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Shaping the Future

Geochemistry and Impacts of Silver Iodide Use in Cloud Seeding

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1 Introduction

Silver iodide and the closely-related silver chloroiodide ($\text{AgI}_{0.8}\text{Cl}_{0.2}$) is one of the most common nucleating materials used in cloud seeding, including projects in the Sierra Nevada range in California. The crystalline structure of silver iodide closely resembles that of ice, and as such it makes a very effective surrogate for ice as nucleating agents in the cloud. The first layer of water molecules to be laid down on a silver iodide particle substrate fits very closely, so the surface energy in the interface is small (Dennis, 1980).

Another reason that silver iodide is so commonly used for cloud seeding is that it is practically insoluble in water. That is, it stays in the solid form rather than dissolving in water. This characteristic is essential to the success of cloud seeding, because if the nucleating agent were to dissolve in water it would no longer be useful as a nucleation site for precipitation. In addition, by remaining in a solid form, the introduced silver iodide does not become biologically available in the environment, and as such does not have an adverse effect to human health and the environment.

Several multiyear studies have been conducted on cloud seeding, including the geochemistry and toxicity of silver iodide, as follows:

- Project Skywater (Howell, 1977), a program of research of weather modification by cloud seeding sponsored by the US Bureau of Reclamation.
- Critical Issues in Weather Modification Research (NAS, 2003), a study by the Academy to evaluate the effectiveness of current cloud seeding efforts.
- California Energy Commission Public Interest Energy Research Program (Hunter, 2007), presents the results of evaluating the state of the art in cloud seeding, and directions for further research.
- Mokelumne Lake and Sediment Study (Stone, 2006), a comprehensive monitoring effort using high-precision analytical techniques to evaluate the effects of cloud seeding using silver iodide on surface waters and sediments.

These studies are unanimous in their conclusion that silver iodide used in cloud seeding is practically insoluble, does not tend to dissociate to its component ions of silver and iodine, and is not bioavailable in the aquatic environment but instead remains in soils and sediments. These studies are the basis for the Department of Water Resources recommending weather modification by cloud seeding in its 2009 California Water Plan Update (DWR, 2009). This section summarizes the information available in the literature on this topic, including toxicity of elemental silver in the environment.

2 Properties of Silver Iodide

This section discusses the most important properties of silver iodide, including:

- Silver speciation, or the different elemental and molecular forms of silver in the environment;
- Silver iodide solubility, or its ability to dissolve in water;

- Silver iodide dissociation, or its ability to break down into its component elements silver and iodine;
- Silver iodide adsorptivity, or its ability to bind to soil and other particles.

2.1 Silver Speciation

Silver is relatively rare in the earth's crust, with an abundance of approximately 0.07 mg/kg. It is found in igneous rocks at concentrations ranging from 0.07 to 0.1 mg/kg (Eisler, 1996). It is concentrated in ore-forming processes, most commonly hydrothermal systems surrounding cooling plutons (subsurface magma bodies), and it is these deposits that are mined for human use. Silver can be found in its elemental state, and as silver sulfide, silver arsenide, silver chloride, silver nitrate, and silver iodide. Each of these is known as a silver species, and the different forms of silver found in the environment are known as silver speciation.

Elemental silver can be found in oxidation states of Ag^0 , Ag^{+1} , Ag^{+2} , and Ag^{+3} , but only the Ag^0 state (solid silver) and the Ag^{+1} state (free silver ion in water) occur in ambient environmental conditions. In water, silver can exist as simply free silver ion, or in various degrees of association with negative ions such as sulfate, bicarbonate, nitrate, iodide, and chloride. The properties of each silver species are very different. The free silver ion in water (Ag^+) is fungicidal, algicidal, and bactericidal at concentrations ranging from 10 – 1,000 $\mu\text{g/L}$. Ionic silver has also been used in medical applications for sterilizing potable water. In contrast, silver iodide, silver sulfide, and silver chloride are practically insoluble. Ratte (1999) has shown that insoluble or complexed silver (that is, not the free silver ion) are virtually non-toxic to terrestrial and aquatic vertebrates. For example, silver thiosulfate was found to be 15,000 times and silver chloride 11,000 times less toxic than the highly soluble silver nitrate (Ratte, 1999). Particulate silver chloride is described by Bury et al. (1999) and Rodgers et al. (1997) as virtually non-toxic.

In addition to forming different silver species which reduce silver's toxicity, the free silver ion (Ag^+) bonds, or forms complexes with, organic matter in water. Therefore, the toxicity of free silver ion can also be reduced by bonding with these particulates.

Most studies of silver in the environment have measured total silver, not the concentrations of the individual silver species. Since the free silver ion is the toxic form of silver, these studies overestimate the actual toxicity of the measured silver concentration. It is important to note that in discussions of toxicity, concentrations of silver iodide are compared to standards for elemental silver. This comparison is not meant to imply that elemental silver and silver iodide are equivalent, because they are not. Rather, the comparison is made to demonstrate that, **even if** one were to make the assumption that all silver iodide dissociates to silver and iodine (which in fact it does not), the concentrations of silver affected by cloud seeding are **still** less than any human health, aquatic life, or terrestrial life standards.

2.2 Solubility of Silver Iodide

Solubility is the measure of a compound’s ability to dissolve in water. Solubility is measured by the solubility product, or K_{sp} . The reaction is expressed as:



The solubility product for this reaction is K_{sp} value = 8.5×10^{-17} , which indicates that the reaction goes strongly to the solid form, AgI. The maximum concentration of free silver ion in contact with solid silver iodide at 25 ° C (standard conditions) is 9.84×10^{-7} g/L, or 9.84×10^{-4} mg/L (parts per million), or 0.984 µg/L (parts per billion) (Stone, 2006). This value of 0.984 µg/L, the maximum concentration of free silver ion that can be found in water that comes in contact with silver iodide particles from cloud seeding, is less than any toxicity standards or guidelines for silver, as described below in Section 3. Furthermore, any water that comes in contact with silver iodide particles will be greatly diluted by water or snow that did not come in contact with the particles. Accordingly the maximum amount of free silver ion that can be derived from contact with silver iodide particles in the natural environment is far less than this maximum possible value derived from the solubility.

2.3 Dissociation of Silver Iodide

Dissociation of a compound is a breaking down into its component parts. For silver iodide, dissociation produces silver (Ag^+) and iodine (I^-) ions in water. These ions will tend to bond and form the silver iodide solid, as described above in the discussion of solubility.

The solubility production of AgI, $K_{sp}=8.3 \times 10^{-17}$, is directly proportional to the dissociation constant, K_D . In a mixture of pure water and silver iodide solid, only a small amount of the silver iodide will dissociate and dissolve, producing a maximum possible concentration of 0.984 µg/L (see solubility discussion above). Table 1 lists the solubility for some common silver salts, including silver iodide (from Stone, 2006).

Table 1 Solubility of Selected Silver Salts

Silver Salts	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 ₂ S	Insoluble	Insoluble

Source: Stone, 2006

In a system with other ions that also bond to silver, such as sulfide ion, chloride ion, or dissolved organic carbon, dissociation of silver iodide can lead to new compounds, such as silver sulfide or silver chloride, forming in addition to silver iodide. The sulfide, chloride, and iodide in the system will preferentially form complexes with silver before silver ion (Ag^+) can remain stable.

Therefore, dissociation of silver iodide and other silver species in water will lead to a new equilibrium distribution of silver species. However, these species tend to be insoluble so that very little free silver ion remains available. In fact, only a high proportion of the very soluble (and dissociative) silver nitrate will produce appreciable amounts of the toxic free silver ion (Table 1).

2.4 Adsorptivity of Silver Iodide

Silver has been shown to strongly adsorb onto particulate matter in water. Some silver complexes and silver ions are readily adsorbed to particulate matter to the extent that only some 25 percent of total silver is estimated to be dissolved as either ion colloid or complexes (Wen et al., 1997, Stone, 2006). Silver also adsorbs to manganese dioxide, ferric compounds, and clay minerals (Stone, 2006).

Therefore, almost all of the silver iodide that is introduced by cloud seeding will remain in the solid form. First, silver iodide has a very low solubility and does not readily dissociate, so most of the silver introduced as silver iodide will stay as a solid silver iodide. The small amounts of free silver ion that may be produced, though less than any health or ecological standards, will in part adsorb to other solids. The solid silver iodide primarily remains as a solid, and resides in soil and sediments.

3 Measurements of Silver Iodide in the Environment

The Concise International Chemical Assessment Document 44 (CICAD 44) (WHO, 2002), has presented data from 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 industrialized areas the levels were typically 0.01-0.1 µg/L. Stone (2006) also uses these techniques, and notes the importance of sample contamination by dirty hands. CICAD 44 notes 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. In the following, the data is presented as reported in the literature, but the improvement in sampling and analytical methods that has occurred since the 1990's has led to a better understanding of the occurrence of silver and silver species at the very low concentrations typical of environmental conditions outside silver mining districts, areas for the manufacture of photographic materials, and other areas of unusual concentration of silver.

Figure 1, taken from the comprehensive study of the effects of cloud seeding by silver iodide sponsored by the US Bureau of Reclamation (Howell, 1977), illustrates the various compartments in the environment where silver species can be found, and their approximate concentrations. The diagram also illustrates the exchange between compartments. The following discussion of the figure is taken from Howell (1977).

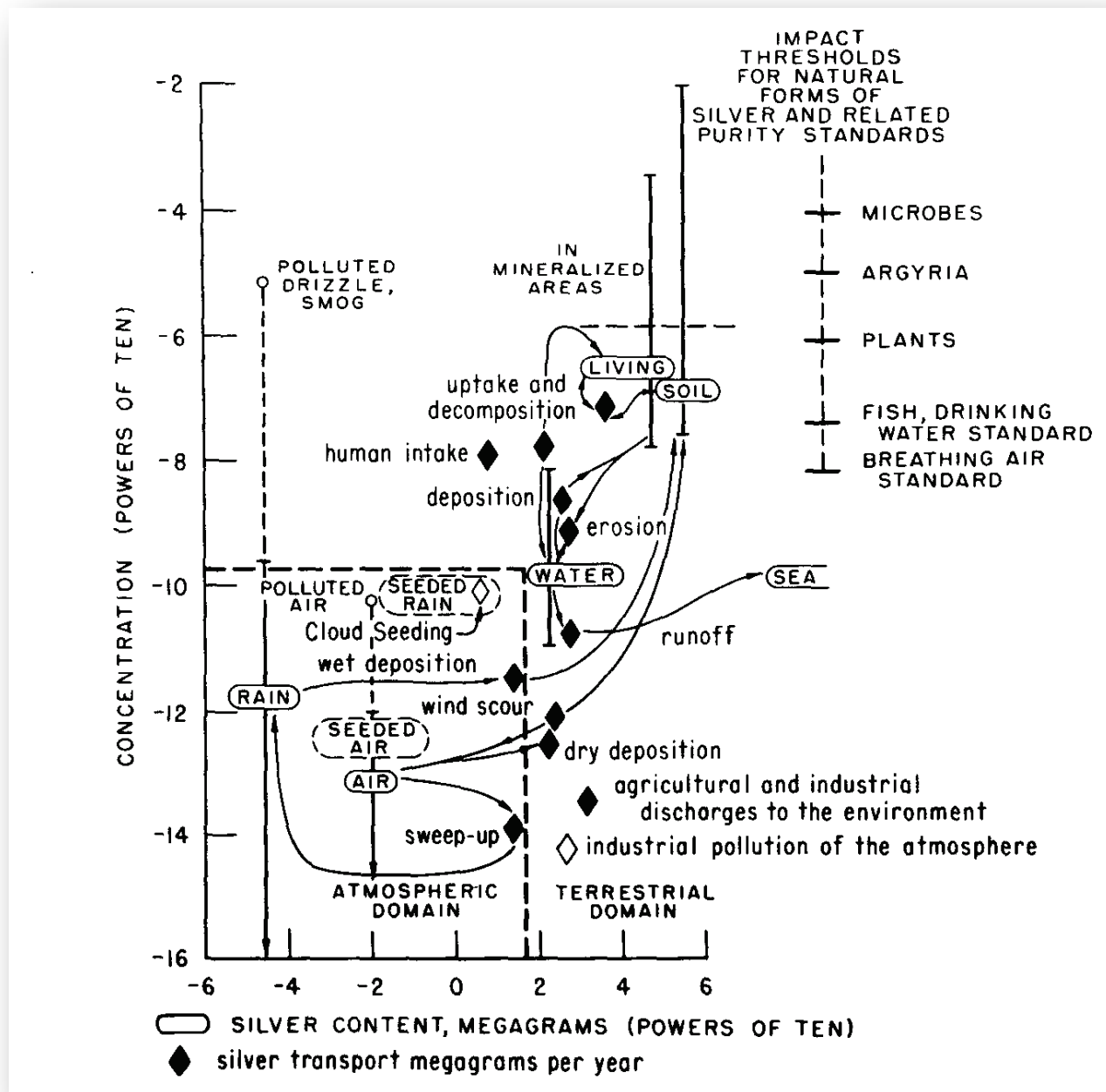


Figure 1 Generalized Approximate Content and Concentration of Silver in Environmental Compartments from the Contiguous United States, Pathways of Exchange between Compartments, and Impact Threshold Concentrations

The soil compartment (including also mud and vegetable litter), calculated for the top 20 cm comprising the root zone, contains by far the largest quantity of silver, at concentrations that may become quite high in areas subject to silver mining. Living matter of all sorts from microbes and fungi to animals (Shown as “Living” in Figure 1), which has on the average a slight tendency to concentrate silver from the soil, contains the next largest quantity. The exchange between living matter and soil through uptake and decomposition (designated by the diamonds

related to the bottom scale) dominates all other exchanges by at least an order of magnitude. The rates of exchanges are slow enough so that contents of these two compartments must change only slowly.

The silver concentration and content in lakes and rivers (shown in Figure 1 as “Water”) are determined mainly by depositional and erosional exchanges with the soil and by runoff to the sea. Whereas, uptake and decomposition exchanges with plants play a lesser role. In the aquatic compartment, annual transports are of the same order of magnitude as contents. Most transport is thought to be waterborne sediment.

The atmospheric domain receives silver in the form of windblown dust, some of which is swept up by particles of precipitation (the label “Rain” includes snow) and is carried with it to the ground, to lakes, or to the sea. The silver content of the atmospheric compartment at any moment is small in comparison with the annual transport through it. Silver transports associated with cloud seeding and with pollution are shown in Figure 1 by open diamonds. Atmospheric pollution causes local temporary changes within the atmosphere compartment that are large in comparison with natural amounts. Industrial atmospheric emissions are variously estimated at 135 to >360 Mg (150-400 tons) per year (Carson and Smith, 1975; USEPA, 1973), at concentrations ranging from $\sim 10^{-10}$ in city air to extreme of 6×10^{-6} measured in the smog water within the downwind plume from a copper smelter (J. Fletcher, 1976, personal communication to Howell in Howell, 1977). The other main source of silver pollution affecting soil and surface waters is fertilizer, either Florida phosphates or processed sewage sludge (Carson and Smith, 1975).

Cloud seeding, if it became widespread, would result in local, temporary concentrations in precipitation of the same order of magnitude as the natural concentration in surface waters. However, the rates of exchange would remain more than an order of magnitude smaller than the principal exchanges affecting the aquatic compartment. The rates of exchange would also be many orders of magnitude smaller than those affecting plants and soil, even in localized areas of precipitation management, using silver iodide as the cloud-seeding agent. This is the case even assuming that all the silver dispersed in the course of a century accumulated in the top 2 cm of soil, would not cause the silver concentration there to exceed the normal background. Silver from seed rain follows a pathway essentially identical to those from natural rain, and the effect of it on the silver transport by wet deposition (an increase of <20%) is too small to be illustrated conveniently in Figure 1.

3.1 Background Concentrations of Silver

As reported in Eisler’s study of silver in the environment (1996), the maximum concentrations of total silver recorded in various locations include the following: 36.5 $\mu\text{g}/\text{m}^3$ in air near a smelter in Idaho; 2.0 $\mu\text{g}/\text{m}^3$ in atmospheric dust; 0.1 $\mu\text{g}/\text{L}$ in oil well brines; 6.0 $\mu\text{g}/\text{L}$ in groundwater near a hazardous waste site; 8.9 $\mu\text{g}/\text{L}$ in seawater from Galveston Bay, Texas; 260 $\mu\text{g}/\text{L}$ in the Genesee River, New York—the recipient of photoprocessing wastes; 300 $\mu\text{g}/\text{L}$ in steam wells; 300 ng/L in treated photoprocessing wastewaters; 31 mg/kg in some Idaho soils; 43 mg/L in water from certain hot springs; 50 mg/kg in granite; as much as 100 mg/kg in crude oils; 150 mg/kg in some Genesee River sediments; and 27,000 mg/kg in some solid wastes from photoprocessing effluents. Eisler (1996) emphasizes that only a small portion of the total silver

in each of these compartments is biologically available. For example, typical publicly owned treatment works receiving photoprocessing effluents show silver removal efficiencies greater than 90%; the mean concentration of free silver ion present in the effluents from these plants ranged from 0.001 to 0.07 µg/L (Lytle, 1987; Bober et al., 1992).

Therefore, the concentration of silver in the environment is variable depending on the location, geology, and past use history. The remainder of this section focuses on the western United States, and in areas outside of significant mining or photographic equipment manufacture.

Several projects and monitoring efforts document the background of silver in reservoirs, steams, and alpine lake settings. The concentration of silver in snow in the Sierra Nevada has been well documented over the past fifty years by a number of investigations for example, Warburton et al. (1994) and Stone (2006) as well as many other studies by Stone that are not referenced in his 2006 paper. Silver concentrations have remained essentially constant over the time span covered by these studies.

Table 2 provides a listing of the mean background silver concentration measured in several programs from other Sierra Nevada locations and seasons beginning in 1966. Assuming normal distribution, the average background concentration of silver can be stated as $[Ag] = 1.88 \times 10^{-3} \mu\text{g/L}$ ($\sigma \pm 1.11 \times 10^{-3} \mu\text{g/L}$). The highest mean concentration of silver was found to be $<5.4 \times 10^{-3} \mu\text{g/L}$ in the Tahoe Basin, Sierra Nevada; and the lowest concentration was found to be $<1 \times 10^{-3} \mu\text{g/L}$ in the Ruby Mountains of Eastern Nevada (Stone, 2006).

Table 2 Natural Silver Background in Snow in the Western U.S.

Location	Period	Number of Samples	Mean [Ag] ($\times 10^{-3} \mu\text{g/L}$)	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

Source: Stone, 2006

Notes: NAA is neutron activation analysis; GFAAS is graphite furnace atomic adsorbtion spectroscopy; ICPMS is inductively coupled plasma mass spectrometry; HR is high resolution

3.2 Concentrations of Silver Found in Precipitation

Silver concentration in precipitation from unseeded storms have been measured from 0.0 to 0.02×10^{-3} $\mu\text{g/L}$, while concentrations in precipitation from seeded storms range from .01 to 0.3 $\mu\text{g/L}$ (Eisler, 1996). In some studies of the effectiveness of cloud seeding, an increase in the silver content of precipitation was used to indicate that the method was successful. Although generally a reasonable assumption, the National Academy of Science's review of weather modification (NAS, 2003) notes that these efforts lacked statistical rigor. For the purposes of this report, however, these values provide an indication of the increased silver concentration in rainfall that can result from the use of silver iodide as a nucleating agent.

3.3 Concentration of Silver Found in Lakes and Streams

Silver in lakes and streams reflects the average concentration of silver in all storms in the contributing watershed, both seeded storms and unseeded storms. In addition to this dilution effect, the concentrations in lakes and streams are further reduced by adsorption on vegetation and sediments. For these reasons, the concentrations of silver in surface waters decrease with distance from the source (Cooper and Jolly, 1970).

As noted in the discussion of background silver concentration, the geology and past use history can have an overriding effect on the abundance of silver. For example, a value of 4.5 $\mu\text{g/L}$ total silver is reported from an alpine lake in the Buckeye Mountains near Leadville, Colorado (Freeman, 1979). Although the area had been subject to cloud seeding in the 10 years prior to the study, the location is in a silver mining district, and Freeman (1979) documents that the lake is substantially supported by groundwater inflow. This result is reported in compilations by the USEPA (1980), the US Public Health Service (1990), and Eisler (1996) as representative of the maximum silver concentration that is known to occur in seeded areas. However, Freeman (1979) does not attribute the value to past cloud seeding. In fact, it is thought that the concentration represents a high background concentration caused by the silver mineralization of the surrounding rocks.

PG&E has conducted cloud seeding operations targeting the Mokelumne watershed under various permits from the United States Forest Service since 1953. Two studies were conducted at Lower Blue Lake and the Salt Spring Reservoir to assure that water samples from target watershed continue to remain well below the "no effect" threshold (Stone, 2006). The 2006 Mokelumne study used an HR-ICP-MS. The addition of high resolution mass spectrometry to the inductively coupled plasma reduces interference in the silver range and in most cases provides detection limits in the parts-per-trillion (ppt) to parts-per-quadrillion (ppq) range. As such, the results are discussed here as they represent the highest resolution analytical results currently available.

Lower Blue Lake is a watershed upwind from the cloud seeding area. Since it is upwind from the target area, detectable silver was found in only one sample. The average silver concentration is 0.00004 $\mu\text{g/L}$. The Salt Spring Reservoir provides an ideal location for measuring any elevated metals concentrations of silver above natural background levels in water or sediment samples. This is because a majority of runoff from the target area flows past this location. Results from Salt Spring Reservoir demonstrate that silver was detectable in four of the five samples. The

average silver concentration observed at Salt Springs Reservoir was <0.0005 µg/L. Overall, both measurements lie well within the natural background concentration.

A recent study (Williams and Denholm, 2009) concerned with a winter cloud seeding program in Australia confirmed these findings. Williams and Denholm (2009) agree that the bioavailability of silver is unlikely to change from the current background levels. Furthermore, extensive investigations undertaken prior to the commencement of the project confirmed background levels of silver and the presence of many ameliorating factors known to limit toxicity of the silver ion.

3.4 Concentrations of Silver Found in Soil

As noted in the section on background concentrations of silver (Section 3.1), the area geology and past use history governs the soil concentration. Howell (1977) notes that, even with prolonged seeding, the soil levels still remain at background levels. This occurs despite the fact that almost all of the applied silver iodide will reside in the soil or sediment of the area. However, the amounts added by cloud seeding are negligible compared to the amount of solid in the upper 20 cm of the soil horizon.

Tsiouris et al. (2002) investigated the soil silver content of an agricultural area subjected to cloud seeding with silver iodide. The research analyzed 2,500 soil samples using a spectrophotometric method capable of detecting Ag in parts per billion. This study reflected low total amount of AgI used in cloud seeding in two regions (469 kg in Hemathia-Pella and 361 kg in Serres, Greece). The average silver concentration in 1,438 soil samples from Hemathia-Pella and 1,063 samples from Serres were 44.5 µg/L and 37.2 µg/L, respectively. These averages were found to be within the range of those in control areas and comparable to those reported in the literature for unaffected soils (Table 3).

Table 3 Silver Concentration (Mg/G Dry Weight) Reported from Various Soils, Sediments and Areas

Location	Mean [Ag] (g Ag/g dry weight x 10 ⁻⁶)
Uncontaminated soils, Wales	0.01 – 1
Surface mineral soils, United States	0.7
Organic soils, United States	2 – 5
Earth's Crust	0.07
Typical Soils	0.1-1
Restronguent Estuary U.K	7*
Acushnet Estuary, New Bedford Hr	40*
Sorjord, Norway	190*
Thermaikos, Greece	2.36*
Eleusina, Greece	3.32*
Elizabeth and Nansemond rivers, Virginia	0.0-0.8*
Axios River, Greece	0.1-0.5

Source: Tsiouris et al. 2002
* samples originate from sediments

The Mokelumne Lake and Sediment study found the average silver concentration of the dissolved sediment samples collected from Lower Blue Lake and Salt Springs Reservoir range between 0.35 µg/L to 1.07 µg/L respectively. These values are thought to be at background levels (Stone, 2006).

4 Silver Iodide and Silver Toxicity Guidelines

There are several water quality objectives for silver that reflect protection of human health and the environment. There are also several proposed standards that have not been adopted and do not have associated regulatory requirements. These are summarized in Appendix A, and a materials safety data sheet (MSDS) for silver iodide is provided in Appendix B.

The compilation of standards is taken from Eisler (1996), of the USFWS. In presenting the compilation, Eisler notes that most measurements of silver in natural waters prior to the use of clean techniques are considered inaccurate. He also notes that most of proposed standards are formulated as total recoverable silver per liter, but total silver measurements do not provide an accurate assessment of the potential hazard because silver ion (Ag^+) is the most toxic of the many silver species. In fact, EPA is considering moving to measurements of acid-soluble silver rather than total recoverable silver, to reflect that the silver ion is the potentially toxic form. Eisler notes that silver and its compounds do not pose serious health concerns to humans, but that lower concentrations may affect freshwater and marine organisms. The drinking water standard for silver is 100 µg/L.

The remainder of this section discusses these standards and objectives. Much of the work summarized in this section is taken from the US National Biological Service Report Silver Hazards to Fish, Wildlife, and Invertebrates: A Synoptic Review (Eisler, 1996), supplemented by other references.

4.1 Impacts of Silver to Human Health

Much of our knowledge of the effects of silver iodide on the human body is derived from experience in the 1930s when doctors prescribed a nasal spray with 1 to 4 percent silver iodide. While there is no evidence that occasional use of this medication had adverse effects, prolonged use resulted in an ashen pigmentation of the skin known as argyria; no other adverse effects were noted (Vonnegut and Standler, 1972). Humans are also routinely exposed to silver from dental fillings and silverware. California and the United States regulate silver in surface water through the Federal Water Pollution Control Act (Clean Water Act), and in the California Code of Regulations. The silver criteria contain values to protect human health from ingestion of contaminated aquatic organisms and maximum acceptable concentrations to protect organisms that live in freshwater and salt water from toxic effects. The human health component of the silver criteria was drawn directly from the drinking water MCL. California and the United States have established a drinking water standard (maximum contaminant level, or MCL) of 100 µg/L for dissolved silver in drinking water. As summarized in the Compilation of Water Quality Goals (RWQCB-CV 2003), the USEPA Integrated Risk Information System (IRIS) reference dose as a drinking water level is set at 35 µg/L. However, RWQCB-CV (2003) recommends that

California-derived limits are preferred within California government. As such, the MCL of 100 µg/L is preferred for regulatory purposes in California.

4.2 Impacts of Acute Silver to Aquatic Species

The EPA has set a guideline of 4.1 µg/L in fresh water with a hardness of 120 mg/L as the acute toxic limit. In solution, high levels of ionic silver are toxic to aquatic plants and animals. Water concentration of 1.2-4.1 µg/L can have adverse effects to representative species of aquatic life, including representative species of insects, daphnids, amphipods, trout, flounders, sticklebacks, guppies, and dace (Eisler, 1996). Adverse effects occur on development of trout at concentration as low as 1.7 µg/L (Eisler, 1996). Freshwater fish and amphibians appear to be the most sensitive vertebrates to dissolved silver. Sensitive aquatic plants accumulated silver from water containing as little as 2 µg/L, and grew poorly at 3.3- 8.2 µg/L (Eisler, 1996).

4.3 Impacts of Silver to Algae.

At higher concentrations of 2-7 µg/L for 3 to 4 weeks, silver inputs caused disappearance of *Anacystis marina*, a mat-forming blue-green alga; increased dominance by *Skeletonema costatum*, a chain-forming centric diatom; and increased silver concentrations in various species of phytoplankton to 8.6-43.7 Ag µg/g DW (Eisler, 1996). Silver Iodide can retard the growth of algae, fungi, bacteria, and fish in fresh water (Cooper and Jolly, 1970).

4.4 Impacts of Silver to Terrestrial Animals.

No data were found on effects of silver on avian life. AgI may be deposited on forages in the seeded target area and enter the food chain of livestock. Only one article was found in the literature that related AgI toxicity in livestock. Younger and Crookshank (1978) documents the effects of silver iodide on sheep. They state that, “AgI complexes used in weather modification operations are not likely to induce overtly toxic effects on livestock. Silver may be absorbed from the gastrointestinal tract during continuous exposure to AgI, and this fact may be a function of time and dose”.

4.5 Impacts of Silver to Terrestrial Plants.

According to Cooper and Jolly (1970), silver levels that may damage plants are many times higher than would occur in precipitation from seeded storms. Further, reports that sprays containing 9,800 µg /L kill corn (*Zea mays*), and sprays containing 100,000-1,000,000 µg /L kill young tomato (*Lycopersicon esculentum*) and bean (*Phaseolus* spp.) plants. Hirsch et al. (1993) planted seeds of corn, lettuce (*Lactuca sativa*), oat (*Avena sativa*), turnip (*Brassica rapa*), soybean (*Glycine max*), spinach (*Spinacia oleracea*), and Chinese cabbage (*Brassica* spp.) in soils amended with silver sulfide and sewage sludge to contain 10, 50, or 100 mg Ag/kg (dry weight) soil. All plants germinated and most grew normally at the highest soil concentration of silver tested, but growth of Chinese cabbage and lettuce was adversely affected at 10 mg Ag/kg DW soil and higher (Eisler, 1996). Silver concentrations in edible portions from all plants at all

soil levels of silver tested, except lettuce, were less than 80 µg/kg. Lettuce grown in soil containing 100 mg Ag/kg had about 1.2 mg Ag/kg DW (Hirsch et al. 1993).

5 Summary of Findings

The geochemistry of silver in the environment generally restricts silver iodide to a solid form. In fact, this property is important for the success of its use for cloud seeding, since dissolution of the nuclei would fail to provide nucleation sites for precipitation. Based on the solubility of silver iodide, the maximum possible concentration in contact with water would be 0.984 µg/L. This value would be much reduced by dilution with snowmelt or rainwater not in direct contact with silver iodide nucleating agents. Once on the ground, the silver in solution then readily forms complexes with sediments and inorganic materials, as well as forming complexes with other negative ions. Therefore, the maximum concentration of the free silver ion, the only silver species shown to be toxic to some biota in the environment, would be far less than 0.9 µg/L.

The human health-based drinking water standard is based on concerns related to change in skin pigment, and the safe level is set at 100 µg/L. Other standards for ecosystem protection are all greater than 1.4 µg/L. Based on the Mokelumne case study and the concurring opinion of Williams and Denholm (2009), the values stated in aquatic water samples do not pose adverse ecotoxicological impacts to human health or the environment. Comprehensive studies and data reviews of the environmental affect of the use of silver iodide for cloud seeding all concur that there is no evidence for adverse effects to human health or the environment from the use of silver iodide for cloud seeding.

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Appendix A

**Proposed Standards
(not regulatory requirements)**

There are several proposed standards that have not been adopted and do not have associated regulatory requirements.

The compilation of standards included below is taken from Eisler (1996), of the USFWS. In presenting the compilation, Eisler notes that most measurements of silver in natural waters prior to the use of clean techniques are considered inaccurate. He also notes that most of proposed standards are formulated as total recoverable silver per liter, but total silver measurements do not provide an accurate assessment of the potential hazard because silver ion (Ag^+) is the most toxic of the many silver species. In fact, the US Environmental Protection Agency is considering moving to measurements of acid-soluble silver rather than total recoverable silver, to reflect that the silver ion is the potentially toxic form. Eisler notes that silver and its compounds do not pose serious health concerns to humans, but that lower concentrations may affect freshwater and marine organisms.

Resource, criterion, and other variables	Effective silver concentration
Agricultural crops	
Soils	<100 mg total silver/kg dry weight soil for most species; <10 mg/kg for sensitive species
Freshwater aquatic life protection	
Acute exposure	
Total recoverable silver	<1.32 µg/L
Acid-soluble silver ^b	4-day average shall not exceed 0.12 µg/L more than once every three years; 1-h average not to exceed 0.92 µg/L more than once every 3 years
Chronic exposure	
Total recoverable silver, in µg/L, should not exceed $e^{(1.72[\ln(\text{hardness})] - 6.52)}$ at any time.	
Examples follow	
50 mg CaCO ₃ /L	<1.2 µg/L
100 mg CaCO ₃ /L	<4.1 µg/L
200 mg CaCO ₃ /L	<13.0 µg/L
Chronic exposure	<0.12-<0.13 µg total recoverable silver/L
Tissue residues	
Adverse effects on growth of the Asiatic clam, <i>Corbicula fluminea</i>	>1.65 mg total silver/kg soft tissues, fresh weight basis
Marine life protection	
Acute exposure	
Total recoverable silver	<2.3 µg/L at any time
Acid-soluble silver ^b	4-day average concentration not to exceed 0.92 µg/L more than once every 3 years on average and the 1-h concentration not to exceed 7.2 µg/L more than once every 3 years
Tissue residues	
Marine clams, soft parts	
Normal	<1 mg total silver/kg dry weight
Stressful or fatal	>100 mg total silver/kg dry weight
Human health	
Air, United States	
Current level of exposure, nationwide	100 µg total silver daily per person
Short-term exposure limit (15 min; up to 4 times daily with 60-min intervals at <0.01 mg Ag/m ³ air)	<0.03 mg total silver/m ³
Threshold limit value (8 h daily, 5 days weekly)	
Aerosol silver compounds	<0.01 mg total silver/m ³
Metallic silver dust	<0.1 mg total silver/m ³
Diet, United States	
Current level of exposure	35 to 40 µg daily per person
Drinking water	
United States	
Long-term exposure (>10 days)	<50 µg total silver/L
Proposed long-term exposure	<90 µg/L total silver
Short-term exposure (1-10 days)	<1,142 µg total silver/L
California	<10 µg/L
Germany	<100 µg/L
Space vehicles	
Former Soviet Union	Max. 200 µg total silver/L
United States	100 to Max. 200 µg total silver/L
Switzerland	<200 µg total silver/L
Ground water	<50 µg total silver/L

Source: Silver Hazards to Fish, Wildlife, and Invertebrates: A Synoptic Review (Eilser, 1996)

Appendix B

MSDS of Silver Iodide and Silver

Material Safety Data Sheet

Silver Iodide MSDS

Available online at: <http://www.espimetals.com/msds/s/silveriodide.pdf>. Accessed Sept 22, 2010.

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.

Material Safety Data Sheet

Silver MSDS

Available online at: <http://www.espimetals.com/msds/s/silver.pdf>. Accessed Sept 22, 2010.

Section 1: Chemical Product and Company Identification

Product Name: Silver

Catalog Codes: SLS4222, SLS2005, SLS3427, SLS1210,
SLS2632, SLS4054, SLS1837

CAS#: 7440-22-4

RTECS: VW3500000

TSCA: TSCA 8(b) inventory: Silver

CI#: Not applicable.

Synonym:

Chemical Formula: Ag

Contact Information:

Sciencelab.com, Inc.

14025 Smith Rd.

Houston, Texas 77396

US Sales: 1-800-901-7247

International Sales: 1-281-441-4400

Order Online: ScienceLab.com

CHEMTREC (24HR Emergency Telephone), call:

1-800-424-9300

International CHEMTREC, call: 1-703-527-3887

For non-emergency assistance, call: 1-281-441-4400

Section 2: Composition and Information on Ingredients

Composition:

Name CAS # % by Weight

Silver 7440-22-4 100

Toxicological Data on Ingredients: Silver: ORAL (LD50): Acute: 100 mg/kg [Mouse].

Section 3: Hazards Identification

Potential Acute Health Effects:

Very hazardous in case of eye contact (irritant), of ingestion, of inhalation. Severe over-exposure can result in death.

Inflammation of the eye is characterized by redness, watering, and itching.

Potential Chronic Health Effects:

CARCINOGENIC EFFECTS: Not available. MUTAGENIC EFFECTS: Not available.
TERATOGENIC EFFECTS: Not available. DEVELOPMENTAL TOXICITY: Not available.
Repeated exposure to an highly toxic material may produce general deterioration of health by an accumulation in one or many human organs.

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: No known effect on skin contact, rinse with water for a few minutes.

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Serious Skin Contact: Not available.

Inhalation: Allow the victim to rest in a well ventilated area. Seek immediate medical attention.

Serious Inhalation:

Evacuate the victim to a safe area as soon as possible. Loosen tight clothing such as a collar, tie, belt or waistband. If breathing is difficult, administer oxygen. If the victim is not breathing, perform mouth-to-mouth resuscitation. Seek medical attention.

Ingestion:

Do not induce vomiting. Examine the lips and mouth to ascertain whether the tissues are damaged, a possible indication that the toxic material was ingested; the absence of such signs, however, is not conclusive. 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: May be combustible at high temperature.

Auto-Ignition Temperature: Not available.

Flash Points: Not available.

Flammable Limits: Not available.

Products of Combustion: Some metallic oxides.

Fire Hazards in Presence of Various Substances: Not available.

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:

SMALL FIRE: Use DRY chemical powder. LARGE FIRE: Use water spray, fog or foam. Do not use water jet.

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.

Large Spill:

Use a shovel to put the material into a convenient waste disposal container. 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:

Keep locked up Keep away from heat. Keep away from sources of ignition. Empty containers pose a fire risk, evaporate the residue under a fume hood. Ground all equipment containing material. Do not ingest. Do not breathe dust. Avoid contact with eyes In case of insufficient ventilation, wear suitable respiratory equipment If ingested, seek medical advice immediately and show the container or the label.

Storage:

Keep container dry. Keep in a cool place. Ground all equipment containing material. Keep container tightly closed. Keep in a cool, well-ventilated place. Highly toxic or infectious materials should be stored in a separate locked safety storage cabinet or room.

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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.

Personal Protection in Case of a Large Spill:

Splash goggles. Full suit. Boots. Gloves. Suggested protective clothing might not be sufficient; consult a specialist BEFORE handling this product.

Exposure Limits:

TWA: 0.01 (mg/m³) from OSHA (PEL) TWA: 0.01 (mg/m³) from OSHA NIOSH Australia:
TWA: 0.1 (mg/m³) Consult local authorities for acceptable exposure limits.

Section 9: Physical and Chemical Properties

Physical state and appearance: Solid. (Solid metallic powder. Metal solid.)

Odor: Not available.

Taste: Not available.

Molecular Weight: 107.87 g/mole

Color: Not available.

pH (1% soln/water): Not applicable.

Boiling Point: 2212°C (4013.6°F)

Melting Point: 961°C (1761.8°F)

Critical Temperature: Not available.

Specific Gravity: 10.4 (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.

Dispersion Properties: Is not dispersed in cold water, hot water.

Solubility: Insoluble in cold water, hot water.

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.

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Special Remarks on Reactivity: Not available.

Special Remarks on Corrosivity: Not available.

Polymerization: No.

Section 11: Toxicological Information

Routes of Entry: Absorbed through skin. Eye contact. Inhalation. Ingestion.

Toxicity to Animals: Acute oral toxicity (LD50): 100 mg/kg [Mouse].

Chronic Effects on Humans: Not available.

Other Toxic Effects on Humans: Very hazardous in case 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 as toxic as the original product.

Special Remarks on the Products of Biodegradation: Not available.

Section 13: Disposal Considerations

Waste Disposal:

Section 14: Transport Information

DOT Classification:

Identification:

Special Provisions for Transport: Not available.

Section 15: Other Regulatory Information

Federal and State Regulations:

Rhode Island RTK hazardous substances: Silver Pennsylvania RTK: Silver Minnesota: Silver Massachusetts RTK: Silver New Jersey: Silver TSCA 8(b) inventory: Silver TSCA 8(a) PAIR: Silver TSCA 8(d) H and S data reporting: Silver SARA 313 toxic chemical notification and release reporting: Silver: 1% CERCLA: Hazardous substances.: Silver: 1000 lbs. (453.6 kg)

Other Regulations:

OSHA: Hazardous by definition of Hazard Communication Standard (29 CFR 1910.1200).
EINECS: This product is on the European Inventory of Existing Commercial Chemical Substances.

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Other Classifications:

WHMIS (Canada):

CLASS D-1B: Material causing immediate and serious toxic effects (TOXIC). CLASS D-2B: Material causing other toxic effects (TOXIC).

DSCL (EEC): R41- Risk of serious damage to eyes.

HMIS (U.S.A.):

Health Hazard: 2

Fire Hazard: 1

Reactivity: 0

Personal Protection: j

National Fire Protection Association (U.S.A.):

Health: 2

Flammability: 1

Reactivity: 0

Specific hazard:

Protective Equipment:

Not applicable. Lab coat. Wear appropriate respirator when ventilation is inadequate. Splash goggles.

Section 16: Other Information

References: Not available.

Other Special Considerations: Not available.

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