7.2x10^{-7}$ |
| Silver iodide<br>AgI | $8.51x10^{-17}$ | $9.2x10^{-9}$ |
| Silver sulfide<br>$Ag_2S$ | $6.69x10^{-50}$ | $2.56x10^{-17}$ |

**Table 9. Solubility product constants for some common silver salts (Gymer, 1973, CRC Handbook, 1984)**

The significance of the data in Table 8 is that for silver chloroiodide, the maximum concentration of silver ion in an aqueous solution in equilibrium with solid silver iodide is less than $1.0\times10^{-7}$ M ($1.0\times10^{-5}$ g/L) and for silver iodide the maximum silver concentration is $9.2\times10^{-9}$ M ($9.84\times10^{-7}$ g/L). For comparison, the maximum silver concentration that can be reached with silver sulphide is $2.56\times10^{-17}$ M ($2.73\times10^{-15}$ g/L).

This means that solid silver chloroiodide or silver iodide will be extremely weak sources of silver ions in solution, particularly for solutions containing significant chloride or iodide concentrations.

## Typical Environmental Levels of Silver

There is a considerable body of literature describing background levels of silver for many regions and ecosystems around the world. The natural background level of silver in snow in the Sierra Nevada has been well documented over the past forty years by a number of investigations e.g., Warburton and Young (1969) Stone (1983) Stone(1989) Stone and Marler (1993) and Stone, et. al.(1997). It has remained essentially constant over the time span covered by these studies. A series of tests conducted as part of the NV/NOAA cooperative program in the central Sierra Nevada towards the end of the 1984 winter season, when no seeding activities were taking place due to record snow packs, showed that the background silver distribution in snow closely follows a log normal distribution (Stone, 1989). The same distribution occurs in the Lake Almanor region of the northern Sierra Nevada and many areas of the western U. S.

The log normal distribution found from the NV/NOAA study follows the function:

$$y = a_0 \exp\left[-0.5\left(\ln\left(x / a_1\right)/a_2\right)\right]^2 ;$$

where

$a_0$ = 0.861 (amplitude of the normalized distribution)

$a_1$ = 1.160 (peak center value of silver concentration)

$a_2$ = 0.975 (width of distribution at half-maximum amplitude)

This relationship was based on a sample size of n=847 and has a remarkably high correlation coefficient of $r^2 = 0.994$ and low standard error, $s_e = 0.012 \times 10^{-12}$ $gAgml^{-1}$. Less than 1% of the background samples in these study would be expected to contain silver exceeding $6.0 \times 10^{-12}$ $gAgml^{-1}$.

For comparison, Table 9 provides a listing of the mean background silver concentration measured in several other programs from other Sierra Nevada locations and seasons beginning in 1966. The mean background levels from all of these areas are basically the same when consideration is given to continued improvement of analytical instrumentation and techniques.

| *Location* | *Period* | *No of Samples* | *Mean [Ag] (gAg/ml x $10^{-12}$)* | *Analytical Technique* |
|---|---|---|---|---|
| **Tahoe Basin, Sierra Nevada** | 1966-1969 | 169 | <3.9 | Ion Exchange – NAA |
| **Tahoe Basin, Sierra Nevada** | 1970-1971 | 18 | <4.7 | Ion Exchange – NAA |
| **Tahoe Basin, Sierra Nevada** | 1971-1972 | 26 | <5.4 | Ion Exchange – GFAAS |
| **Tahoe Basin, Sierra Nevada** | 1972-1973 | 12 | <4.5 | Ion Exchange – GFAAS |
| **Tahoe Basin, Sierra Nevada** | 1973-1974 | 9 | <3.8 | Ion Exchange – GFAAS |
| **Tahoe Basin, Sierra Nevada** | 1973-1974 | 24 | <3.0 | Ion Exchange – GFAAS |
| **Walker River Watershed, Sierra Nevada** | 1976-1977 | 24 | 3.0 | GFAAS |
| **Mokelumne Watershed, Sierra Nevada** | 1976-1979 | 18 | 1.6 | GFAAS |
| **Tahoe Basin, Sierra Nevada** | 1978-1979 | 10 | 1.7 | GFAAS |
| **Central Sierra Nevada** | 1983 | 847 | <1.5 | GFAAS |
| **Ruby Mountains, Eastern Nevada** | 1983, 1996 | 20 | <1.0 | GFAAS |
| **Lake Almanor Watershed, Northern Sierra Nevada** | 1983-1989 | 200 | <2.0 | GFAAS |
| **Tushar Mountains, Southern Utah** | 1982-1984 | 35 | 2.0 | GFAAS |
| **Upper San Joaquin, Southern Sierra Nevada** | 1994 | 30 | <1.9 | GFAAS, ICPMS |
| **Payette Basin, Idaho*** | 1996 | 74 | <1.3 | GFAAS |
| **Payette Basin, Idaho** | 2004 | 15 | 1.17 | HR-ICPMS |

*** Estimated Value – based on profiles collected at Scott Mountain and Deadwood Summit**

**Table 10. Natural silver background in snow in the western U. S.**

The metal composition of snow has also been studied in a number of environments including the Greenland and Antarctica. For example, Warburton *et al* (1995) have examined trace metal levels in snow in the Antarctic and concluded that the silver found was derived from mainly from marine sources. They also found that the natural silver background levels of silver in snow from the Antarctica were very similar to those observed in the pristine high elevation mountains of the western U. S.

Although they did not report silver levels in the ocean generally, Martin *et al* (1983) showed that silver levels in the north-eastern region of the Pacific Ocean ranged from $1.0 \times 10^{-13}$ gAg/ml to $2.3 \times 10^{-12}$ gAg/ml at a depth of 2440 m. Silver concentrations near the coastline can occur at much higher levels. Stone (1980) observed silver concentrations ranging from $6.9 \times 10^{-9}$ gAg/ml to $82 \times 10^{-9}$ gAg/ml from samples collected off the California coast in the Monterey Bay collected at depths of 20 to 60 m below the surface.

The Concise International Chemical Assessment Document 44 (2002), (CICAD 44), has recorded some recent silver levels in various environmental compartments found using ultra-trace sampling and analysis techniques. For pristine, unpolluted areas such as rivers, lakes and estuaries, levels of < 0.01 µg/L were found, while for urban and industrialised areas the levels were typically 0.01-0.1 µg/L.

CICAD 44 includes an important caveat however, which is that because ultra-clean metal sampling did not begin until the late 1980's, silver analyses reported for environmental studies and toxicity research prior to that period should be treated with caution.

Environmental concentrations of silver are elevated in areas associated with abandoned silver mines or a silver-based industry such as the manufacture of photographic film. Several of these sources exist immediately downwind of the Mokelumne watershed.

Although background total silver levels in non-pristine areas are similar to effect concentration levels, the key issue is whether the local environmental conditions favour a lesser or greater bioavailability of the silver ion, before concern as to the toxicity of the silver ion is warranted.

Silver is more bioavailable under conditions of low anion concentrations, low levels of reactive sulfide or sulfur containing ligands, low concentrations of organic ligands (humates), lower suspended sediment and lower pH. In soils and fresh water, the primary silver compounds under oxidizing conditions were believed to be chlorides, bromides and iodides, whereas under reducing conditions the free metal and silver sulfide are the principal species (CICAD 44). Although recent published work has shown that sulfides are very important even in oxic conditions.

For brackish and marine environments increasing salinity leads to increasing concentrations of silver-chloro complexes because of the affinity of free silver ion for the chloride ion. Recent work has shown that levels of reactive sulfide in oxygenated natural waters are stable and high enough to ensure that silver sulfide or silver thiol complexes dominate (Bianchini *et al* 2002; Bowles *et al* 2002; Bielmyer *et al* 2002).

Sunda and Huntsman (1998) have pointed out that photochemical and biological reduction of $Ag^+$ leads to a substantial decrease in biological uptake and toxicity. Redox conditions play a role in determining bioavailability since the elemental form is unreactive towards complex formation. Although Adams and Kramer (1999), found that silver ($Ag^+$) is not reduced to the metal when complexed to ligands for which it has a high affinity.

Concentrations of silver in air have been occasionally reported. For example, silver concentrations in air near a smelter have been measured at 36.5 ng/m$^3$ and a level of 2.0 µg/m$^3$ in atmospheric dust (CICAD 44). The workplace airborne limit for silver is 0.1 µg/m$^3$. The level of silver in the air in polluted environments has been reported by Bowen (1986), for both Britain (0.0001 – 0.001 µg/m$^3$) and the US (0.01–0.02 µg/m$^3$). Downwind of cloud seeding activities similar to those conducted in the Mokelumne project ambient silver concentrations are much lower. Typical concentrations at distances of 10-20 km downwind of ground-based generators range from 0.1 to 50 x $10^{-12}$ gAg/m$^3$. Over the course of a season involving several hundred hours of seeding Stone (1980) measured a mean concentration of [Ag] = 3.5 x $10^{-12}$ gAg/m$^3$, which was about seven times the natural background concentration.

Silver is a normal trace constituent of many organisms. Terrestrial plants for example usually contain silver at less than 0.1 mg/kg dry weight, with seeds nuts and fruits containing higher concentrations than other plant parts (USEPA (1980), cited in CICAD 44 (2002)).

The toxicity of the silver ion ($Ag^+$) in water to a range of aquatic species has been the subject of a great number of studies reported in the scientific literature. These wide-ranging studies have been comprehensively reviewed by Eisler (1997), Ratte (1999) and others.

The source of the silver ion used in these studies was generally derived from the readily soluble silver nitrate ($AgNO_3$) which dissociates completely and gives essentially free silver ion. In contrast to the situation found in most laboratory studies, Hogstrand and Woods (1998) note that only a small proportion of total dissolved silver in natural waters, <40%, exists in the free form, and very often will be much less.

In studies where the silver ion was derived from silver salts that are insoluble, such as silver thiosulfate $Ag_2(S_2O_3)$ and silver chloride (AgCl), the toxicity decreased significantly as the solubility decreased. For silver chloride for example the 96-hr $LC_{50}$ was reported as > 100 µg/L (Wood *et al* 1996). Davies and Goetl (1978) were successful at testing the effects of silver iodide within the limits of its solubility on rainbow trout. They conducted a thirteen month exposure test and found a "no-effect" silver concentration of 0.03 to 0.06 µg/L or 30 to 60 parts per trillion. Mortaility rates increased to 5-22% at silver concentration of 110 parts per trillion. These concentrations are 30 to 110 times the silver levels observed in the Mokelumne watershed in lake water samples and it is unlikely that silver concentrations of this magnitude could ever be attained in the lakes because of the extremely low buffering capacity and relatively neutral pH.

LeBlanc *et al* (1984) reported that for fathead minnows, silver ion was 300 times more toxic than silver chloride, 15,000 times more toxic than silver sulfide and 17,500 times more toxic that the silver thiosulfate complex.

Similar results were found by Hogstrand *et al* (1996), who also reported that toxicity decreased as hardness was increased from 50 to 250 mg $CaCO_3$/L. Increasing concentrations of humic acid were also found to decrease silver ion toxicity, as noted elsewhere in this report.

Occasionally silver toxicity studies have been attempted using the insoluble silver salts, but most researchers had to resort to indirect methods to achieve the desired silver salt's concentration see for example Wood *et al* (1996).

As noted above, a number of researchers studying the toxicity of insoluble silver salts have attempted to "get-around" the problem of the very low solubility by preparing the required salt in solution prior to toxicity testing using, as an example, a solution of sodium chloride and adding silver nitrate. This overlooks the fact that these anions, often in some excess, will act to reduce the available silver ion concentration in solution (solubility product) leading to AgCl (precipitate) and or may produce a silver ion complex $AgCl_2^-$ which is negatively charged (Pavlostathis and Maeng, 1998)

### *Silver Levels in Snow Following Seeding Operations*

Cloud seeding operations result in negligible additions of insoluble silver chloroiodide of silver iodide to the soluble silver budget of the Mokelumne watershed.

The ground-based generators used to seed clouds passing over the target area release 20 gAgI/hr. During any particular storm up to four-five generators are operated giving an aggregate release rate of 80-100 gAgI/hr. An average of forty twelve-hour long seeding events occur each season yielding a total release of about 25kg of Ag in the form of AgI. Silver measurements from snow samples collected from eight target area sampling locations show that typical concentrations range from the natural background level of $1.0\text{-}2.0 \times 10^{-12}$ gAg/ml to peak values as high as $40\text{-}60 \times 10^{-12}$ gAg/ml in 10-30% of the samples. Higher silver concentrations were found in less than 10% of the samples at levels higher than twelve parts per trillion, $[Ag] > 12 \times 10^{-12}$ gAg/ml. This additional silver iodide must then dissolve and dissociate to enhance the extremely low levels of silver ions which can act, subject to the factors described below, to moderate and reduce the bioavailability of the silver ions.

The proportion of these ultra-trace concentrations of incremental silver ion that could become bioavailable is determined by the relative importance of each of the moderating factors described in the next few sections. These factors affect the bioavailability of silver ions in both soil and water environments.

### *Role of Sediments and Organic Matter in the Binding of Silver*

Organic matter in lake sediments will bind silver ions in the same way that dissolved organic matter in water binds other metals ions as shown in several studies sponsored by the California Air Resources Board (e.g., Melack and Stoddard (1991), Engle and Melack (1997), Leydecker (1999), Bradford (1992), Bradford, et.al. (1994), Amudson, et. al. (1988)). As part of a recent study on the influence of aeolian dust deposits in New South Wales, AU, Johnston (2001) reported that the percentage of organic carbon in the top ten centimetres of soil profiles collected from alpine elevations were 12.1% and 12.7% respectively. Concentrations of this order would be expected to be very significant in immobilizing silver in the ecosystem. Sediment samples collected from the SSR would also fall into this range and similar results would be expected to occur in terms of binding of silver on organic matter. Any clay minerals that seeding materials encounter in the Mokelumne watershed would bind of silver chloroiodide or silver iodide seeding materials.

The role of groundwater soils in controlling the spreading and filtering of catchment run-off before it enters streams was also noted by Costin (2002). Silver also adsorbs to manganese dioxide, ferric compounds and clay minerals meaning that these compounds are involved in silver deposition in soil and sediments.

Tsiouris and co-workers (2002) recently reported on the silver content of agricultural soils in Greece following a number of years of cloud seeding using silver iodide. They surveyed soils from two areas of Greece, one of some 200,000 ha to which 469 kg of AgI had been applied, and the other some 100,000 ha to which 361 kg AgI had been applied. The silver concentrations found in the soils from the treated areas were within the range found for the three control areas.

Silver concentrations in the treated soils ranged from 37.2 – 44.5 µg/kg, compared with the concentrations in the control areas which ranged from 30.4 – 6.7 µg/kg. These levels are similar to those calculated for a worst-case scenario which assumes that all the silver iodide proposed to be used in the planned trial is incorporated in the top 10 cm of soil in the enhancement area.

### *Factors Affecting the Bioavailability and Toxicity of Silver Ion in Water*

It is clear from a large number of studies, that the toxicity of silver ion in water is significantly moderated by the presence in water of chloride ion, carbonate, sulfide ion and dissolved organic carbon. In addition, silver is strongly adsorbed onto particulate matter. As long as the molar concentration of these moderating factors in total, is greater than the number of moles of silver added to the watershed, there is a negligible risk of toxicity due to silver occurring. The explanation for this is discussed below.

Bell and Kramer (1999) found that in the aqueous phase, silver at the lowest concentrations exists either as a simple sulphur-hydrate (AgSH) or as a simple polymer HS-Ag-S-Ag-SH. Many studies have shown that because of the possibility of binding to colloids or through the formation of covalent and other complexes, the toxicity of dissolved silver ion in the environment is generally less than that found in laboratory tests.

It has recently been shown by Bianchini *et all* (2002), Bowles *et al* (2002) and others, that reactive sulfides occur at concentrations ranging from pico-molar to nano-molar concentrations in natural oxygenated waters. Bianchini *et al* (2002) have observed that these reactive sulfides probably account for the fact that waterborne chronic silver toxicity has never been shown for natural field situations.

Attempts has been made to extrapolate current laboratory results to field sites where silver is found has resulted in extremely low regulatory limits (Karen *et al* 1999). Differences in laboratory test methods and local water quality characteristics are further confounding factors in the application of laboratory results to field situations.

### *Dissolved Organic Carbon*

Many published studies have identified DOC as a significant factor in reducing the bioavailability of silver ion. For example, Karen *et al* (1999) studied the effect of DOC (as humic acid) on the toxicity of silver nitrate to rainbow trout (*Oncoryhyncus mykiss*), fathead minnows (*Pimphales promelas*) and water fleas (*Daphnia magna*).

For all three species, increased concentrations of humic acid, measured as the percentage of carbon, significantly increased the $LC_{50}$ values in all treatments. In other words as the dissolved organic carbon concentration increased, the silver ion became much less toxic. This clearly illustrates the protective effect of DOC.

In a study on the toxicity of silver to fathead minnows and water fleas, reported by Erickson *et al* (1998), they were able to demonstrate that for the fathead minnows, increasing the organic carbon to 2.5 mg C/L increased the 96-hr $LC_{50}$ by 350%, and increasing organic carbon to 10 mg C/L increased the 96-hr $LC_{50}$ by 450%.

As they noted, this is similar to other metals for which complexation by organic matter also reduces bioavailability.

Figure 8 shows the effect of organic carbon on the acute toxicity of silver nitrate to juvenile fathead minnows.

In addition, Erickson *et al* (1998) also found that the toxicity of silver ion to both organisms was much reduced when water from the St Louis River was used in the test rather than normal laboratory water.

The reduction in toxicity was some 60-fold for water fleas although this is regarded as a more sensitive organism than the fathead minnow.

They surmised that the higher organic carbon content in the St Louis River water was responsible for the reduced toxicity. Their data are reproduced as Table 11.

**Table 11. Acute toxicity of silver nitrate to juvenile fathead minnows and < 1-d-old *Daphnia magna* in laboratory water and St. Louis River water.**

| **Test Organism** | **Test Water** | **$LC_{50}$ [a] (µg Ag/L) [a]** | **95 % Confidence Limits** |
|---|---|---|---|
| Fathead minnow | Laboratory | 10.4 | 8.6 – 12.5 |
| | River | 106 | 97 – 114 |
| *Daphnia magna* | Laboratory | 0.58 | 0.56 – 0.61 |
| | River | 35 | 32 - 39 |

a $LC_{50}$ = median lethal concentration

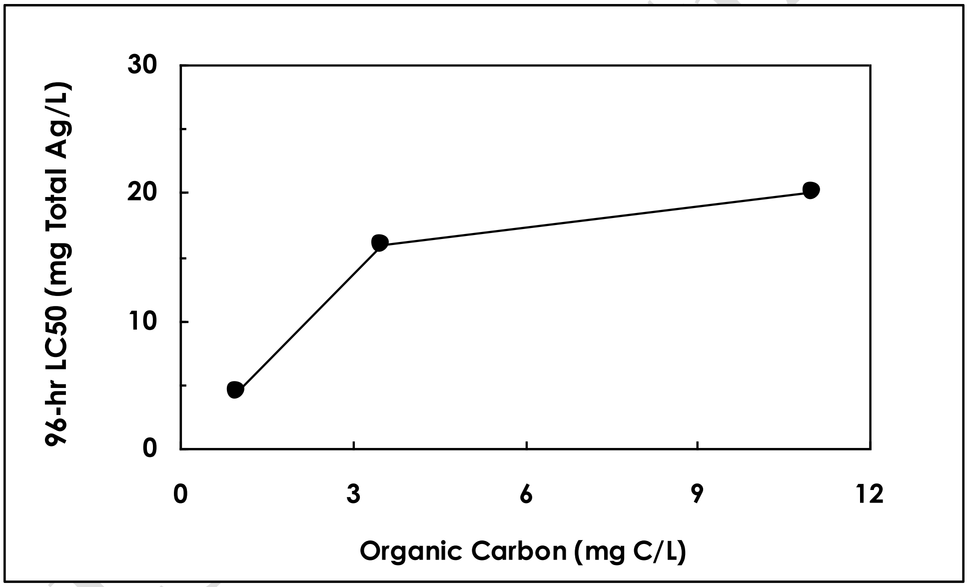

**Figure 8. The effect of organic carbon on the acute toxicity of silver nitrate to juvenile fathead minnows.**

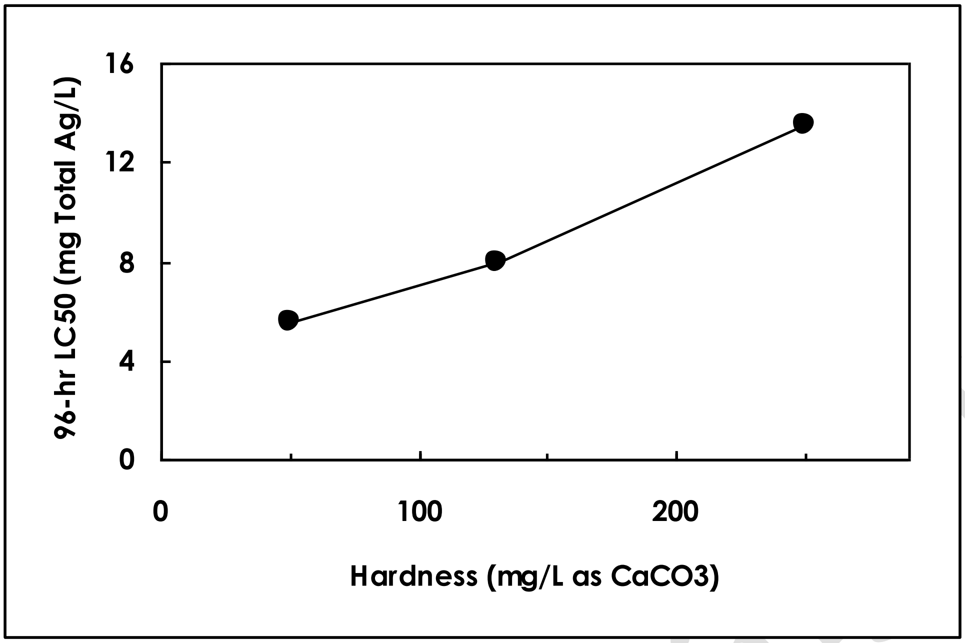

**Figure 9. General effect on silver ion toxicity due to hardness.**

Importantly they also showed that $LC_{50}$ values for flow-through exposures were lower than for aged static exposures. A result they ascribe to organic matter accretion in the aged exposures.

In a study of silver complexation in river waters in central New York, Whitlow and Rice (1985) had noted that the determined values for silver in the river waters were lower than calculated from a speciation model. They attributed the discrepancy to additional complexes formed with dissolved organic carbon and or colloids that were not further identified.

The importance of DOC complexes with silver, has also been emphasized by Hogstrand and Woods (1998) in their review of the bioavailability, physiology and toxicity of silver in fish. They noted that Janes and Playle (1995) have estimated a log $K$ ~ 9 for natural DOC collected from a marsh.

The greater protectiveness of DOC compared with that due to hardness, is seen as particularly important for regions of soft-water which contain much organic carbon. This can clearly be seen in a comparison of Figure 8 and Figure 9.

Because of the importance of DOC in moderating silver toxicity, it is relevant to note an important example of a so-called "hot moment" (McClain *et al* 2003) which could be expected to occur in the Mokelumne watershed. A "hot moment" is an isolated zone of enhanced biogeochemical cycling (referred to as a "hotspot"), which is itself "hot" in a temporal dimension (referred to as a "hot moment").

In this specific case, the "hot moment" is the pulse of DOC that leaches from near-stream soils during snowmelt in alpine areas and which would be expected to play a key role in binding any silver ions arising from the silver iodide associated with the snowpack.

Dissolved organic carbon measurements therefore become a critical parameter in the present circumstance. Boyer *et al* (2000) reported that in Deer Creek, Colorado, DOC increased rapidly from 1 to more than 4 mg/L on initiation of snowmelt, remained high for about one month then decreased quickly as runoff peaked. The effect of snowmelt is to flush DOC accumulated under the snowpack and this DOC then binds silver.

Dissolved organic carbon analyses together with organic carbon determinations on key soils will be important. Their presence is significant in reducing bioavailable silver ion and it is essential that this data be available in order to make an assessment of any environmental impact of silver ion from silver iodide.

### *Chloride Ion*

In their review, Hogstrand and Woods (1998) point out that the ability of native chloride and sulfide to significantly reduce the toxicity of silver by precipitating it out of solution in natural waters should not be overlooked. Silver ion forms complexes with chloride ion including AgCl, $AgCl^{2-}$, $AgCl^{3-}$ and $AgCl^{4-}$.

Increasing the chloride ion concentrations will increase the concentration of these chloro-complexes. There is some evidence that the neutral AgCl may represent the most bioavailable form Bryan and Langston (1992) and others.

It has been suggested by some researchers that chloride levels >35 mg/L will affect silver solubility in fresh waters. However, lower concentrations can also be effective (see following).

In their study examining the toxicity of silver to seawater-acclimated rainbow trout, Ferguson and Hogstrand (1998) note that in brackish water, with a typical chloride concentration of 50 mM NaCl (1775 mg/L $Cl^{-}$), total silver at a concentration of 0.1 g/L was not toxic over 168 hr. These silver concentrations however are well outside the ranges expected in the planned trial.

In a study on rainbow trout (*Oncorhynchus mykiss*), Galvez and Wood (1997) showed that increasing calcium by 100-fold increased the median lethal time by a factor of 10. However, increasing chloride ion levels by 100-fold increased the median lethal time by a factor of at least 100-fold. As they observed in their paper, "… complexation processes are expected to reduce silver ion concentrations to well below acute toxicity concentrations".

The reduction in free silver ion concentration in the presence of small amounts of chloride ion is shown in Figure 10.

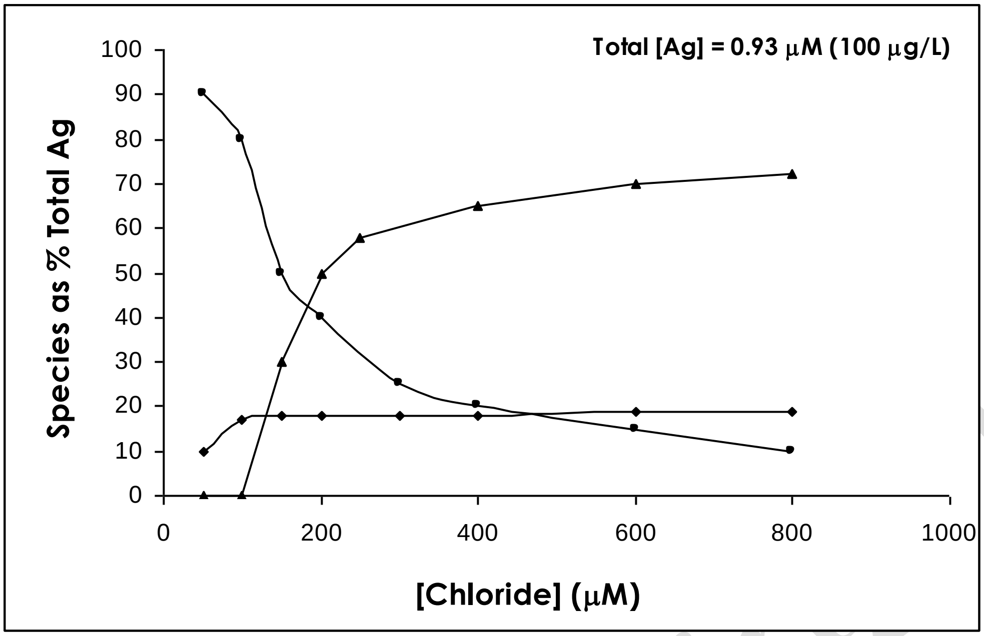

**Figure 10. Concentration of free silver with the presence of small amounts of chlorine ion (adapted from Galvez and Woods (1997). The figure shows how the concentration of free silver is expected to decrease rapidily in the presence of relatively small amounts of chloride ion.**

The importance of complexes in reducing silver toxicity is well illustrated in the study of silver thiosulfate toxicity to freshwater rainbow trout Wood *et al* (1996). In this study, rainbow trout were able to tolerate a 3000-fold higher concentration of silver where it was complexed as $Ag(S_2O_3)^{n-}$ compared with free $Ag^+$ from silver nitrate.

During exposure to silver thiosulfate there was a doubling of liver silver concentrations compared with that found for silver nitrate. This may reflect the increased octanol-water partition coefficient of these neutral species (Warburton *et al* (1995), Ratte (1999), Reinfelder and Chang (1999) & Fortin and Campbell (2000)).

***Sulfides and Sulfur Containing Ligands***

There is a growing recognition that because reactive sulfides are found in oxic as well as anoxic environments, silver – "sulfide" complexes may have a greater impact in reducing acute silver toxicity than many if not most of the factors described above.

Probably the most important chemical fact to note is the strength of the silver – sulfur bond. The presence in the environment of tiny concentrations of inorganic sulfides and organic mercaptans plays a major role in the environmental behaviour of silver. As mentioned earlier, silver binds strongly to the sulfide ion (see $K_{SP}$) data, which results in nanogram per litre concentrations of aqueous dissolved silver. This outcome is also found for sulfide ion associated with inorganic and organic species.

Occluded mercaptans as well as $HS^-$ or $H_2S$ trapped within colloids or particulate matter will act as reaction sites for $Ag^+$. Silver sorbs rapidly onto amorphous FeS giving an aqueous silver ion concentration similar to that for $Ag_2S$ solubility.

Trace levels of dissolved silver in the presence of FeS are rapidly adsorbed (Bell and Kramer, 1999) with any silver remaining in solution as silver sulfide. Silver thiolate complexes are often the dominant dissolved species in waters with high levels of natural organic matter (Adams and Kramer, 1998).

At low silver concentrations, when silver is adsorbed onto sulfide particles, the local presence of a high concentration of an organic mercaptan can lead to an exchange reaction leading to the formation of a silver thiolate. This process will move silver into solution phase as either a silver thiolate or as a silver-other-metal thiolate at levels of the order of <5 nanomolar. This "dissolved silver" is not bioavailable however.

In their study, Adams and Kramer (1998) showed, using X Ray Diffraction (XRD), that dissolved silver ion in the presence of amorphous iron sulfide rapidly equilibrated, to give ultra-trace levels (~ 5 ng/L) of silver ion. This concentration is consistent with that calculated from the solubility product constant (see earlier). They also calculated that sulfur containing ligands especially thiols are more important than chloride until the total sulfur species is less than $10^{-13}$ M.

Bielmyer *et al* (2002) have argued that silver thiol complexes dominate all other dissolved silver species when organic molecules containing sulfur are present and other metal sulfide concentrations are negligible. Silver thiol complexes are bioavailable due to increased lipophilicity and have shown chronic effects in *Ceriodaphnia dubia* at lower concentrations than for silver ion.

In a comprehensive (ultra-clean) study of silver concentrations in tailings and stream sediments and rooted vegetation associated with an old mining site in Canada, Kramer *et al* (1999) looked at, inter alia, the association of silver to acid volatile sulfide (AVS) ratio. They found acid-volatile sulfides (AVS) at the nanomolar concentration in most samples.

The procedure they used detected many colloidal sulfides, soluble sulfides and part of the polysulfides but not the thiols. Concentrations ranged from 570 nM to <1 nM. Interestingly, corresponding dissolved oxygen levels were between 10.2 – 6.8 mg/L with dissolved organic carbon levels of 18.7 – 3.2 mg/L. They noted that, although all water samples were nearly saturated with respect to atmospheric oxygen, over half the samples had measurable AVS ranging from tens to hundreds of nM.

They concluded that the silver is strongly bound to the solid phase and is at low nanogram per litre concentrations in the apparent soluble phase. Their data indicate that the majority of the operationally defined soluble (<0.45 µm) silver ion occurs in the colloidal phase. One conclusion from their study was that as long as the AVS (mole) >$Ag^+$ (mole), $Ag^+$ should not accumulate in plant material.

Hirsch (1998) looked at the toxicity of silver sulfide to the juvenile freshwater amphipod (*Hyalella azteca*), an epibenthic organism that burrows into the sediment surface. Using sediments from a non-contaminated source, spiked with varying amounts of silver sulfide, there was no difference found in survival rates between treatments and controls up to a level of silver of 753.3 mg Ag/kg sediment. The sediments had average AVS concentrations of 5.35 µmol/gm and total organic carbon values of the order of 1.5%. Hirsch noted that the concentration of AVS in the sediment would have favoured the formation of $Ag_2S$ had any free silver ion been present.

Call and co-workers (1999) showed that the capacity of river sediments to bind silver effectively occurs at relatively low levels of total organic carbon and acid volatile sulfides. This capability is important in reducing silver bioavailability in pore waters to which benthic organisms would be exposed.

Sediments were spiked with silver nitrate until silver ion was detected in the pore water. One sediment with a TOC of 0.87% and an AVS of < 0.1 µmol/g was spiked at 2.2 g Ag per kilogram before silver appeared in the pore water.

In contrast, the other sediment with a TOC of 0.22% and AVS < 0.1 µmol/g showed silver in the pore-water at a spiking level of only 0.08 g Ag /kg. The authors believed that the differences might in part be explained by the interaction of several sediment characteristics such as particle size distribution and geochemical composition.

It should be noted that this work involved sediments, which are very likely to be anoxic, whereas the work reported by Kramer *et al* (1999), involved oxic waters which were shown to contain AVS.

Other research groups have found that in more oxic sediments, amorphous Fe oxides or manganese oxides or colloids are important sinks for binding silver and other metals.

Because of the large stability constants found for metals such as silver sulfide, the importance of a pool of sulfides including zinc and iron sulfides (AVS) in detoxifying metals such as silver in natural waters cannot be overstated.

In a recent study of multinuclear sulfide clusters in natural waters, Rozan *et al* (2000), showed that the most abundant metal sulfides were iron sulfides and that they were composed mainly of a soluble FeS cluster. They found that FeS predominated in rivers that drained less-urbanised watersheds". Metal sulfide clusters were kinetically stable and as a result persisted in oxic waters.

On the basis of their observations it was suggested that sulfur complexation might dramatically lower the acute toxicity of "b"-class metals including silver.

### *Hardness*

Water hardness, principally in the form of calcium, was recognised by the USEPA (1980) as having a critical role in reducing harm to aquatic organisms from acute silver toxicity.

The maximum total recoverable silver in water was related to hardness by the equation:

$$\text{Max. total recoverable Ag } (\mu g/L) = e^{(1.72[\ln \text{hardness}] - 6.52)}$$

More recently however, it has become clear that this expression is under protective at high hardness levels and is overly conservative where waters have low hardness (Galvez and Wood, 1997). In the study reported by Galvez and Wood (1997), they found that the protective effect of chloride is much more significant than that due to calcium. CICAD 44 notes that silver was less toxic to fathead minnows when water hardness increased from 50 to 250 mg $CaCO_3$/L.

The current view however is that hardness due to calcium ion is now thought to be less effective in modifying the toxicity of silver ion than the other factors discussed, unless it is the only significant ameliorating factor present.

### *Colloids*

The strong affinity of silver for suspended particulates in river and estuarine water was demonstrated in a study reported by Wen *et al* (1997). In experiments to determine phase speciation, they used cross-flow ultrafiltration to separate water samples into particulate >0.45 µm or >0.1 µm, colloidal (0.1 – 0.45 µm), or truly dissolved (<0.1 µm) fractions.

They were able to show that between 33-89% of the silver was bound to the particulate fraction.

The high affinity of silver for suspended particulates was reflected by a high mean particle/water partition coefficient of log $K_D = 5.0$. They also noted that the ratio of colloidal silver to filter-passing silver was similar to the ratio of colloidal organic carbon to total dissolved organic carbon.

They further concluded that silver is complexed by organic macromolecules and that the functional groups with affinity for silver are evenly distributed across the different molecular weight fractions.

In their detailed study, the particulate silver was found to be associated mainly with an iron – manganese oxyhydroxide/sulfide phase. Because of the close relationship between silver and iron in both the colloidal and particulate phases a common surface complex, believed to be sulphydryl groups, was proposed. Of particular relevance to this project was their finding that particulate silver from riverine inputs was rapidly removed from water.

Further support for the effectiveness of colloids in removing silver from water is provided by Shafer *et al* (1998). They examined the removal of silver from influent water in POTW's and found that more than 94% of the influent silver was removed during treatment. The percentage of filterable silver was directly related to DOC.

The amount of silver passing a 0.4 µm filter (often regarded as the dissolved fraction) represented just 2% of the total Ag in the sample.

They found that 92% of dissolved silver was associated with colloidal particles. In their study, DOC concentrations were typically 4.5 – 11.6 mg/L, and log $K_D$ values ranged between 4.75 and 6.14.

A useful illustration of the operational significance of all these factors on the bioavailability of silver, following the release of silver iodide into the environment over a 40 year period, is shown in the report on the Mokelumne watershed lake water and sediment survey (Stone *et al* 1995).

This report showed that, although there were detectable concentrations of silver in the lake sediments (average value 0.035 mg/kg), the silver level in the watershed averaged $6.7\times10^{-12}$ g Ag/ml which was not significantly different than the natural background silver levels measured historically in Eastern Sierra Nevada rivers and streams.

More importantly, no detectable free silver could be measured in leachates of the sediment samples at pH 5 showing that the silver in the sediments was tightly bound and not generally bioavailable to the environment.

## Acute Toxicity of Silver Ion to Aquatic Species

### *Silver Toxicity General Issues*

Reviewing the toxicity of $Ag^+$ to algae, bacteria and macroinvertebrates, Taylor (cited by Bell and Kramer, 1999) recorded silver concentrations in the nanomolar (10 µg/L) range for threshold effects. More subtle effects were found at concentrations of 10–100 ng/L.

Eggs of rainbow trout continuously exposed to silver ions at 0.17 µg/L had increased embryotoxicity and hatched prematurely. The fry also had a reduced growth rate Davies *et al* (1978).

CICAD 44 notes that aqueous concentrations of silver in the range 1-5 µg/L killed sensitive species of aquatic organisms including representative species of insects, daphnids, amphipods, trout, flounder and dace. Wood *et al* (1996) noted that 96-hr $LC_{50}$ values for freshwater fish generally lie in the range 6.5 – 65 µg/L.

In a detailed study of the mechanism of toxicity of silver ion (using silver nitrate) Grosell *et al* (2000) found a difference in tolerance to free silver ion between European eels and rainbow trout of 3.4 fold. The 96-hr $LC_{50}$'s ranged from 5 – 70 µg/L. For trout, the silver ion inhibited both sodium ion and chloride ion influx whereas for eels only the sodium ion influx was inhibited.

The key target of inhibition in trout and eels was found to be branchial $Na^+$, $K^+$-ATPase, an enzyme that drives uptake of $Na^+$ needed to counter diffusive loss of

$Na^+$ to the hypo-osmotic environment. This is similar to the findings of Webb and Wood (1998) who examined physiological responses in rainbow trout rather than toxicity. In each case the source of the silver ion was silver nitrate.

The EPA has set a guideline of 4.1 µg total Ag/L in fresh water with a hardness of 120 mg/L as the acute toxic limit. There is no chronic guideline value. The State of California has also established a maximum contaminant level of 0.1 mg/L for silver in drinking water, in secondary standards which are defined as having potential effects on the taste, odor or appearance of drinking water. California law also requires that any guideline established by the US EPA will also be followed within the state. Canadian Water Quality Guidelines specify a limit of 0.1 µg/L total silver as both the acute and chronic limits while Australia has set a total dissolved silver concentration of 0.02 mg/L.

Freshwater fish and amphibians appear to be the most sensitive vertebrates to dissolved silver. The leopard frog, *Rana pipiens*, is among the most sensitive amphibians with an $LC_{50}$ of 10 µg/L silver ion. The most sensitive fish species are even less tolerant with $LC_{50}$'s between 2.5 and 10 µg/L.

### Toxicity of Silver to Aquatic Species

Table 12, adapted from the CICAD 44 document, shows the range of aquatic species used in toxicity tests with silver ion. The toxic silver concentration for each species is also given.

**Table 12. Toxicity of Silver to Aquatic Species**

| **Organism** | **End-point** [a] | **Silver ion concentration (µg/litre)** [b] |
|---|---|---|
| **Microorganisms** | | |
| ***Marine*** | | |
| Marine bacteria (isolated from tubes of deep-sea polychaete annelids) | 10-day $EC_{50}$ (growth) | 3000 |
| Silver-resistant strains | 10-day NOEC | 20 000 – 40 000 |
| Marine algae (*Prorocentrum mariae lebouriae*) | 5-day $EC_{50}$ (growth) at 7.5% salinity | 3.3 |
| | 5-day $EC_{50}$ (growth) at 15-22.5% salinity | 6.7 |
| Marine diatom (*Skeletonema constatum*) | 5-day $EC_{50}$ (growth) at 30% salinity | 8.2 |
| | 5-day $EC_{50}$ (growth) at 7.5% salinity | 5.9 |

| **Organism** | **End-point** [a] | **Silver ion concentration (µg/litre)** [b] |
|---|---|---|
|  | 5-day $EC_{50}$ (growth) at 15% salinity | 15.4 |
|  | 5-day $EC_{50}$ (growth) at 22.5-30% salinity | 20 |
|  | 96-h $EC_{50}$ (cell numbers) | 130-170 |
| ***Freshwater*** |  |  |
| Alga (*Selenastrum capricomutum*) | 7-day NOEC | 10 000 [c] |
| Alga | $EC_{100}$ (growth) | 100 - 200 |
| (*Scenedesmus* sp.) |  |  |
| Protozoan | 24-h $LC_{50}$ at 2.8 mg $CaCO_3$/litre | 8.8 |
| (*Spirostomum ambiguum*) | 24-h $LC_{50}$ at 250 mg $CaCO_3$/litre | 15.3 |
| **Invertebrates** |  |  |
| ***Marine*** |  |  |
| Bay scallop | 96-h $LC_{50}$ | 33 |
| (*Argopecten irradians*) juvenile |  |  |
| Scallop | 115-h $LC_{50}$ | 100 |
| (*Chlamys varia*) adult |  |  |
| Pacific oyster | 209-h $LC_{50}$ | 100 |
| (*Crassostrea gigas*) adult |  |  |
| American oyster (*Crassostrea virginica*) embryo | 48-h $LC_{50}$ | 5.8 |
| American oyster juvenile | 12-day $LC_{50}$ | 25 |
| Quahog clam (*Mercenaria mercenaria*) embryo | 48-h $LC_{50}$ | 21 |
| Quahog clam juvenile | 10-day $LC_{50}$ | 32.4 |

| **Organism** | **End-point** [a] | **Silver ion concentration (µg/litre)** [b] |
|---|---|---|
| Clam (*Scrobicularia plana*) adult | 96-h LC $_{50}$ | 200 |
| | 250-h LC $_{50}$ | 100 |
| Mussel | 21-month LOEC | 1 |
| (*Mytilus edulis*) | (histopathology [d]) | |
| | | |
| Mussel | 110- h LC $_{50}$ | 100 |
| (*Mytilus galloprovincialis*) | | |
| ***Freshwater*** | | |
| Asiatic clam | 21-day NOEC (survival) | 7.8 |
| (*Corbicula fluminea*) | 21-day NOEC (growth) | 2.6 |
| | 21-day LOEC (growth) | 7.8 |
| Flatworm | 96-h LC $_{50}$ | 30 |
| (*Dugesia dorotocephala*) | 96-h LC $_{50}$ | > 1 000 000 [e] |
| | 96-h LC $_{50}$ | > 1300 [c] |
| Oligochaete (*Lumbriculus variegatus*) | 96-h LC $_{50}$ | > 1 000 000 [e] |
| Snail (*Planorbella trivolis*) | 96-h LC $_{50}$ | 300 |
| | 96-h LC $_{50}$ | > 1 000 000 [e] |
| | 96-h LC $_{50}$ | > 1300 [c] |
| Free-living nematode (*Caemorhabditis elegans*) | 96-h LC $_{50}$ | 102 (10 - 4980) |
| Copepod (*Acartia tonsa*) | 96-h LC $_{50}$ | 36 |
| Copepods (*Acartia tonsa* and *A.hudsonica*) | 48-h LC $_{50}$ | 43 |
| Amphipod | 10-day LC $_{50}$ | 20 |
| (*Ampelisca abdita*) | | |
| Scud (*Gammarus pseudolimnaeus*) | 96-h LC $_{50}$ at 44mg $CaCO_3$/litre | 4.5 (3.7-5.5) |

| **Organism** | **End-point** [a] | **Silver ion concentration (µg/litre)** [b] |
|---|---|---|
| Amphipod | 96-h $LC_{50}$ | 1.9 (1.4 – 2.3) |
| (*Hyalella azteca*) | 21-day NOEC (survival) | 0.96 |
| | 21-day LOEC (survival) | 1.9 |
| Daphnid | 48-h $EC_{50}$ | 0.9 |
| (*Daphnia magna*) | 96-h $LC_{50}$ | 5 |
| | 96-h $LC_{50}$ | 20 [f] |
| | 96-h $EC_{50}$ | > 1 000 000 [e] |
| | 96-h $LC_{50}$ | > 1330 [c] |
| | 96-h $LC_{50}$ at 38-75mg $CaCO_3$/litre | 0.4-15.0 |
| (*Daphnia magna*) | 96-h $LC_{50}$ at 255mg $CaCO_3$/litre | 45-49 |
| | 21-day $EC_{50}$ (growth) | 3.5 |
| Daphnids (*Daphnia* spp.) | 96-h $LC_{50}$ | 10 (0.25-49.0) |
| Cladocerans (*Simocephalus* sp. and *Ceriodaphnia dubia*) | 48-h $LC_{50}$ at 16mg $CaCO_3$/litre | 27 |
| Chironomid | 10-day $LC_{50}$ | 57 |
| (*Chironomus tentans*) | 10-day $LC_{50}$ | 1 170 000 – 2 750 000 [g] |
| Mayfly | 7-to 15-day $LC_{50}$ | 4.0 – 8.8 |
| (*Ephemerella grandis*) | | |
| Mayfly | 96-h $LC_{50}$ | 6.8 (5.5 – 7.8) |
| (*Isonychia bicolor*) | 14-day NOEC (moult) | 0.3 |
| | 14-day LOEC (moult) | 1.6 |
| Mayfly (*Stenonema* sp.) | 96-h $LC_{50}$ | 3.9 (2.5-5.7) |
| Stonefly (*Leuctra* sp.) | 96-h $LC_{50}$ | 2.5 (1.7-3.2) |
| **Fish** | | |
| ***Marine*** | | |

| **Organism** | **End-point** [a] | **Silver ion concentration ($\mu$g/litre)** [b] |
|---|---|---|
| Rainbow trout (*Oncorhynchus mykiss*) | 96-h NOEC at 15-20% salinity; seawater acclimatized | 401 |
| | 96-h $LC_{50}$ at 25% salinity; seawater acclimatized | 401 |
| Tidepool sculpin (*Oligocottus maculosus*) | 96-h $LC_{50}$ | 331 (25% salinity) |
| | 168-h $LC_{50}$ | 119 (25% salinity) |
| | 96-h $LC_{50}$ | 664 (32% salinity) |
| | 168-h $LC_{50}$ | 472 (32% salinity) |
| Sheepshead minnow (*Cyprinodon variegatus*) juvenile | 96-h $LC_{50}$ | 1400 |
| ***Freshwater*** | | |
| Mottled sculpin | 96-h $LC_{50}$ at 30mg $CaCO_3$/litre | 5.3 |
| (*Cottus bairdi*) | 96-h $LC_{50}$ at 250mg $CaCO_3$/litre | 14 |
| Mosquitofish (*Gambusia affinis*) juvenile | 96-h $LC_{50}$ | 23.5 (17.2-27.0) |
| Flagfish<br>(*Jordanella floridae*) | 96-h $LC_{50}$ at 44mg $CaCO_3$/litre | 9.2 (8.0-10.7) |
| Bluegill<br>(*Lepomis macrochirus*) | 96-h $LC_{50}$ | 31.7 (24.2-48.4) |
| Atlantic silverside (*Medinia medinia*) larvae | 96-h $LC_{50}$ | 110 |
| Atlantic silverside juvenile | 96-h $LC_{50}$ | 400 |
| Coho salmon (*Oncorhynchus kisutch*) alevin | 96-h $LC_{50}$ | 11.1 (7.9-15.7) |
| Coho salmon juvenile | 96-h $LC_{50}$ | 12.5 (10.7-14.6) |
| Rainbow trout (*Oncorhynchus mykiss*) eyed embryo to adult | 70-day LOEC (survival) | 1.2 |

| **Organism** | **End-point** [a] | **Silver ion concentration (µg/litre)** [b] |
|---|---|---|
| | at 20-31mg $CaCO_3$/litre | |
| | 18-month LOEC (survival) | 0.17 |
| | at 20-31mg $CaCO_3$/litre | |
| | | |
| Rainbow trout juvenile | 144-h $LC_{50}$ | 4.8 |
| | 96-h $LC_{50}$ at 20-31mg $CaCO_3$/litre | 5.3-8.1 |
| | 96-h $LC_{50}$ | 7.6-10.9 |
| | 96-h $LC_{50}$ | 11.8 |
| | 96-h $LC_{50}$ | 161 000 [c] |
| | 168-h $LC_{50}$ | 9.1 |
| | 168-h $LC_{50}$ | 137 000 [c] |
| | 168-h $LC_{50}$ | > 100 000 [h] |
| | 96-h $LC_{50}$ at 350mg $CaCO_3$/litre | 13 |
| Rainbow trout adult | 96-h $LC_{50}$ in soft, low chloride (10µmol/litre) water | 10.2 |
| Rainbow trout alevin | 96-h $LC_{50}$ | 16.1 (12.8-20.2) |
| Rainbow trout juvenile | 96-h $LC_{50}$ | |
| | 28-day $LC_{50}$ at 93-105mg $CaCO_3$/litre | 10 |
| | 96-h $LC_{50}$ | 9.2 |
| Rainbow trout embryo/larva | 60-day LOEC (growth) | 0.1 |
| | 60-day LOEC (survival) | 0.5 |
| Rainbow trout embryo | 32-day LOEC (survival) | 13.5 |
| | at 120mg $CaCO_3$/litre | |
| | | |
| Summer flounder (*Paralichthys dentatus*) larvae | 96-h $LC_{50}$ | 4.7 |
| Summer flounder embryos | 96-h $LC_{50}$ | 8.0-48.0 |

| **Organism** | **End-point** [a] | **Silver ion concentration ($\mu$g/litre)** [b] |
|---|---|---|
| Fathead minnow (*Pimephales promelas*) | 96-h $LC_{50}$ at 25-75mg $CaCO_3$/litre | 5.3-20.0 |
| | 96-h $LC_{50}$; flow-though tests | 5.6-7.4 |
| | 96-h $LC_{50}$; static tests | 9.4-9.7 |
| | 96-h $LC_{50}$ at 44mg $CaCO_3$/litre | 10.7 (10.6-10.8) |
| | 96-h $LC_{50}$ at 255mg $CaCO_3$/litre | 110-270 |
| | 96-h $LC_{50}$ | 16 (12-20) |
| | 96-h $LC_{50}$ | > 280 000 [c] |
| | 96-h $LC_{50}$ | > 240 000 [g] |
| Winter flounder (*Pleuronectes americanus*) embryo | 96-h $LC_{50}$ | 200-450 |
| Speckled dace (*Rhinichthys osculus*) | 96-h $LC_{50}$ in soft water | 4.9 |
| | 96-h $LC_{50}$ in hard water | 14 |
| Arctic grayling (*Thymallus arcticus*) alevin | 96-h $LC_{50}$ | 6.7 (5.5-8.0) |
| Arctic grayling juvenile | 96-h $LC_{50}$ | 11.1 (9.2-13.4) |
| European eel | 96-h $LC_{50}$ in soft, low chloride (10$\mu$mol/litre) water | 34.4 |
| (*Anguilla anguilla*) | | |
| **Amphibians** | | |
| Leopard frog | $EC_{10}$ based on mortality or abnormal development of embryos and larvae | 0.7-0.8 |
| (Rana pipiens) | $EC_{50}$ based on mortality or gross terata of embryos and larvae | 10 |

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a $EC_{50}$ = median effective concentration; $EC_{100}$ = effective concentration for 100% of the population; $LC_{50}$ = median lethal concentration; NOEC = no-observed-effect concentration; LOEC = lowest-observed-effect concentration; $CaCO_3$ = calcium carbonate.

b Tests performed using silver nitrate, unless stated otherwise.

c Silver thiosulfatet

d Accumulations of yellowish-brown to black particulates in the basement membrane and connective tissue of the body organs; black particulate-laden macrophages were noted throughout the connective tissue and accumulated in large groups in the intertubular connective tissue of the digestive diverticula and the kidneys.
e silver sulfide.
f silver sulfate.
g sediments supplemented with silver nitrate, in µg silver/kg dry weight sediment.
h silver chloride.

### *Chronic Toxicity of Silver Ion*

In their paper detailing a study on the physiology of silver ion toxicity to freshwater rainbow trout, Wood *et al* (1996) note that during chronic exposure to 0.5 µg/L $Ag^+$ (as silver nitrate) the principal sub-lethal effect was a small depression of plasma $Na^+$ and $Cl^-$.

Diamond and co-workers (1990) carried out a series of chronic silver toxicity tests using a range of representative aquatic species including six invertebrates and three fish species. Their results suggested that some of the invertebrates were more sensitive than the fish species tested. As a general statement they concluded that for water of moderate hardness a chronic value could be obtained by multiplying the acute value by 0.5. Chronic tests are significantly influenced by the binding of silver ion to the food used during the test period.

Guadagnolo *et al* (2001) showed that silver concentrations in different compartments of rainbow trout eggs were greatest just before hatch. However, they noted that the silver burden was not correlated with mortality.

### *Uptake of Silver by Terrestrial Plants*

Accumulation of silver by terrestrial plants is low even when the plants are grown on silver amended sewage sludge or mine spoil (Hirsch, 1998). Where uptake occurs, the silver is found mainly in the root systems (Ratte, 1999). As a general rule most of the toxicity testing on plants, reported in the recent literature, involved the use of appropriate concentrations of silver nitrate giving ($Ag^+$) concentrations in the mg/L (ppm) range.

In sensitive plant species, growth and germination were reported to be affected at a concentration of 7.5 mg/kg with germination the most sensitive stage. As expected, soluble silver salts were markedly more toxic than insoluble silver salts.

Silver uptake by seedlings of perennial ryegrass (*Lolium perenne L.*) and white clover (*Trifolium repens L.*) was studied in detail by Ward *et al* (1979). They found that some 90% of the silver was immobilised in the root systems of both species.

Uptake was rapid and essentially complete after 10 days. While the silver concentrations in the roots of both species approached that of the added silver, the aerial parts of the plants were much lower, and seldom exceeded 10% of that in the roots.

The silver concentrations used in this study ranged from 0 – 1000 mg/L (ppm) which are significantly higher than those observed in the Mokelumne watershed.

More importantly, they concluded that there would be little danger to stock grazing on pastures with these high levels of plant silver.

In some much earlier work Freeman (1979), looked at silver levels in algae and emergent aquatic plants in an alpine lake in Colorado and found concentrations of the order of 0 – 2.6 mg/kg in several species. However, this work was conducted well before the introduction of ultra-trace chemical techniques and no detail was given of the analytical procedures followed.

Hirsch (1998) has looked at the germination of a range of crop plants grown on soils amended with silver-laden sludge derived from photographic industry waste. It was found that germination or emergence in all crop species studied was not adversely affected. And further, for silver levels up to 106 mg Ag/kg in the sludge, the growth and yield of corn and oats was not different from the controls.

Hirsch (1998) also reported that yields of plant species such as lettuce, cabbage and spinach were affected at amended soil levels greater than 14 mg Ag/kg. With the exception of lettuce, there was no difference in silver concentrations in the tissues of the treated crops compared with the controls. Hirsch's conclusion was that land application of silver rich sludge would not adversely affect plant growth.

Sensitive aquatic plants were found to grow poorly at 3.3 – 8.2 µg Ag/L and died at concentrations greater than 130 µg Ag/L (CICAD 44).

There is no published research which has looked specifically at the impact of silver ions on alpine plant species. There is nothing in the existing research into the toxic effects of silver ions on terrestrial plant species to suggest that alpine species would behave in a different way from the species that have been studied.

### *Bioaccumulation of Silver in Organisms*

Bioaccumulation of substances occurs via body surfaces (often referred to as bioconcentration) and through intake of food (often referred to as biomagnification). Bioconcentration factors (BCF's) are given by the ratio of the concentration of the compound in the organism with that of the surrounding medium, usually water (also food). For terrestrial plants, uptake is generally through the roots and leaves. For terrestrial animals uptake occurs via the surface or the gastro-intestinal tract (GIT).

For aquatic vertebrates uptake is possible via the body surface or the GIT, or in the case of fish, via the gills. Uptake from water can be due to passive diffusion, active transport and adsorption. There is no significant evidence of substantial silver uptake via food for aquatic organisms.

It is clear that BCF's appear to be correlated with the silver compound's solubility.

Some silver bioconcentration factors and the species studied are shown in Table 14, adapted from Ratte (1999).

**Table 13. Silver Bioconcentration Factors for Selected Organisms**

| Organisms | **Quantity [a]** | **Parameter [b]** | **Ag compound** | **Type [c] of experiment** |
|---|---|---|---|---|
| **Algae** | | | | |
| Selenastrum capricornutum | 3 | C | $AgNO_3$ | L |
| | 4.8 | BCF | 1 µg/L Ag | |
| Green algae | 150 | BCF | $NaAgS_2O_3$ | L |
| Scenedesmus obliquus | 1.8-25x$10^5$ DW | BCF | $^{110}AgCN$ | L |
| | (= 3-42x$10^4$ WW) | | | |
| *Periphyton* | 0.1-3.6 | C | Ag, river | F |
| *Several species* | 50 | BCF, cells/ sediments | | |
| Scenedesmus obliquus | 6,818 WW | BCF | $NaAgS_2O_3$ | LM |
| | 750 mg/kg WW | C | | |
| | | | | |
| ***Microphytes*** | | | | |
| Lemma gibba | 135.3 | C | $AgNO_3$ | |
| *Duckweed* | 1.5 | BCF | 6 µg/L Ag | |
| | 25.4 | BCF | 118.5 µg/L Ag | L |
| | | | | |
| ***Crustaceans*** | | | | |
| Daphnia magna | 61 | BCF | $AgNO_3$ | L |
| | | | 0.5 µg/L Ag | |
| | 9 | BCF | $NaAgS_2O_3$ | L |
| | > 2,200 | BCF | $NaAgS_2O_3$ | LM |
| | 130 | C | | |

| | | | | |
|---|---|---|---|---|
| Gammarus pulex | 1,100 | BCF, water | $^{110}AgCN$ | LM |
| | 1.9 | BCF, sediment | | |
| | | | | |
| ***Insects*** | | | | |
| Chironomus luridus | 1,100 | BCF, water | $^{110}AgCN$ | LM |
| | 0.67 | BCF, sediment | | |
| Chironomus *sp.* | 0.5 | BCF | $NaAgS_2O_3$ | FM |
| Hydophilidae *sp.* | 0.08 | BCF | $NaAgS_2O_3$ | FM |
| Notonecta *sp.* | 0.08 | BCF | $NaAgS_2O_3$ | FM |
| | | | | |
| ***Oligochaetes*** | | | | |
| Lumbriculus variegatus | 0.18 | BCF | $Ag_2S$ | L |
| | 80.3 | C | 444 mg Ag/kg | L |
| | | | | |
| ***Molluscs*** | | | | |
| Ligumia *sp.* | 8.5 | BCF | $NaAgS_2O_3$ | LM |
| | 1,400 WW | BCF | $NaAgS_2O_3$ | LM |
| Margaritifera *sp.* | 110 WW | C | | |
| Organisms | **Quantity [a]** | **Parameter [b]** | **Ag compound** | **Type [c] of experiment** |
| ***Amphibians*** | | | | |
| Bufo *sp.* | 0.5 | BCF | $NaAgS_2O_3$ | FM |
| | | | | |
| ***Fish*** | | | | |
| Lepomis macrochirus | Below DL | C | $NaAgS_2O_3$ | L |
| | | | 05 µg Ag/L | L |

| | | | | |
|---|---|---|---|---|
| Oncorhynchus mykiss | 335 | BCF | $NaAgS_2O_3$ | L |
| *(168-h static bioassay)* | | | | |
| Campostomum anomalum | 1.32-2.73 | C | Ag | F |
| Lepomis microlophus | | | | |
| *Contaminated site* | 0.458 | C | Ag | F |
| *Noncontaminated site* | 0.001 | | | |
| Cyprinus carpio | 106 | BCF, water | $^{110}AgCN$ | LM |
| | 1,100 | BCF, sediment | | |
| Pimephales promelas | 1.8 | BCF | $NaAgS_2O_3$ | FM |
| | 303 WW | BCF | $NaAgS_2O_3$ | LM |
| | 32 WW | C | | |

a DL = detection limit; DW = relation to dry weight; WW = relation to wet weight.
b BCF = bioconcentration factor; C = silver concentration (mg/kg).
c F = field measurement; L = laboratory experiment; LM = indoor microcosm.

The US EPA (1980) has reported BCF's of 210 in diatoms, 240 in brown algae, 330 in mussels, 2300 in scallops and 18700 in oysters. In contrast, bluegills showed no significant accumulation when exposed to 0.5 μg/L silver (Coleman and Cearley, 1974).

Concern over the possible accumulation of silver in both marine and freshwater environments has arisen because of bioaccumulation observed in benthic organisms (Bell and Kramer, 1999).

Silver is a soft or "b"-class metal and would be expected to coordinate and complex strongly with soft bases which, in this context, are organic molecules containing sulfur (S) or nitrogen (N) atoms. Silver exhibits a great affinity for sulfur-containing ligands (organic compounds).

This is reflected in the higher stability constants (K) between silver ion ($Ag^+$) and organosulfur complexes such as thiols, $K \sim 10^{13}$ compared to those of $Ag^+$ carboxylate complexes (monodicarboxylic acids, $K \sim 10^2 - 10^4$ and polycarboxylates such as EDTA, $K \sim 10^7$.

In biological systems thiolate complexes include mercaptans, glutathione and cysteine and for many of these complexes stability constants are available (Bell and Kramer, 1999). Higher stability constants indicate strong binding between silver and the complexing agent which decreases bioavailability.

Fisher and Wang, (1998) in their review of trophic transfer of silver note that trophic transfer has been shown to be insignificant in several aquatic animals, for example particularly oysters and shrimp. Oysters were able to accumulate dissolved silver but did not acquire silver from various phytoplankton species. Shrimp could accumulate dissolved silver but did not acquire silver from planktonic or detrital food.

Uptake from marine sediments was reported by Bryan and Langston (1992), leading to the view that sediments are an important source of silver. However, in a reported laboratory exposure experiment over some 20 days, net uptake of silver only occurred when the concentration of silver in the sediment exceeded 1 mg/kg.

Connell *et al* (1991) found that incorporated silver was tightly bound to the cell membrane and was not released by mechanical disruption.

They also observed that food-chain biomagnification was unlikely at concentrations normally found in the environment.

Given the extremely low silver levels observed in the Mokelumne watershed, it is unlikely that bioaccumulation of silver through food chains will be a concern.

Further support for this conclusion can be drawn from a consideration of the food chains briefly described below, see also Table 14.

### *Algae, Pelagic and Benthic Food Chains*

The accumulation of dissolved silver into algae is very high. Uptake into algal cells would be expected to influence biogeochemical cycling if the algae are subsequently consumed by animals. Algae show high bioconcentration factors (BCF's), although differences in experimental conditions can significantly influence the value.

In the pelagic food chain, typically including protozoans, rotifers and small crustaceans, significant bioaccumulation is not likely. For example, bioconcentration was markedly lower in daphnids than in algae.

The benthic food chain, typically including snails, some insect larvae, bivalves and worms, feed on algae on the bottom of the water body. For gammarids such as midge larvae and chironomids, the BCF exceeded the BCF found for daphnids. In contrast, bivalves showed BCF's that corresponded to the daphnids' BCF.

### *Bioaccumulation by Fish*

Bioaccumulation of silver in fish will be subject of a more detailed treatment in another section. However the following general findings are worth noting here.

Pelagic carnivores such as fathead minnows showed low bioaccumulation potential compared with their prey. Other studies involving fish have shown that concentration of metals was dependent on its contact with sediment or contact with the sediment by its prey, rather than trophic position within the food chain (Ratte, 1999).

The toxicity of rainbow trout to dissolved silver has been the subject of many studies into the toxicity of silver ion. These studies have generally used the highly soluble silver nitrate and have largely focused on laboratory conditions although some researchers have considered the effect of water parameters such as hardness and DOC (Hogstrand and Wood, 1998; Erickson *et al,* 1998; and Rodgers *et al* 1997).

Where bioavailability, due to the presence of these ameliorating factors has been considered, toxicity was shown to be reduced. Given the low silver ion bioavailability expected due to action of the factors considered above, and given the low levels of silver iodide used in the PG&E Mokelumne cloud seeding program, significant bioaccumulation of silver in fish is very unlikely.

### *Terrestrial Animals*

While the bioaccumulation of silver on terrestrial animals is considered more fully elsewhere in the report, some studies are worth noting at this point.

Studies into the effects of silver ions on terrestrial species are limited.

Exposure of earthworms to increasing concentrations of $Ag_2S$ in artificial soil did not lead to an accumulation of silver, but there was evidence of reduced growth. The No Observed Effect Concentration (NOEC) was given as 62 mgAg/kg) (Hirsch,1997).

Silver has also been found in fur seals and sea lions in the North Pacific Ocean (Saeki *et al,* 2001). Some 70 of the body burden was found in the liver with the remaining silver associated with body hair and other organs. Their data suggested that bioaccumulation increased with age.

Given the extremely low levels of bioavailable silver from the PG&E Mokelumne cloud seeding program, toxic effects and bioaccumulation for terrestrial species are considered unlikely.

## Summary Conclusions

The expected environmental impact of each of these compounds can be summarized as being insignificant for the reasons set out below:

- although silver ions from soluble silver salts have been shown to be toxic to aquatic species, this is not the case for insoluble silver iodide or silver chloroiodide;
- since water solubility generally controls bioavailability, silver compounds that are insoluble or not readily soluble are of less environmental concern;
- silver toxicity studies have been attempted using the insoluble silver salts, however researchers have had to resort to indirect methods to achieve the desired concentration of the silver ion;
- the majority of studies investigating acute and chronic effects of silver ion have used soluble silver nitrate;
- the studies that have used silver iodide have relied on sodium iodide as a complexing agent which allows part per billion and higher concentrations of silver iodide to be tested. These studies have clearly shown that the iodide ion released by the sodium iodide complexing agent and present orders of magnitude higher levels than measured in the Mokelumne and other Sierra Nevada watersheds can be toxic to fish, fry and fish eggs as demonstrated by the mortality rate in control tanks containing only sodium iodide;
- the studies that have only used silver iodide have failed to prove that it is toxic to fish;
- a number of studies have shown that the toxicity of silver ion in water is significantly ameliorated by the presence in water of chloride ion, carbonate ion, sulphide ion and dissolved organic carbon. In addition, silver is strongly adsorbed onto particulate matter in water or clay soil types. Findings from recent studies point to the fact that silver ion concentrations in natural waters are negligibly small and virtually undetectable.
- Studies conducted in the Mokelumne Watershed have shown that silver concentrations exist at trace levels in lakes naturally and no evidence has been obtained to suggest that seeding activities will contribute to the detectable bioavailable silver burden, principally due to the limiting factors discussed above.

### Appendix B – Silver Iodide Material Safety Data Sheet

# Material Safety Data Sheet

## Silver iodide MSDS

## Section 1: Chemical Product and Company Identification

**Product Name:** Silver iodide
**CAS#:** 7783-96-2
**Chemical Formula:** AgI

## Section 2: Composition and Information on Ingredients

**Composition:**
**Name CAS # % by Weight**
Silver iodide 7783-96-2 100
**Toxicological Data on Ingredients:** Silver iodide: ORAL (LD50): Acute: 2820 mg/kg [Rat].

## Section 3: Hazards Identification

**Potential Acute Health Effects:** Hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation.
**Potential Chronic Health Effects:**
CARCINOGENIC EFFECTS: Not available.
MUTAGENIC EFFECTS: Not available.
TERATOGENIC EFFECTS: Not available.
DEVELOPMENTAL TOXICITY: Not available.
Repeated or prolonged exposure is not known to aggravate medical condition.

## Section 4: First Aid Measures

**Eye Contact:** Check for and remove any contact lenses. Do not use an eye ointment. Seek medical attention.
**Skin Contact:**
**Dispersion Properties:** Not available.
**Solubility:** Insoluble in cold water, hot water.
After contact with skin, wash immediately with plenty of water. Gently and thoroughly wash the contaminated skin with running water and non-abrasive soap. Be particularly careful to clean folds, crevices, creases and groin. Cover the irritated skin with an emollient. If irritation persists, seek medical attention.
**Serious Skin Contact:**
Wash with a disinfectant soap and cover the contaminated skin with an anti-bacterial cream. Seek medical attention.
**Inhalation:** Allow the victim to rest in a well ventilated area. Seek immediate medical attention.
**Serious Inhalation:** Not available.
**Ingestion:**
Do not induce vomiting. Loosen tight clothing such as a collar, tie, belt or waistband. If the victim is not breathing, perform mouth-to-mouth resuscitation. Seek immediate medical attention.
**Serious Ingestion:** Not available.

## Section 5: Fire and Explosion Data

**Flammability of the Product:** Non-flammable.
**Auto-Ignition Temperature:** Not applicable.
**Flash Points:** Not applicable.
**Flammable Limits:** Not applicable.
**Products of Combustion:** Not available.
**Fire Hazards in Presence of Various Substances:** Not applicable.
**Explosion Hazards in Presence of Various Substances:**
Risks of explosion of the product in presence of mechanical impact: Not available.

Risks of explosion of the product in presence of static discharge: Not available.
**Fire Fighting Media and Instructions:** Not applicable.
**Special Remarks on Fire Hazards:** Not available.
**Special Remarks on Explosion Hazards:** Not available.

## Section 6: Accidental Release Measures

**Small Spill:**
Use appropriate tools to put the spilled solid in a convenient waste disposal container. Finish cleaning by spreading water on the contaminated surface and dispose of according to local and regional authority requirements.
**Large Spill:**
Use a shovel to put the material into a convenient waste disposal container. Finish cleaning by spreading water on the contaminated surface and allow to evacuate through the sanitary system. Be careful that the product is not present at a concentration level above TLV. Check TLV on the MSDS and with local authorities.

## Section 7: Handling and Storage

**Precautions:**
Do not ingest. Do not breathe dust. Wear suitable protective clothing In case of insufficient ventilation, wear suitable respiratory equipment If ingested, seek medical advice immediately and show the container or the label. Avoid contact with skin and eyes
**Storage:**
No specific storage is required. Use shelves or cabinets sturdy enough to bear the weight of the chemicals. Be sure that it is not necessary to strain to reach materials, and that shelves are not overloaded.

## Section 8: Exposure Controls/Personal Protection

**Engineering Controls:**
Use process enclosures, local exhaust ventilation, or other engineering controls to keep airborne levels below recommended exposure limits. If user operations generate dust, fume or mist, use ventilation to keep exposure to airborne contaminants below the exposure limit.
**Personal Protection:**
Splash goggles. Lab coat. Dust respirator. Be sure to use an approved/certified respirator or equivalent. Gloves.
**Personal Protection in Case of a Large Spill:**
Splash goggles. Full suit. Dust respirator. Boots. Gloves. A self contained breathing apparatus should be used to avoid inhalation of the product. Suggested protective clothing might not be sufficient; consult a specialist BEFORE handling this product.
**Exposure Limits:**
TWA: 0.01 (mg/m3) from ACGIH
Consult local authorities for acceptable exposure limits.

## Section 9: Physical and Chemical Properties

**Physical state and appearance:** Solid.
**Odor:** Not available.
**Taste:** Not available.
**Molecular Weight:** 234.79 g/mole
**Color:** Not available.
**pH (1% soln/water):** Not applicable.
**Boiling Point:** 1506°C (2742.8°F)
**Melting Point:** 552°C (1025.6°F)
**Critical Temperature:** Not available.
**Specific Gravity:** 5.675 (Water = 1)
**Vapor Pressure:** Not applicable.

**Vapor Density:** Not available.
**Volatility:** Not available.
**Odor Threshold:** Not available.
**Water/Oil Dist. Coeff.:** Not available.
**Ionicity (in Water):** Not available.

## Section 10: Stability and Reactivity Data

**Stability:** The product is stable.
**Instability Temperature:** Not available.
**Conditions of Instability:** Not available.
**Incompatibility with various substances:** Not available.
**Corrosivity:** Non-corrosive in presence of glass.
**Special Remarks on Reactivity:** Not available.
**Special Remarks on Corrosivity:** Not available.
**Polymerization:** No.

## Section 11: Toxicological Information

**Routes of Entry:** Eye contact. Inhalation. Ingestion.
**Toxicity to Animals:** Acute oral toxicity (LD50): 2820 mg/kg [Rat].
**Chronic Effects on Humans:** Not available.
**Other Toxic Effects on Humans:** Hazardous in case of skin contact (irritant), of ingestion, of inhalation.
**Special Remarks on Toxicity to Animals:** Not available.
**Special Remarks on Chronic Effects on Humans:** Not available.
**Special Remarks on other Toxic Effects on Humans:** Not available.

## Section 12: Ecological Information

**Ecotoxicity:** Not available.
**BOD5 and COD:** Not available.
**Products of Biodegradation:**
Possibly hazardous short term degradation products are not likely. However, long term degradation products may arise.
**Toxicity of the Products of Biodegradation:** The products of degradation are more toxic.
**Special Remarks on the Products of Biodegradation:** Not available.

## Section 13: Disposal Considerations

**Waste Disposal:**

## Section 14: Transport Information

**DOT Classification:** Not a DOT controlled material (United States).
**Identification:** Not applicable.
**Special Provisions for Transport:** Not applicable.

## Section 15: Other Regulatory Information

**Federal and State Regulations:**
Pennsylvania RTK: Silver iodide
Massachusetts RTK: Silver iodide
TSCA 8(b) inventory: Silver iodide
CERCLA: Hazardous substances.: Silver iodide
**Other Regulations:** Not available..
**Other Classifications:**
**WHMIS (Canada):** Not controlled under WHMIS (Canada).
**DSCL (EEC):** R36/38- Irritating to eyes and skin.

**HMIS (U.S.A.):**
**Health Hazard:** 2
**Fire Hazard:** 0
**Reactivity:** 0
**Personal Protection:** E
**National Fire Protection Association (U.S.A.):**
**Health:** 2
**Flammability:** 0
**Reactivity:** 0
**Specific hazard:**
**Protective Equipment:**
Gloves.
Lab coat.
Dust respirator. Be sure to use an approved/certified respirator or equivalent.
Splash goggles.

## Section 16: Other Information

**References:** Not available.
**Other Special Considerations:** Not available.

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