Environmental Effects of Silver Iodide from Cloud Seeding Operations

Sacramento Municipal Utility District

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EXECUTIVE SUMMARY

SMUD has conducted cloud seeding since 1968 in the South Fork American River watershed upstream of the Upper American River Project (UARP) over a 190-square mile target area, with a currently planned expansion to 444-square miles. Silver iodide (AgI) is a compound of silver used in cloud seeding activities to promote the formation of ice crystals and enhance total snowpack accumulation. Silver iodide is used for cloud seeding because its crystalline structure makes the compound ideally suited for ice formation, it exhibits very low solubility in natural waters (i.e., less than 1 microgram per liter [ug/L]), and it is not bioavailable or toxic to organisms in the environment.

In general, studies of cloud seeding using silver iodide have demonstrated increased total silver concentrations in associated precipitation, but no corresponding, statistically significant systematic increase or accumulation of total silver in freshwater, soil, or in stream, lake, or reservoir sediments in the areas experiencing cloud seeding.

Silver iodide is not typically measured in isolation in the environment, with existing analytical methods relying upon measurements of total silver. Cloud seeding using silver iodide has been found to increase total silver concentrations in precipitation between two and three times on average when compared to unseeded precipitation.

In studies conducted in the California Sierra Nevada, total silver concentrations in snow from areas seeded with silver iodide were typically less than 0.02 ug/L but reached a maximum of approximately 0.115 ug/L. Freshwater total silver concentrations in areas cloud seeded with silver iodide were usually less than analytical detection limits (between 0.0005 and 0.04 ug/L depending on the method used), but they were occasionally measured between 0.09 - 0.74 ug/L in the Feather River-Lake Almanor watershed and less than 0.0005 ug/L on average in the Mokelumne River watershed. In general, total silver concentrations have not been shown to increase above background levels in terrestrial, stream, and lake sediments in areas seeded with silver iodide.

There are no documented environmental hazards associated with silver iodide and to date no studies have identified adverse environmental impacts due to cloud seeding with silver iodide. There are no federal, state, or local regulations establishing acceptable levels of exposure for silver iodide. In natural waters, silver iodide has such extremely low solubility (0.984 ug/L) that it is generally considered to be insoluble and is thus not bioavailable or toxic.

In contrast, there are known environmental hazards and regulations associated with *dissolved* silver (free silver ion [Ag^+]) because, unlike insoluble silver iodide, dissolved silver is bioavailable and potentially toxic to sensitive organisms. Dissolved silver is a negligible environmental hazard for humans, but federal and state regulations set the maximum contaminant level for dissolved silver in drinking water at 100 ug/L to prevent a cosmetic gray or blue-gray discoloration of skin that may occur from chronic exposure to high levels. Dissolved silver is a potential hazard to aquatic and terrestrial organisms

at a wide range of concentrations depending on the species, life-stage, and water hardness with 1.2 to 4.9 ug/L lethal to sensitive aquatic organisms. Accordingly, the USEPA has set an acute freshwater criterion or criteria maximum concentration (CMC) for dissolved silver as a function of water hardness with a CMC of 3.2 ug/L at a hardness of 100 mg/L. Lower water hardness results in a lower CMC for silver. There is no chronic freshwater criterion for dissolved silver. Dissolved silver also is an environmental hazard to terrestrial plants and animals, but the concentrations causing adverse effects are much higher than found under typical natural conditions. However, despite the hazards associated with dissolved silver, there is no equivalent hazard with silver iodide because it is insoluble and thus not bioavailable.

Historically, SMUD has measured total and dissolved silver in water samples within the Upper American River watershed at various times. Total silver would include any contributions from silver iodide, while dissolved silver would not include any silver iodide since silver iodide is insoluble in water under natural conditions. Measurements of total silver, including both dissolved and particulate silver, in all years ranged from <0.008 – 0.86 ug/L, which in all cases is below the USEPA secondary drinking water threshold (100 ug/L dissolved silver). Dissolved silver was analyzed in 2004 and ranged from <0.0045 – 0.02 ug/L with the hardness-adjusted freshwater CMC for aquatic biota being exceeded in two reservoir samples and one riverine sample. Total and dissolved silver concentrations in water and fish tissue measured more recently have been consistently at or near the lowest analytical detection limits.

SMUD currently monitors total and dissolved silver in the Upper American River watershed every five years as part of a suite of trace metals. Monitoring is conducted seasonally at 22 sites across seven stream reaches and 20 sites across 11 reservoirs in the watershed, where monitoring sites range in elevation from approximately 500 – 6,500 feet, covering the full elevational extent of SMUD cloud seeding activities. Of the 42 total riverine and reservoir monitoring sites, 23 are located directly within the existing 190-square mile cloud seeding target area, and the remaining sites are located downstream of both the existing and the expanded target area, allowing for an assessment of potential downstream transport of silver. The current trace metals monitoring program would detect long-term seasonal trends in total and dissolved silver concentrations in specific reservoir and river locations within the existing cloud seeding target area, and it would also detect spatial variations in concentrations within this area (e.g., particular locations that may exhibit higher concentrations than others). While the frequency and spatial coverage of the current monitoring program is not able to attribute variations in concentrations of these forms of silver to individual cloud seeding events, it would measure long-term changes in the amount of dissolved (i.e., bioavailable) silver directly within the existing 190-square mile cloud seeding target area, and downstream of both the existing and the expanded target area, which could be compared to long-term trends in SMUD application rates of silver iodide.

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1.0 INTRODUCTION

Cloud seeding with silver iodide (AgI) has been conducted in California for over 50 years with many projects dispersing silver iodide along the central and southern Sierra Nevada to enhance snowpack accumulation (Hunter 2007; DWR 2013, 2016). Silver iodide is used in cloud seeding because it is insoluble, able to be dispersed by ground- or aerial-based methods, and has a crystalline structure similar to ice that promotes the formation of snow from water vapor in the atmosphere. Silver iodide and the impacts of its use in cloud seeding have been frequently studied by industry, government, and academia to quantify its efficacy at increasing snow accumulation as well as its environmental impact. While some studies have directly evaluated silver iodide under laboratory conditions, most studies have focused on field monitoring of total silver concentrations in the environment (see also Section 4.1) .

In 2017, the Sacramento Municipal Utility District (SMUD) received questions about the use of silver iodide in cloud seeding during public comments on the proposed expansion of SMUD's El Dorado Cloud Seeding Program. The objective of this report is to generally address those questions through discussion of the following topics:

- Cloud seeding practices
- Properties of silver and silver iodide
- Silver iodide levels in the environment
- Potential human and environmental hazards of silver and silver iodide
- Relevant regulatory thresholds
- Overview of SMUD's cloud seeding program

2.0 BACKGROUND

2.1 CLOUD SEEDING

Cloud seeding is the introduction of very small particles into clouds to increase the amount of precipitation the clouds would naturally produce. Clouds are formed when temperatures in the atmosphere reach saturation or a relative humidity of 100 percent, causing water vapor in the air to condense around a particle and form a droplet. Naturally occurring particles, such as dust from wind erosion or salt formed by evaporation from the ocean, are the "cloud condensation nuclei" critical to condensing water vapor in the air into clouds composed of water droplets, ice crystals, or a mixture of both. The two types of cloud formation processes are "warm cloud" and "cold cloud". Warm cloud formation occurs when cloud temperatures are above freezing and water droplets in the cloud collide until they form droplets with sufficient weight to fall as rain. Cold cloud formation occurs when cloud temperatures are below freezing, such that cloud droplets remain unfrozen as pure water until coming into contact with a particle or ice nuclei that causes the pure water to freeze and form an ice crystal. The ice crystal grows as more water vapor or unfrozen water droplets freeze onto the ice crystal, until it forms a snowflake that falls to the ground as snow or rain (Hunter 2007).

In either warm or cold cloud formation processes, microscopic airborne particles are critical to water droplet or ice crystal formation, which then produces precipitation. In cold cloud formation, particles are especially important for causing ice crystal development and precipitation because pure water droplets do not freeze until well below 32°F (Hunter 2007; SMUD 2017). In some cold storm systems, natural particles in the air are too few to promote ice crystal formation of the pure water droplets, so no precipitation occurs. Cloud seeding introduces a sufficient number of additional small particles to stimulate the formation of water droplets or ice crystals and create precipitation (County of Los Angeles 2015).

The main types of cloud seeding that commonly occur are cold-season orographic cloud seeding, hail and fog reduction cloud seeding, and warm-season convective cloud seeding. As SMUD conducts cold-season orographic cloud seeding with silver iodide, the remainder of this report focuses primarily on the processes involved in this type of cloud seeding. Cold-season orographic cloud seeding relies on cold cloud formation processes. It generally occurs in California when moist air flowing from the Pacific Ocean rises as it reaches the western side of the Sierra Nevada and subsequently cools, causing water vapor to condense into clouds. However, if there are insufficient natural particles in the cloud to cause the pure water to form ice crystals, no precipitation will occur. Artificial particles introduced by ground- or aerial-based cloud seeding methods can provide the additional particles needed to initiate or increase precipitation.

Silver iodide (AgI) is the most common artificial particle used in cloud seeding because it has a crystal structure similar to ice which enables it to easily promote ice crystal formation. Silver iodide is most effective at producing ice crystals when air temperatures are below 23°F (-5°C), so effective cloud seeding with silver iodide would only occur under those conditions. As a cloud seeding agent, silver iodide is released in smoke from ground-based cloud-nuclei generators (CNGs), flare "trees", or from aerial-based flares mounted to an aircraft that flies through the clouds. Specific details of the methods used to disperse silver iodide in cloud seeding conducted by SMUD are discussed in Section 6.

While cloud seeding has been used for many decades and in numerous locations throughout the western United States, the efficacy of cloud seeding is still debated amongst experts in the field and in the scientific literature. In a 2003 report, the National Academy of Sciences (NAS) notes there is strong evidence that some cloud seeding programs have induced precipitation changes, but more tests of significance and reproducibility are needed to prove cloud seeding increases precipitation. Garstang et al. (2005) and Super and Heimbach (2005) summarize the main viewpoints and evidence of experts related to cloud seeding efficacy. While NAS concludes that there was no convincing scientific proof of the efficacy of weather modification efforts at that time (NAS 2003), multiple studies have been conducted since which indicate that cloud seeding does increase precipitation. For example, using air- and ground-based radar

measurements, Huggins (2007) documents that ice crystal concentrations were over an order of magnitude greater in the seeded cloud zone area than those outside. A five-year experimental program in the Snowy Mountains of southeastern Australia indicates that cloud seeding increased precipitation between 7% and 14% in the targeted area compared to unseeded areas (Manton et al. 2011; Manton and Warren 2011).

Cold season orographic cloud seeding in California has been practiced since the early 1950s and in the last 20 years cloud seeding programs have occurred in 11 to 14 watersheds annually. Cloud seeding is recognized as a precipitation enhancement method by the California Department of Water Resources (DWR 2016) and the California Water Plan Update 2013 (DWR 2013). Most cloud seeding projects in California are located along the central and southern Sierra Nevada and use silver iodide as the active seeding agent (DWR 2016). Cloud seeding projects are required to provide the National Oceanic and Atmospheric Administration (NOAA) with activity reports, detailing the number of days, hours of operation, and amounts of seeding material used. The State of California requires cloud seeding project sponsors to file a notice of intent initially and every five years for continuing projects, record keeping by operators, and annual or biennial reports to DWR. All cloud seeding projects must comply with the California Environmental Quality Act (DWR 2016).

2.2 PROPERTIES OF SILVER AND SILVER IODIDE

Silver is a relatively rare, naturally occurring element with an abundance of approximately 0.07 mg/kg in the earth's crust. It is found primarily in mineral ores containing other elements. In its elemental state, silver can be found in oxidation states of Ag^0, Ag^{+1}, Ag^{+2}, and Ag^{+3}, but only the solid state (Ag^0), dissolved (Ag^+), or free silver ion in water (Ag^{+1}) occur under typical environmental conditions (Eisler 1996). Dissolved silver is the primary form of silver that is an environmental concern because it interferes with biological processes in aquatic organisms (EPA 1980). Dissolved silver is fungicidal, algicidal, and bactericidal at concentrations ranging 10–1,000 ug/L so it is frequently used in medical applications and to sterilize potable water (Williams and Denholm 2009).

Silver also forms compounds with a range of other substances including arsenic, sulfate, bicarbonate, nitrate, iodide, and chloride with each silver compound exhibiting very different properties (Cardno ENTRIX 2011). As noted previously, silver iodide is one of the most common particles used in cloud seeding because the crystalline structure of silver iodide closely resembles ice, making it an effective surrogate for ice as a nucleating agent in clouds (PG&E 2011). The reaction to form silver iodide (AgI) from dissolved silver (Ag^+) and iodide (I^-) is expressed as:

$$Ag^+ \text{ (liquid)} + I^- \text{ (liquid)} \rightarrow AgI \text{ (solid)} \qquad \text{(Equation 1)}$$
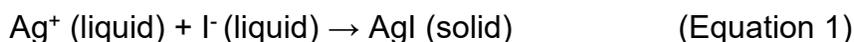
2.2.1 Solubility of Silver Compounds

Solubility is the ability of a compound to dissolve in a solvent. In the environment, solubility in water generally controls bioavailability so silver compounds that are not readily soluble (or "insoluble") in water are of significantly less environmental concern (Karen et al. 1999; Williams and Denholm 2009). Table 1 provides a comparison of the solubility of several silver compounds in water, along with two common substances (table salt, sand/quartz) for comparison. The solubility of silver compounds varies widely, with some silver compounds (e.g., silver nitrate) being very soluble and readily forming dissolved silver ions in water, while other silver compounds (e.g., silver iodide) are very insoluble, producing very few dissolved silver ions when in contact with water. Solubility is also represented by a solubility product or K_{sp}. The solubility product for the silver iodide reaction expressed above in Equation 1 is 8.5×10^{-17} indicating the reaction is strongly driven toward the solid form. The maximum concentration of dissolved silver that can form in water that is in contact with solid silver iodide at 25°C (standard conditions) is 0.984 ug/L (parts per billion [ppb]) (Stone 2006). Solid silver iodide in water will not form any dissolved silver if the concentration of dissolved silver is 0.984 ug/L or higher (Williams and Denholm 2009).

Table 1. Solubility of Selected Silver Compounds.

Compound	Solubility (g/100 mL)	
	Cold Water	Hot Water
Sodium chloride (NaCl or table salt)	35.9	
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
Silicon dioxide (SiO$_2$ or sand/quartz)	Insoluble	Insoluble

Source: Williams and Denholm (2009) for silver compounds.

Silver iodide is soluble in hydroiodic acid (pH < 3) and ammonia solutions (pH > 10), as well as aqueous solutions of other compounds (e.g., potassium iodide, sodium chloride, potassium cyanide, ammonium hydroxide sodium thiosulfate), and concentrated solutions of compounds such as alkali bromides, chlorides, thiocyanates, thiosulfates, mercuric and silver nitrates (Firsching 1960; Lewis 1997; O'Neil 2001). These solutions can be generated in a laboratory or industrial setting, but they are not present under typical environmental conditions.

The extremely low environmental solubility of silver iodide, along with a crystalline structure closely resembling ice, makes it an ideal particle for cloud seeding. In clouds, silver iodide remains a solid nucleating site as water vapor forms droplets and/or ice crystals around it. On the ground, it does not readily disassociate into biologically available dissolved silver ions (PG&E 2011).

2.2.2 <u>Adsorptivity of Silver and Silver Iodide</u>

In the environment, sorption (the physical and chemical process by which one substance becomes attached to another) is the dominant process controlling silver partitioning in water and its movement in solids and sediments. Silver strongly adsorbs to manganese dioxide, ferric (iron) compounds, and clay minerals commonly present in watershed and forms precipitates with naturally occurring fluorine, chlorine, bromine, and iodine, reducing the concentration of dissolved silver (free silver ions) in water (Eisler 1996). Silver also readily adsorbs to particulate matter, to the extent that only approximately 25 percent of the total silver is estimated to be dissolved as either ion colloids or complexes (Wen et al. 1997; Stone 2006). Silver adsorption to particulate matter in water contributes to silver deposition into sediments when particulate matter settles out of the water column (Eisler 1996). The U.S. Environmental Protection Agency (USEPA) ambient water quality criteria also notes that silver may adsorb to organic material in natural waters and form metal-organic complexes (USEPA 1980). Silver may desorb under reducing conditions in the sediment after which it may either reduce to metallic silver or combine with reduced sulfur to form insoluble silver sulfide (USEPA 1980). The silver iodide compound is not likely to strongly adsorb to surfaces as it is a relatively uncharged, insoluble solid.

3.0 SILVER IODIDE IN THE ENVIRONMENT

3.1 MEASUREMENT OF SILVER IODIDE IN THE ENVIRONMENT

The silver iodide compound is not typically measured in the environment, even during studies focused on evaluating the impacts of using silver iodide in cloud seeding. Readily available analytical techniques measure total silver concentrations, where the latter include all forms of silver in a sample (e.g., dissolved silver ions, silver iodide, other silver complexes). Total silver concentrations are used to estimate silver iodide released from cloud seeding, assuming that other sources of silver in the sample are minimal or constant. Since the total silver concentration includes both the bioavailable dissolved silver that correlates with aquatic toxicity and the insoluble silver iodide particles, measurements of the total silver concentration cannot be directly compared with regulatory thresholds based on dissolved silver concentrations in water.

Total silver is typically measured with a high resolution inductively-coupled plasma mass spectrometer (HP-ICP-MS) (Huggins et al. 2004; Manton et al. 2011; PG&E 2011), but it also can be measured with inductively coupled plasma optical emission spectrometry (ICP-OES) or inductively coupled plasma atomic emission spectrometry (ICP-AES) (Fajardo et al. 2016). Total silver is also measured in soil using soxlet extraction followed by flame atomic absorption spectrometry and in vegetation using acid digestion then electrothermal atomic absorption spectrometry for grass (Tsiouris et al. 2003). USEPA Method 200.8 and Method 6020A detail HP-ICP-MS procedures for ultra-trace sampling and analysis techniques for trace elements like silver (USEPA 1994; USEPA 1998). SMUD currently uses USEPA Method 200.8 HP-ICP-MS with

detection limits of 0.070 ug/L for total silver and 0.15 ug/L for dissolved silver (SMUD 2016).

Measurements of total silver concentrations have been reported for many locations with the total silver concentration varying significantly depending on geology and past land use activities (Strandler and Vonnegut 1972; Eisler 1996; Williams and Denholm 2009; Cardno ENTRIX 2011). Silver measurements before the late 1980s should be treated cautiously because ultra-clean metal sampling procedures to ensure an uncontaminated sample, especially for trace metals like silver, did not begin until after that period. Eisler (1996) and Williams and Denholm (2009) summarize the total silver concentrations measured at locations around the world in air, water, snow, soils, and aquatic sediments from the Concise International Chemical Assessment Document 44 (CICAD 44) and other publications. Eisler (1996) reports total silver concentrations in the air of 1.0 nanograms per cubic meter [ng/m^3] in rural areas with cloud seeding using silver iodide and 0.04 – 0.17 ng/m^3 in rural areas without cloud seeding (Table 2). Total silver concentrations in air samples taken directly adjacent to a silver iodide ground based cloud-seeding generator are considerably higher (e.g., >10,000 ng/m^3) (Eisler 1996).

3.2 SILVER CONCENTRATIONS IN PRECIPITATION

Silver concentrations in precipitation have been regularly monitored in cloud seeding operations (Super and Huggins 1992; Warburton et al. 1995; Eisler 1996; Sanchez et al. 1999; Huggins et al. 2004; Cardno ENTRIX 2011; Manton and Warren 2011). Silver concentrations in snow in seeded regions have been found to be higher than in unseeded regions. In studies of the central Sierra Nevada, the background silver concentration in snow was measured at 0.002 ug/L, while mean total silver concentration in snow after cloud seeding with silver iodide ranged from approximately 0.003 – 0.0894 ug/L (Table 2; Warburton et al. 1995; Huggins et al. 2004). USEPA (1981) concludes in an exposure and risk assessment for silver that the total silver concentrations in precipitation from silver iodide used in cloud seeding are not expected to contribute significant amounts to water.

3.3 SILVER CONCENTRATIONS IN FRESHWATER

Measured silver concentrations in lakes and streams represent a long-term average of silver concentrations from the area upstream of the measurement point, and integrate silver signals from both seeded and unseeded storms. Silver concentrations in freshwater are also reduced by adsorption on vegetation and sediments such that silver concentrations in surface waters tend to decrease with distance from the source of silver (Cooper and Jolly, 1970). Dissolved silver (Ag^+) has exhibited rapid removal in freshwater environments, with a one to two-week half-life (Wen et al. 2002). Eisler (1996) reports average total silver concentrations of 0.3 ug/L in rivers, 2.6 ug/L in surface waters, and 2.2 ug/L in tap water across a large number of samples. In the California Sierra Nevada, the freshwater total silver concentrations from cloud seeded areas range from less than detection levels to 0.74 ug/L with most measurements within the range of typical freshwater silver concentrations (Table 2).

3.4 SILVER CONCENTRATIONS IN SOIL AND LAKE SEDIMENTS

Studies of silver concentrations in soils and lake sediments in cloud seeded areas document that silver concentrations in seeded areas have not increased above background levels found in non-seeded areas (Table 2). Measurements of total silver concentrations in soil at three different depths report higher surface concentrations, but the differences between the surface and middle layer or the middle and bottom layer were not statistically significant (Tsiouris et al. 2003). While seeded areas were not found to have elevated silver concentrations, a 1975 study found silver concentrations to be higher in the top 2 cm of soil within 50 m of a cloud seeding generator (USEPA 1981). In a study of the Mokelumne River watershed, average silver concentration in sediment samples ranged from 0.35 ug/L in Lower Blue Lake upwind of the cloud seeding area to 1.07 ug/L in Salt Springs Reservoir where runoff from the seeded area flows past (Stone 2006). Cloud seeding with silver iodide was reported to have a negligible enrichment impact on silver concentrations in lake sediments in a remote alpine lake in Australia (Stromsoe et al. 2013).

Table 2. Comparison of Measured Total Silver Concentrations in Seeded Areas with Typical Background Silver Concentrations.

Location	Total Silver Concentration Measured in Silver Iodide Seeded Areas	Source	Typical Background Total Silver Concentration	Source
AIR (ng/m³)				
Composite of U. S. measurements in rural areas	0.1 - 1.0	Eisler 1996	0.04 – 0.17	Eisler 1996
SNOW PRECIPITATION (ug/L or ppb)				
Composite of U. S. measurements	0.01 – 0.3	Eisler 1996	0 – 0.02	Eisler 1996
Lake Tahoe-Truckee River	0.003 – 0.022	Warburton et al. 1995	0.002	Warburton et al. 1995
Lake Almanor	0.004 – 0.02	Warburton et al. 1995	0.002	Warburton et al. 1995
Lake Tahoe -Truckee River (2003 – 2004)	0.0126 – 0.0894	Huggins et al. 2004	0.002	Warburton et al. 1995
Snowy Mountains, Australia	0 – 0.055	Manton and Warren 2011	0 – 0.025	Manton and Warren 2011
FRESHWATER (ug/L or ppb)				
Feather River – Lake Almanor (2000)	0 - 0.74	PG&E 2011	0.09 – 0.55	USEPA 1980; Eisler 1996
Feather River – Lake Almanor (2002 – 2003)	0.090 - 0.153	PG&E 2011	0.09 – 0.55	USEPA 1980; Eisler 1996
Mokelumne watershed	< 0.0005	Stone 2006	0.09 – 0.55	USEPA 1980; Eisler 1996
SOIL AND LAKE/RESERVOIR SEDIMENT (ug/L or ppb)				
Soil	37.2 – 44.5	Tsiouris et al. 2002	30.4 – 56.7	Tsiouris et al. 2002
Mokelumne watershed	0.35 - 1.07	Stone 2006	n/a	Stone 2006

4.0 ENVIRONMENTAL HAZARDS OF SILVER AND SILVER IODIDE

Studies of the environmental hazards of silver and silver iodide indicate that the toxicity of silver is primarily dependent on the type of silver present in the environment. The toxicity of silver in the environment strongly correlates with dissolved silver (Ag^+) (USEPA 1980, 1981, 1987, 2010a, 2010b; Eisler 1996; Ratte 1999; Williams and Denholm 2009; Cardno ENTRIX 2011; Fajardo et al. 2016). While silver and its compounds, including silver iodide, do not pose a serious health concern to humans (USEPA 1980, 1981, 2010a, 2010b), dissolved silver has been found to impact aquatic organisms, plants, and other biota at a range of concentrations depending on the organism and ambient conditions (Cardno ENTRIX 2011). An exposure and risk assessment for silver details some of the environmental hazards and toxicity of silver on both biota and humans (USEPA 1980, 1981, 1987), while Eisler (1996) provides an extensive list of the threshold silver concentrations at which adverse effects have been found on many species of invertebrates, aquatic organisms, terrestrial plants, and wildlife.

While dissolved silver (Ag^+) is the main form of silver that presents an environmental hazard, silver is typically analyzed and reported as total silver concentration, particularly in studies of silver iodide used in cloud seeding (Section 4.1). However, total silver concentrations overestimate the amount of bioavailable, toxic dissolved silver, particularly if any particulate silver (e.g., silver iodide) is present.

4.1 SILVER

There is a negligible environmental hazard to humans from silver in the environment, with silver impacting human health only at levels far greater than those found in the environment (USEPA 1981; Eisler 1996). Toxicity tests report silver having no effect on humans at concentrations of 200 ug/L. Chronic exposure to high levels of silver over a long time can cause a cosmetic gray or blue-gray discoloration of skin (USEPA 1981).

Dissolved silver is an environmental hazard to aquatic life with concentration of dissolved silver between 1.2 and 4.9 ug/L lethal to sensitive aquatic organisms, with trout experiencing adverse effects at dissolved silver concentrations as low as 0.17 ug/L in lab tests (Eisler 1996; Williams and Denholm 2009). Field measurements often find higher tolerances to silver than laboratory toxicity tests because dissolved silver toxicity is significantly influenced by the presence of other ions found in natural waters (Eisler 1996; Williams and Denholm 2009). Dissolved silver ions are fungicidal, algicidal, and bactericidal at low doses with bactericidal concentrations occurring between 10 – 1000 ug/L (Williams and Denholm 2009).

Dissolved silver has adverse impacts on terrestrial life at much higher concentrations than would be encountered from cloud seeding (Cooper and Jolly 1970; Eisler 1996). Eisler (1996) summarizes the impacts and threshold silver concentrations from a wide range of silver concentrations on tested crops, domestic poultry, livestock, and other small laboratory mammals. Adverse impacts were observed in crops from sprays

containing 9,800 – 100,000 ug/L dissolved silver. Poultry, livestock and small mammals experienced adverse effects after exposure over several months to drinking water with dissolved silver concentrations from 250 ug/L (rabbits) to 1,586,000 ug/L (rats). There were very limited data describing the effects of silver on laboratory poultry and mammalian life, and there were no studies of the potential effects on wildlife.

4.2 SILVER IODIDE

There are no documented environmental hazards associated with the standard silver iodide concentrations used in cloud seeding because it is insoluble and does not have the toxic properties of dissolved silver (Standler and Vonnegut 1972; USEPA 1980, 1981, 2010a, 2010b; Cardno ENTRIX 2011; PG&E 2011; Fajardo et al. 2016). Insoluble silver compounds are virtually non-toxic to terrestrial and aquatic vertebrates (Ratte 1999). USEPA (1981) specifically evaluates the exposure and risk from silver iodide in cloud seeding concluding that it is not likely to result in significant exposure levels for natural populations or microorganisms. Silver iodide in general and specifically as used in cloud seeding also is not a hazard to human health based on the historical medical usage in nasal sprays and tooth fillings and the evaluation of the health of cloud seeding generator operators (Standler and Vonnegut 1972).

Silver iodide used in cloud seeding is not likely to be an environmental hazard to the environment, with laboratory studies reporting no adverse effects on plants (Cooper and Jolly 1970), soil microbial populations (Klein and Molise 1975), methanogenic organisms (Castignetti and Klein 1979), freshwater phytoplankton (Fajardo et al. 2016), or livestock (Younger and Crookshank 1978). While Cooper and Jolly (1970) noted that there was a possibility that silver iodide impacts the growth of algae, fungi, bacteria, and fish in fresh water and recommended further research into the subject, subsequent studies of silver iodide have not documented impacts at concentrations expected from cloud seeding activities.

Silver iodide used in cloud seeding is not considered an environmental hazard by the California Department of Water Resources (DWR 2013, 2016). The California Water Plan Update 2013 concludes silver iodide from cloud seeding should not result in any chronic effect on sensitive aquatic organisms from a review of silver measurements in water, sediment, and fish from areas with cloud seeding (Hunter 2007; DWR 2013, 2016). The U.S. Bureau of Reclamation (USBR) determined the environmental hazard of silver iodide from cloud seeding is insignificant (USBR 1977; Harris 1981; Howell 1977; Hunter 2007).

4.3 DISPERSAL METHODS FOR SILVER IODIDE

There are no documented environmental hazards or risks associated with the dispersal methods for silver iodide assuming reasonable safe handling and operation of the individual components (Standler and Vonnegut 1972; Hunter 2007; PG&E 2011; County of Santa Barbara 2013; DWR 2013, 2016; Reynolds 2015). Cloud seeding disperses silver iodide by either burning a silver iodide solution with propane or burning flares

containing silver iodide. An analysis by the Northern Sierra Air Quality Management District found burning of the silver iodide solution with propane was a minimal environmental hazard (PG&E 2011). Flares used for cloud seeding are similar to a standard road flare with silver iodide added. The burning of the flares and the compounds released (e.g., silver iodide) are not considered an environmental hazard because the amount of compounds released is less than the irritant level listed in the manufacturer material safety data sheet (MSDS) and the combustion products are generally considered "inert" since they do not readily react with plants or animals (County of Santa Barbara 2013).

5.0 REGULATORY THRESHOLDS FOR SILVER AND SILVER IODIDE

There are no federal or state regulations for silver iodide because it is considered effectively insoluble and not bioavailable in the aquatic environment (Williams and Denholm 2009; Cardno ENTRIX 2011). USEPA does not have an ambient water quality criterion for silver iodide. The existing water quality criterion is based the bioavailable dissolved silver, which correlates with toxicity data (USEPA 1980, 1981, 1987). Cloud seeding with silver iodide is not regulated by the USEPA (PG&E 2011). In California, there are no water quality standards or criteria for silver iodide, and silver iodide is currently not discussed in the Central Valley Regional Water Quality Control Board's Basin Plan (RWQCBCV 2016). The Basin Plan does not identify silver iodide from cloud seeding as an activity that can impact water quality and it does not stipulate discharge requirements for silver iodide. In addition, the State of California's current 303(d) list of impaired water bodies (SWRCB 2017a) does not identify any water bodies in the target area as water quality limited for silver.

5.1 SILVER WATER QUALITY REGULATORY THRESHOLDS

All regulatory water quality standards for silver are focused primarily on the bioavailable dissolved silver with the silver concentration criteria set to protect human health and aquatic life. At the federal level, silver and its compounds are broadly designated as a toxic pollutant because of its impacts to aquatic life and historical usage as a disinfectant (USEPA 1980, 1981). Regulatory thresholds for silver are detailed in Table 3 below. The USEPA establishes both primary maximum contaminant levels (MCLs) and secondary MCLs for many substances. Primary MCLs are enforceable standards to prevent a risk to human health, while secondary MCLs are non-mandatory standards designed to manage aesthetic conditions like taste, color, or odor. There is no risk to human health at secondary MCLs. The USEPA has no primary maximum contaminant level (MCL) for silver in drinking water, but the USEPA secondary MCL for dissolved silver is 100 ug/L in drinking water (USEPA 2010a, 2010b, 2013). Similarly, the California State Water Resources Control Board lists no primarily MCL and sets the secondary MCL for dissolved silver in drinking water as 100 ug/L (SWRCB 2017b). The USEPA guideline for silver in freshwater is 3.2 ug/L with a hardness of 100 mg/L as the acute toxic limit, but there is no chronic guideline value (USEPA 2004, 2017).
While not regulatory thresholds, Eisler (1996) proposed total silver concentration criteria for the protection of natural resources and human health based on an exhaustive review

of the ecological and toxicological hazards of silver found in scientific literature and reports.

5.2 SILVER AIR QUALITY REGULATORY THRESHOLDS

Cloud seeding with silver iodide has been evaluated by regulatory agencies that found emissions from the dispersal of silver iodide do not exceed any regulatory thresholds (Williams and Denholm 2009; USEPA 2010b; PG&E 2011). Table 3 summarizes the regulatory thresholds for silver in the air. Silver iodide emitted by ground-based cloud seeding methods was not a concern in an analysis by the Northern Sierra Air Quality Management District (NSAQMD) of the ground-based dispersal of silver iodide (PG&E 2011).

Silver iodide particles produced from burning the silver iodide solution in CNGs or silver iodide flares are approximately 0.1 micrometers [micron or um], but the amount emitted by cloud seeding has been found to be far less than federal and state triggers for permits controlling emissions of 10 micron (PM 10) and 2.5 micron (PM 2.5) sized particles (PG&E 2011). The California ambient air quality standards for PM 10 is 50 ug/m^3 per 24 hours and the annual arithmetic mean is 20 ug/m^3, while for PM 2.5 the annual arithmetic mean is 12 ug/m^3. The national ambient air quality primary standards for PM 10 is 150 ug/m^3 per 24 hours while for PM 2.5 is 35 ug/m^3 per 24 hours and the annual arithmetic mean is 12 ug/m^3 (CARB 2016). The El Dorado County Air Pollution Control District (EDCAPCD) uses the California and national ambient air quality standards for PM 10 and PM 2.5 (EDCAPCD 2002).

Table 3. Silver Regulatory Thresholds.

Regulatory Threshold Description	Regulatory Agency	Regulatory Threshold	Source
DRINKING WATER			
Primary maximum contaminant level (MCL)	USEPA, SWRCB	None	USEPA 2013; SWRCB 2017b
Secondary maximum contaminant level (SMCL)	USEPA, SWRCB	100 ug/L	USEPA 2013; SWRCB 2017b
FRESHWATER			
Acute toxic limit (Criteria Maximum Concentration [CMC])	USEPA	3.2 ug/L[A]	USEPA 2004, 2017
Chronic toxic limit (Criterion Continuous Concentration [CCC])	USEPA	None	USEPA 2017
AIR			
U.S. workplace airborne limit	NOHSC	0.1 g/m^3	NOHSC 1995; Williams and Denholm 2009
Occupational exposure limit for silver metal, silver compounds, and soluble silver compounds	OSHA	0.01 mg/m^3	USEPA 2010a

[A] At hardness of 100 mg/L

6.0 SMUD CLOUD SEEDING PROGRAM

6.1 TARGET AREA

SMUD has conducted cloud seeding in the Sierra Nevada since the 1968–1969 rainy season. SMUD cloud seeding typically disperses silver iodide particles from November through April. Cloud seeding has occurred over a 190-square mile target area in the South Fork American River watershed upstream of the UARP, where the latter is operated by SMUD for hydroelectric power generation. SMUD is currently planning to expand its target area to 444-square miles (Figure 1). The target area is located primarily in El Dorado County, California, east of Sacramento County and west of the Tahoe Basin.