TO: Colorado Water Conservation Board Members

FROM: Joe Busto, Staff
Watershed and Flood Protection Section

DATE: January 11, 2018

AGENDA ITEM: Agenda Item 14, Silver Iodide in the Environment

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Background: The CWCB just completed five public hearings around the state to solicit public input on renewing permits for ground based winter time cloud seeding programs. Three winter time cloud seeding permits were renewed through the DNR process to get a State of Colorado weather modfiication permit for the general areas of a: Gunnison, Dolores/Telluride, and the Central Colorado Mountains cloud seeding programs. At the November Finance Committee a citizen spoke to the Board and expressed concerns about silver iodide. Staff will give an overview of the weather modification permitting process. Staff will explain what is in the literature about silver iodide (AgI) and its use in cloud seeding.   Frank McDonough of Desert Research Institute will attend the CWCB meeting as well. Desert Research Institute is a world class research facility in Reno, Nevada that operates and evaluates cloud seeding programs in the west. DRI does trace chemistry analysis for silver as well. DRI will look for minute amounts of silver in snowpack above background concentrations. Trace Chemistry of snowpack will help give you evidence of cloud seeding's contribution to total snowpack. If you sample snowpack downwind in your intended target area and find traces of silver then you are likely targeting the area properly. This type of evaluation is helpful for this discussion.

It is not uncommon to have periodic concerns expressed for the environment. A Pacific Gas and Electric and question and answer document, and published abstract about a silver toxicity monitoring project are attached for the Board to review. Staff and DRI will discuss this issue, comment on the previous statements made to the Board in November.

Summary
This is an informational itme with no board action requested.

Responses to Questions Regarding Cloud Seeding in the Lake Almanor Basin

Updated: September 13, 2011

1 Foreword

Pacific Gas and Electric (PG&E) received a number of questions regarding its cloud seeding program from the Almanor Basin Water Advisory Committee (ABWAC) and local residents. On May 26, 2011, ABWAC sponsored a community forum in Chester to facilitate further discussion between experts, ABWAC Board Members and the public. PG&E was requested to prepare a written response to questions following the public forum. Questions received by PG&E and responses are provided in Appendix A of this document. Each question is answered by reference to page number and paragraph in the following overall response.

The responses are organized by the following major headings:

- Introduction
- PG&E Seeding Program in the Lake Almanor Watershed
- Environmental Effects
- Air Quality
- Regulatory Setting
- Nanoparticles

2 Introduction

Cloud seeding has steadily increased since its discovery early in the 20th century. In California, cloud seeding has been implemented since the early 1950s, one of the longest records of seeding in the world. Nationally, cloud seeding is used primarily to augment water supplies for domestic use, for agriculture, and to augment stream flows for hydroelectric generation. Most programs in California have been conducted in winter over the Sierra Nevada, and are intended to augment the snowpack. The additional snowpack melts and runs off, providing water for multiple beneficial uses. As climate change has led to reduced snowpack and other hydrologic impacts, the Intergovernmental Panel on Climate Change (IPCC, 2007) and the California Department of Water Resources (DWR, 2009) have embraced cloud seeding as one adaptation technique.

Cloud seeding is being conducted in numerous areas of the western United States in order to augment public water supply, hydro-electric power, increase summer precipitation for agriculture and grazing, aquifer recharge and hail suppression (Figure 1). Winter cloud seeding programs in California began more than 50 years ago and in the last 20-years cloud seeding has been conducted in 11 to 14 watersheds annually (Figure 2). Sponsors of these programs include public water supply agencies, agricultural water agencies, and power generation agencies.

The seeding particles are typically in a size range of 0.05 to 0.10 micron. At this size they float in the air with the wind and have a negligible settling velocity. They are dispersed by the turbulence of the wind and they rise with the lift of the air that occurs in the mountains during storms. The silver iodide – silver chloride bismuth oxide portion of the particle is very insoluble and it acts as an ice nucleus (freezes water) upon contact with super-cooled (sub-freezing) liquid water cloud droplets (ASCE 2006). The potassium chloride (KCl) portion of the particle is hygroscopic (attracts water) and it is soluble in water.

4 Environmental Effects

This section describes the environmental effects of cloud seeding particles, starting with introduction to the air by the cloud seeding burner, through snowfall, snow melt, and subsequent transport. The results of specific studies evaluating the environmental effects of cloud seeding are then presented.

4.1 Environmental Transport

Silver iodide and the closely related silver chloroiodide ($AgI_{0.8}Cl_{0.2}$) 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. 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 (Williams and Denholm, 2009).

Several multi-year studies, summarized in Cardno ENTRIX 2011, 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.

Cloud seeding aerosol is formed by ground-based burners, as described previously. After leaving the burner, the seeding particles are carried by the wind and rising air currents into the clouds. Some of the seeding particles are swept from the air to the earth surface by existing falling snow particles. However, a portion of the seeding particles enter the cloud. At cloud temperatures below minus 5° C and when super-cooled liquid water is available the seeding particles trigger the formation of ice crystals upon contact with the cloud droplets. The new ice crystal with particle grows in size and falls from the cloud as snow (ASCE 2006). Release into the atmosphere does not change the physical or chemical properties of the seeding particles. The physical shape changes as the new ice crystals that contain the seeding particles grow by vapor deposition and aggregation to sizes large enough to fall from the clouds to the earth's surface (Mason, 1962; Bras, 1990, ASCE, 2006).

Once on the ground, the snow melt water carries the seeding particles to the soil surface where they adhere to the surface dirt particles, decayed plant material and plant life (moss, algae) (Williams and Denholm, 2009; Cardno ENTRIX, 2011). Since the silver iodide is practically insoluble, it does not tend to percolate downward in the soil column. The potassium chloride would be dissolved (ionized) and would chemically combine with other ions in the soil to form solids. Potassium is a plant nutrient and it would likely be absorbed by live plant roots. Previous studies in cloud seeding areas have examined the upper 20 cm (about 8 inches) to find seeding chemical concentrations within the range of background concentrations (Cardno ENTRIX, 2011), and more recent soil studies of cloud seeding areas in Australia have focused on the upper 2 cm (<0.8 inch) of soil (Lincoln-Smith, et al., 2011) with the same results.

During snowmelt, some of the seeding particles are carried in the runoff to surface water courses. (William and Denholm, 2009). The seeding particles that fall upon surface water enters the water as does that which falls upon ice covered surface water upon ice melt. The particles move with the water, and eventually become part of the sediments that collect at the bottom of lakes, stream beds, and rivers. The physical and chemical properties of the insoluble seeding particles do not change in the water and sediments. The potassium chloride dissolves in water and subsequently combines with other water chemicals and/or becomes nutrients for aquatic plants.

4.2   Effects of Silver on Humans, the Environment, and Related Testing

Silver iodide is the chemical species of silver that is most commonly used cloud as seeding nuclei, because it is practically insoluble and has a structure that closely mimics that of ice. In contrast, the free silver ion (Ag^+) has been used as a disinfectant. The similarity in nomenclature between silver iodide and free silver ion has led to concerns about the environmental fate of silver iodide particles, but it is important to understand that silver iodide is used in cloud seeding, not silver ions. Silver is not toxic to humans, and it is used for tooth fillings, silverware, and other common consumer items. The drinking water standard, or secondary maximum contaminant level (MCL), was developed to reduce nuisance conditions, and is set at 100 μg/L (micro-gram per liter, or part per billion) dissolved silver. There are no toxicity-based drinking water standards (primary standards) for silver in drinking water set by EPA or California because it is not toxic to humans.

Studies of the free silver ion (Ag^+) have found adverse consequences to plants and other biota, and most ecological guidelines are lower than the drinking water standard. The lowest freshwater aquatic life protection guideline found in the literature, and reported in Cardno ENTRIX 2011, is 1.4 parts per billion. 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 silver iodide, which is practically insoluble and so does not produce free silver ions. It is important to note that in discussions of toxicity, concentrations of silver iodide are compared to standards for total silver. This comparison is not meant to imply that total silver (including the free silver ion) 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 ion and iodine (which in fact it does not), the concentrations of silver affected by cloud seeding are still less than any drinking water, aquatic life, or terrestrial life standards.

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PG&E's tests in the Feather River-Lake Almanor between 2000 and 2003 examined total silver (from all sources) in the water and sediments (Appendix E). The 2000-01 tests used a method detection limit of 0.36 parts per billion, and all results were below freshwater aquatic life protection guidelines. In a study conducted in 2002 and 2003, PG&E collected water samples and analyzed them for several constituents, including dissolved silver. The method detection limit used in these studies for water was 0.090 parts per billion. A total of 35 water samples analyzed in these studies had concentrations below method detection limits, one sample showed 0.093 parts per billion. Another showed 0.153 parts per billion, and this value is about 10 to 20 times lower than freshwater aquatic life protection guidelines and 650 times below the secondary maximum contaminant level (SMCL), or drinking water standard, of 100 parts per billion.

Total silver concentrations in water sampled at Salt Springs and Lower Blue Lakes (Mokelumne River where PG&E has seeded for 59 years) average less than 0.0005 part per billion in 2006, similar to background concentrations in other central Sierra lakes (Stone, 2006). This is more than 200,000 times below human water standards and 1,000 times below freshwater aquatic life protection guidelines).

Cardno ENTRIX 2011 summarizes the evidence-based studies related to cloud seeding and public health correlations; no studies have indicated a correlation between cloud seeding and public health concerns. Measured concentrations are typically many times safer than the drinking water standard.

5 Air Quality

Based on Air Quality Index values as determined by monitoring at Chester and Mt. Lassen National Park, PG&E's cloud seeding operations occur during dates of satisfactory (Good) or acceptable (Moderate) air quality index values (see Appendix B). Inversions, which could inhibit successful cloud seeding, are generally associated with calm, fair weather, with night-time and very early morning hours frequently having a surface base temperature inversion. Also, high pressure systems aloft can be associated with temperature inversions occurring over the Plumas County region. PG&E cloud seeding operations are conducted during windy, stormy condition as low pressure systems and weather fronts move across the area. These windy, stormy conditions are not typically associated with inversions, and cloud seeding aerosols released during these conditions would not concentrate near the ground nor create health problems for the Plumas County residents.

The NSAQMD is the regulatory agency with jurisdiction over the emission of criteria pollutants for Plumas County. Cloud seeding in California does not require an air permit, and to confirm this, the NSAQMD calculated the emissions from PG&E cloud seeding and compared the results to the criteria for an air permit. The calculation method overestimates potential exposure in order to apply to any case the District may consider. Using this conservative approach, p-dichlorobenzene was the only chemical of any concern in the cloud seeding solution. The results of the NSAQMD calculation was that the potential emission rate of p-dichlorobenzene is 30 times lower than the level that might trigger the need for a permit. As previously discussed, p-dichlorobenzene is not released to the air but is consumed by combustion, so NSAQMD's

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analysis is hypothetical and extremely conservative. In addition, the calculation assumed that all the emissions were released from a single burner, rather than more dispersed by the actual use of 10 burner units. The NSAQMD email summarizing their approach and results is provided in Appendix C.

6   Regulatory Setting

6.1   Pertinent Monitoring Programs

PG&E has conducted comprehensive monitoring studies of the effects of cloud seeding in the Lake Almanor Basin and the Mokelumne watershed as part of relicensing the hydroelectric projects through the Federal Energy Regulatory Commission. These studies have not identified human health or ecological concerns related to cloud seeding, even using ultra-low laboratory detection limits. The PG&E studies are consistent with and supported by the literature on the environmental effects of cloud seeding using silver iodide (Cardno ENTRIX, 2011). The Federal Energy Regulatory Commission, supported by the agencies participating in the relicensing studies, did not recommend long-term monitoring for cloud seeding. However, as part of the Project Number 2105 Relicensing Settlement Agreement (April 2004) for Lake Almanor and the North Fork Feather River, silver is included as one of the constituents in PG&E's proposed water quality monitoring program. The silver monitoring is not required as a result of cloud seeding, but is a component of the suite of metals that are included in the water analyses.

Cloud seeding is not directly regulated by the EPA, but PG&E's cloud seeding activity complies with regulatory guidelines for the protection of air quality, water quality, human health, and the environment.

6.2   Materials Safety Data Sheets for Worker Safety

The MSDS for silver iodide, and many other materials, are prepared by the manufacturer and lists hazards due to ingestion, skin contact, and inhalation. For *ingestion*, the MSDS cites a study on rats that required a very high intake of silver iodide for the hazard; the cited level is the equivalent of feeding the animal one-fourth its body weight in silver iodide. These levels would not be encountered in the environment. The animal testing dose level would result in the least hazardous classification possible in the Globally Harmonized System of Hazard Classification (UN, 2010) being implemented around the world. For *skin contact*, the hazard identified is as an irritant. While skin irritation can be considered a hazard in some contexts, it is reversible once the irritant is removed, and it does not have long-term effects. Workers handing bulk silver iodide may be exposed to this irritant. For *inhalation*, the concern is related to inhalation of fine and ultrafine levels that may occur in the manufacture of this material. The amount of dust necessary to cause lung irritation is far higher than would be encountered in the environment with cloud seeding.

In short, the MSDS is written to cover the range of exposures and hazards that may occur, from manufacture to end use. The hazards identified are ones that could occur to workers handling the bulk material, and health and safety plans address these concerns. The hazards identified in the

MSDS do not apply to cloud seeding related environmental levels of exposure because of the resulting very small chemical concentrations. The effects of environmental levels of exposure are summarized in Cardno ENTRIX, 2011.

All chemicals can be toxic to humans; toxicity is determined in large part by the dosage. In toxicology this is referred to as the dose-repose relationship (Schiefer, et al., 1997). The cloud seeding particles, silver iodide-silver chloride- bismuth oxide-potassium chloride, are shown in the MSDS as non-carcinogenic but do potentially produce toxic effects similar to table salt (sodium chloride) and toothpaste (sodium fluoride), depending on dosage. The MSDS for sodium fluoride indicates its potential toxic hazards are more severe than the seeding particles (Appendix D); however, sodium fluoride is used in very low concentrations (dosage) in toothpaste, resulting in a non-toxic response. Environmental concentrations of the seeding chemicals are extremely small (parts per trillion range) and for practical purposes can be considered non-toxic, for the same reason as for sodium fluoride in toothpaste (dose-response relationship).

6.3   Other Considerations

Some comments have referred to silver iodide being considered "Class C chemical" by the UC Berkeley, Office of Environmental Health and Safety, although to date PG&E has not received this documentation from any commenter. However, this designation pertains to the disposal of waste chemicals down drains at UC Berkeley. This designation stems from the discharge limit imposed on East Bay Municipal Utilities District (EBMUD) which receives waste water from UC Berkeley. It addresses much higher concentrations than are used for cloud seeding.

7   Nanoparticles

Questions were asked about nanosilver, or nanoparticles of silver. Nano refers to the size of particles; a nanoparticle is by definition less than 100 nanometers (nm) in any dimension. Cloud seeding particles are approximately 100 nm. Submicron (nano) sized particles are most effective in cloud seeding, and this has been the case since program inception.

The USEPA is evaluating the toxicity of nanosilver as it is applied in consumer products such as clothing, medical equipment, shampoo, toothpaste, nutritional supplements, and other consumer uses. These studies are summarized in *State of the Science Literature Review: Everything Nanosilver and More* (USEPA 2010 a), and *Nanomaterial Case Study: Nanoscale Silver in Disinfectant Spray* (USEPA 2010 b). These studies summarize product testing and related information to set research goals, as well as summarizing the environmental information such as that provided in the Cardno ENTRIX 2011 study. USEPA (2010 a) does note that silver iodide is used in cloud seeding, but the focus of their review was on the use of the antimicrobial form of silver (silver ion) as nanoparticles in commercial uses by consumers.

Engineered nanoparticles are specifically made to retain their nanosize in commercial applications such as surface coatings or consumer and medical products. They lose their nano size, and much of their effectiveness as antimicrobial agents, in the environment as they grow or clump and stick together (agglomerate) (USEPA 2010 a). Engineered nanosilver is also

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specifically made to be predominantly the ionic form of silver, which is the effective anti-microbial agent.

In the case of cloud seeding, however, the particles are not engineered nanosilver. The particles are produced by combustion, some of which are approximately 100 nm and therefore meet the size definition of a nanoparticle. In addition, the nanoparticles produced by cloud seeding are silver iodide particles, which do not have the anti-microbial effects of engineered ionic silver nanoparticles.

7.1   Toxicity of Silver Nanoparticle

Environmental studies indicate that the forms of silver that dissolve and release free silver ions (Ag+) are more toxic than insoluble silver species such as silver iodide. Most researchers believe that the toxic effects of silver-containing materials are directly related to the release of ionic silver (USEPA, 2010 a, b). Silver iodide, the form of silver used in cloud seeding, is practically insoluble, and retains its composition through cloud seeding, snowfall, and snowmelt, ultimately bonding to soil particles (see Cardno ENTRIX, 2011). As such, silver iodide behaves very differently in the environment than do silver ions, and silver iodide does not share the toxic properties of silver ions. The toxic effects of silver ions are principally in the aquatic environment and affect bacteria. This is the reason that nanosilver is engineered to be applied in consumer products: the silver ion makes an effective anti-microbial agent.

In comparing the effects of nanosilver to the regular metal, the relatively large surface area compared to the volume of the nanoparticle leads to increased antimicrobial benefits due to the increased activity of free silver ions released by the nanoparticles. Since silver iodide is practically insoluble, nanoparticles of silver iodide would not have the antimicrobial property of nanosilver engineered to consist of elemental or ionic silver.

The USEPA (2010a, 2010b) is clear that silver is not a human carcinogen. According to the USEPA (2010a, 2010b), no such evidence has been presented despite long-term industrial use of silver, the natural occurrence of silver in the environment, and the growing use of nanosilver in commercial products.

7.2   Status of Research

Contemporary research on nanosilver is well summarized in both of the 2010 USEPA documents cited above. There is good data on manufacturing nanosilver and products with nanosilver. The intent of manufacturing is to ensure that the antimicrobial form of silver (silver ion) is available at the surface, and to keep the nanoparticles from agglomerating and thereby losing their nano size and properties. The USEPA (2010a) recommend further study in several areas, focused on the potential effects of engineered nanosilver on human health and the environment. The emphasis is on how nanoparticles interact with various types of cells, and the fate of nanoparticles in the environment. The USEPA cites the information on regular silver in the environment (also summarized in Cardno ENTRIX, 2011), and recommends validating those findings when applied to the nano scale, particularly with respect to the possibility that engineered nanosilver may have toxicity due to the small particle size itself introducing ionic silver into cells.

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AN ASSESSMENT OF THE ENVIRONMENTAL TOXICITY OF SILVER IODIDE – WITH REFERENCE TO A CLOUD SEEDING TRIAL IN THE SNOWY MOUNTAINS OF AUSTRALIA

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Abstract. The objectives of the Snowy Precipitation Enhancement Research Project are to determine the technical, economic and environmental feasibility of augmenting snowfalls in the Snowy Mountains region of New South Wales. The project commenced during 2004, following proclamation of special enabling legislation, the *Snowy Mountains Cloud Seeding Trial Act 2004* (NSW). Amongst other things, the legislation prescribed a target area of approximately 1000 square kilometres (mostly within the Kosciuszko National Park), and scheduled completion date of 2009. The legislation also mandated the use of silver iodide as the seeding agent. The *Snowy Mountains Cloud Seeding Trial Act 2004* (NSW) was amended in May 2008, expanding the size of the target area to around 2150 square kilometres, and authorising the continuation of cloud seeding activities until April 2015. An extensive review of the literature was undertaken prior to commencement of the project to determine if the use of the silver iodide (AgI) seeding agent would have an adverse impact on the environment. Although silver ions from water-soluble silver salts have been shown to be toxic to aquatic species, this is not the case for the insoluble silver iodide. Many studies have shown that the toxicity of silver ion in water is significantly ameliorated by the presence in water of chloride ion, carbonate ion, sulfide ion and dissolved organic carbon. In addition, silver has been shown to strongly adsorb onto particulate matter in water. Recent research has shown that silver ion concentrations in natural waters are negligibly small, and an investigation in the study area has confirmed many of these ameliorating factors to be present. Consequently the bioavailability of silver is unlikely to change from the current background levels. 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 silver the ion. An analysis of ecotoxicity monitoring data collected over the first four years of the SPERP has shown that the monitoring program has sufficient power to detect any adverse trend in silver concentration well before a level of environmental concern is reached. The SPERP monitoring results to date have all shown mean concentrations of total silver to be well below any level of concern, and we consider the risk of an adverse ecotoxicological impact resulting from the use of silver iodide for this project to be negligibly small.

1. INTRODUCTION AND BACKGROUND

The Snowy Precipitation Enhancement Research Project ("SPERP") is an eleven year cloud seeding research program designed to assess the technical, economic and environmental feasibility of augmenting snowfalls in the Snowy Mountains Region of New South Wales ("NSW").

The SPERP commenced during 2004, following proclamation of special enabling legislation, the *Snowy Mountains Cloud Seeding Trial Act 2004* (NSW) (the "Act"). Amongst other things, the Act prescribed a target area of approximately 1000 square kilometres, and a scheduled completion date of 2009. The legislation also mandated the use of silver iodide (AgI) as the seeding agent.

The Act was amended in May 2008, expanding the size of the target area to approximately 2150 square kilometres, and providing for a continuation of cloud seeding activities until April 2015.

Most of the SPERP target area lies within the Kosciuszko National Park ("KNP"), a place with legislated Australian National Heritage Significance, and also a UNESCO declared World Biosphere Reserve. A large proportion of the SPERP infrastructure and monitoring equipment is located within the KNP.

Given the environmental setting of the SPERP target area, a comprehensive investigation of the potential environmental impacts was undertaken prior to commencement of the project in 2004. This investigation included an extensive review of the literature:

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- To determine if the use of AgI would result in a significant adverse impact on the environment; and
- Design a monitoring program and environmental management plan appropriate to the project setting and environmental risks identified.

In this paper we present the key elements of the literature review and its relevance to the SPERP, and provide a brief overview of the SPERP ecotoxicity monitoring program and brief interpretation of the monitoring results to date.

2. GENERAL CHEMICAL AND PHYSICAL PROPERTIES OF SILVER AND SILVER COMPOUNDS

The element silver occurs naturally in the earth's crust at a concentration of 7×10^{-2} mg/kg (Handbook of Chemistry and Physics) and is found in the free state as the metal, and as ores such as the sulfide, arsenide and chloride (Cotton and Wilkinson, 1962). The metal is not soluble, but salts such as silver nitrate ($AgNO_3$) are very soluble. Other silver salts, such as the sulfide (Ag_2S), chloride (AgCl) and iodide (AgI) are insoluble in water (Purcell and Peters, 1998).

Insoluble or complexed silver compounds were found to be much less toxic or essentially nontoxic to a range of terrestrial and aquatic vertebrates (Ratte, 1999). Silver thiosulfate was found to be 15,000 times less toxic, and AgCl 11,000 times less toxic than silver nitrate (Ratte, 1999). Particulate AgCl is described as virtually nontoxic (Bury et al. 1999; Rodgers et al. 1997). The importance of speciation of trace metals such as silver is well understood (Allen and Hansen 1996).

The silver cation (Ag^+) binds strongly with ligands found in natural waters, hence its toxicity will be reduced by the presence of substances with which it can associate or form covalent bonds. Some silver complexes and silver ions are readily adsorbed to particulate matter to the extent that only some 25% of total silver is estimated to be dissolved as either ion, colloid or complex (Wen et al. 1997).

Free silver ion is known to be fungicidal, algicidal and bactericidal at relatively low doses. Typically, bactericidal concentrations are of the order of 0.01 to 1.0 mg/L, which are well below human health hazard levels. Soluble silver compounds are used in medicine and for sterilising potable water, in part due to the sensitivity of bacterial metabolism to Ag^+ inhibition of the thiol functionality in enzymes.

2.1 Solubility of Silver Salts

Silver is known to be a particular hazard in aquatic environments, however research over the last decade and more has shown that the toxicity is essentially a function of silver speciation, rather than total dissolved silver ion concentration (Bowles et al. 2002, Shafer et al. 1998, and others). Nevertheless, a consideration of solubility is a useful starting point in an assessment of its likely bioavailability.

The solubility in water of some selected silver compounds is shown in Table 1 below.

In solution, the silver ion (Ag^+) has been shown to be toxic to aquatic plants and a range of animals (see for example Table 3), however the toxicity has been clearly demonstrated to be dependent on the chemical form, and has been shown to correlate with free ionic silver (Ag^+).

For silver salts such as silver nitrate (which dissociate strongly) the concentration of silver ion equates to the concentration of the silver salt.

Table 1: Solubility of Selected Silver Salts		
Salt	**Solubility (in g/100 ml)**	
	Cold water	**Hot water**
Silver nitrate $AgNO_3$	122	952
Silver chloride AgCl	0.000089	0.0021
Silver iodide AgI	insoluble	insoluble
Silver sulfide Ag_2S	insoluble	insoluble

Most importantly, as Ratte (1999) has noted *inter alia*, "...the perception of high silver toxicity has long been due to the fact that most laboratory toxicity trials used $AgNO_3$, which readily dissolves releasing the highly toxic free silver ion".

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

The concentration of Ag^+ derived from an insoluble silver salt is determined by the dissociation constant K_{SP} which (in the case of silver iodide) limits the concentration of silver ion to ca. 9×10^{-9} M. This means that the concentration of Ag^+ in a solution containing silver iodide cannot be greater than this value. In contrast, the Ag^+ concentration derived from silver nitrate (as shown in Table 1), is many orders of magnitude greater than that of silver iodide.

For the insoluble silver salts, the concentration of silver ion in equilibrium with the solid silver salt can be determined from the solubility product constant. The solubility product constants for the silver salts of interest are shown in Table 2 below. The calculated silver ion concentrations that would exist in aqueous solution (at equilibrium) are also shown.

The significance of the data in Table 2 is that for silver iodide, the maximum concentration of silver ion in an aqueous solution in equilibrium with solid silver iodide is 9.2×10^{-9} M (9.84×10^{-7} g/L). In comparison, the maximum silver concentration that can be reached for silver sulfide is 2.56×10^{-17} M (2.73×10^{-15} g/L).

This means that solid silver iodide is an extremely poor source of silver ions in solution.

3. TYPICAL LEVELS OF SILVER IN THE ENVIRONMENT

Silver is a widely distributed element, and until relatively recent times used for many applications and extensively in the photographic industry. Waste water from that industry is known to have accounted for significant silver fluxes into the environment (Hirsch, 1998). Although that use is declining, silver is being used more widely in medicinal applications. Silver ions have also been reported in waters adjacent to silver mine sites and municipal waste waster treatment plants (Kramer *et al.* 1999).

Silver is a normal trace constituent of many organisms. Terrestrial plants for example usually contain silver at less than 0.1 mg/kg dry-weight, with seeds, nuts, and fruits containing higher concentrations than other plant parts (USEPA (1980), cited in The Concise International Chemical Assessment Document 44 (2002) ("CICAD 44") and Irwin (1997).

3.1 Soils, Sediments and Water

The CICAD 44 monograph reports silver levels for various environmental matrices. For pristine, unpolluted areas such as rivers, lakes and estuaries, levels of about 0.01 µg/L were found, while for urban and industrialised areas the levels were typically 0.01 to 0.1 µg/L.

Estuarine waters in San Francisco Bay were found to range from 6 to 250 pM (0.65 to 27 ng/L), while in a number of Wisconsin rivers, silver concentrations ranged from 1.2 to 72 ng/L. Wen *et al.* (2002) note rapid removal rates in freshwater environments of the Ag^+, with a one to two weeks half-removal time even for pristine environments.

Table 2: Solubility Product Constants for Some Silver Salts (Handbook of Chemistry and Physics)

Salt	Solubility product constant K_{SP} at 25°C	Silver ion concentration (M)
Silver chloride AgCl	1.77×10^{-10}	1.33×10^{-5}
Silver iodide AgI	8.51×10^{-17}	9.2×10^{-9}
Silver sulfide Ag_2S	6.69×10^{-50}	2.56×10^{-17} M

Silver is more bioavailable under conditions of low anion concentrations, low levels of reactive sulfide or sulfur containing ligands, low concentrations of organic ligands (humates), lower suspended sediment and lower pH (Hogstrand and Wood, 1998). In soils and fresh water, the primary silver compounds under oxidizing conditions were believed to be chlorides, bromides and iodides. Under reducing conditions the free metal and silver sulfide are the principal species (CICAD 44).

Recent published work (Bowles *et al.* 2002a) has shown that sulfides are very important regulators of silver ion concentration, even under oxic conditions.

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

Although they did not report silver levels in the ocean generally, Martin *et al.* (1983) showed that silver levels in the north-eastern region of the Pacific Ocean were ca. 1 pmol/kg (1.07 x 10^{-7} mg/L) and increased with depth to 23 pmol/kg at 2440 m.

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

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

Silver concentrations in the treated soils ranged from 37.2 to 44.5 µg/kg, compared with the concentrations in the control areas which ranged from 30.4 to 6.7 µg/kg.

Contamination by silver in aquatic environments has been reviewed by Flegal *et al.* (1997).

3.2 Air

Concentrations of silver in air have been reported from time to time. For example, silver concentrations in air near a smelter have been measured at 36.5 ng/m^3 and a level of 2.0 µg/m^3 in atmospheric dust (CICAD 44). Concentrations of up to 0.075 ppm (0.075 mg/kg) Ag in dust collected over the SPERP target area have been observed by Kamber *et al.* (2009). It is clear from this work that silver travels great distances from its source.

The level of silver in the air in polluted environments has been reported by Bowen (1986) for both Britain (0.0001 to 0.001 µg/m^3) and the US (0.01–0.02 µg/m^3). It is worth reiterating that the levels allowed in air are typically much higher than levels reported in snow following cloud-seeding operations (Warburton *et al.* 1995b, Snowy Hydro Limited 2008).

Estimating acceptable exposures in non-occupationally exposed populations can be difficult, as data or recommended exposures are lacking. The US workplace airborne limit for silver is 0.1 g/m^3 (NOHSC 1995).

3.3 Silver Concentrations in Snow

The metal composition of snow has also been studied in a number of environments including the US and the Antarctic. For example, Warburton *et al.* (1981) have examined trace metal levels in snow in the Antarctic and concluded that the silver found was derived from marine sources. They also reached the same conclusion following a study of levels of metals in snow across the continental US.

The natural background level of silver in snow in the Snowy Mountains Main Range was determined during the course of an earlier study on snow enhancement (Snowy Mountains Council Meteorology Working Group 1989). Typical levels were reported to be 5 ng/L (5x10^{-12} g/L) and generally were less than 2 ng/L.

Detection limits were stated to be between 2 to 5 ng/L. One site, next to an alpine village, showing between 3 to 10 times background (10 to 30 ng/L), was believed to reflect emissions from over-snow vehicles, chair lifts and fossil fuel emissions. The silver concentration in stream runoff was below the detection limit of 1×10^{-7} g/L (SMHEA 1993).

4. TOXICITY OF SILVER ION

The toxicity of the silver ion (Ag^+) in water to a range of aquatic species has been the subject of a great number of studies reported in the scientific literature. These studies have been comprehensively reviewed by Eisler (1996), Ratte (1999) and others.

4.1 Acute Silver Toxicity

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

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

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

In a detailed study of the mechanism of toxicity of silver ion (using silver nitrate), Grosell et al. (2000) found a difference in tolerance to free silver ion between European eels and rainbow trout of 3 to 4 fold. The 96-hr LC_{50}'s ranged from 5 to 70 µg/L. For trout, the silver ion inhibited both sodium ion and chloride ion influx whereas for eels only the sodium ion influx was inhibited.

The key target of inhibition in trout and eels was found to be branchial Na^+, K^+-ATPase, an enzyme that drives uptake of Na^+ needed to counter diffusive loss of Na^+ to the hypo-osmotic environment. This is similar to the findings of Webb and Wood (1998) and Wood et al. (1999),

who examined physiological responses in rainbow trout rather than toxicity. In each case the source of the silver ion was silver nitrate.

In the Australian context, acute silver ion toxicity is generally considered to be of the order of 1×10^{-7} g/L, although the Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZECC and AMRCANZ 2000) give 0.005 µg/L as a Guideline Trigger Value ("GTV"). The Australian Drinking Water Guidelines (National Health and Medical Research Council 2004) cite a guideline value of total dissolved silver of 0.1 mg/L.

In the US the EPA has set a guideline of 4.7 µg total Ag/L in water with a hardness of 120 mg/L as the acute toxic limit. There is no chronic guideline value.

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

The CICAD 44 monograph has tabulated the range of aquatic species that have been used in toxicity tests with silver ion. The toxic silver concentration for each species is also given in CICAD 44.

4.2 Chronic Toxicity of Silver Ion

The importance of exposure pathways in sub-lethal toxicity testing of silver on zooplankton has been examined by Hook and Fisher (2001).

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

Diamond et al. (1990) carried out a series of chronic silver toxicity tests using a range of representative aquatic species including six invertebrates and three fish species. Their results suggested that some of the invertebrates were more sensitive than the fish species tested. As a general statement they concluded that for water of moderate hardness a chronic value could be ob-

tained by multiplying the acute value by 0.5. Chronic tests are significantly influenced by the binding of silver ion to the food used during the test period.

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

5.   FACTORS AFFECTING THE BIOAVAIL-ABILITY AND TOXICITY OF SILVER

5.1 General Discussion

It is now clear from a large number of studies, that the toxicity of silver ion in water is significantly ameliorated by the presence in water of species such as chloride ion, sulfide ion, carbonate and dissolved organic carbon.   In addition, silver is strongly adsorbed onto particulate matter. Where the number of moles of each of these ameliorating factors in total, is greater than the number of moles of silver added there is a negligible risk of toxicity due to silver occurring. The explanation for this is discussed below.

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

It has recently been shown by Bianchini *et al.* (2002), Bowles *et al.* (2002) and others, that reactive sulfides occur at concentrations ranging from picomolar to nanomolar concentrations in natural oxygenated waters.   These concentrations are sufficient to strongly bind soft metals such as Ag(I) (Bowles *et al.* 2002).

Bianchini *et al.* (2002) have observed that these reactive sulfides probably account for the fact that waterborne chronic silver toxicity has never been shown for natural field situations.

Attempts to extrapolate current laboratory results to field sites where silver is found have resulted in extremely low regulatory limits (Karen *et al.* 1999).   Differences in laboratory test methods

and local water quality characteristics are further confounding factors in the application of laboratory results to field situations.

It is worth reiterating that the source of the silver ion used in these studies was generally derived from the readily soluble silver nitrate ($AgNO_3$) which dissociates completely and gives essentially free silver ion.

In contrast to the situation found in most laboratory studies, Hogstrand and Wood (1998) note that only a small proportion of total dissolved silver in natural waters, <40%, exists in the free form, and very often will be much less.

In studies where the silver ion was derived from silver salts that are insoluble, such as silver thiosulfate $Ag_2(S_2O_3)$ and silver chloride (AgCl), the toxicity decreased significantly as the solubility decreased. No studies have been reported for silver iodide, presumably due to its insolubility. For silver chloride, for example, the 96-hr LC_{50} was reported as > 100 µg/L (Wood *et al.* 1996).

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

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

From time to time silver toxicity studies have been attempted using the insoluble silver salts, but the researchers had to resort to indirect methods to achieve the desired silver salt's concentration, see for example, Wood *et al.* (1996). A number of researchers investigating the toxicity of insoluble silver salts have attempted to circumvent the problem of the very low solubility by preparing the required silver salt in solution by chemical reaction prior to toxicity testing. For example, adding silver nitrate to a solution of sodium chloride to produce silver chloride.

This overlooks the fact that these anions, often in some excess, will act to reduce the available silver ion concentration in solution (K_{SP}) leading to AgCl (precipitate) and or may produce a silver

ion complex $AgCl^{2-}$ which is negatively charged (Pavlostathis *et al.* 1998).

Each factor is discussed in more detail in the following sections.

5.2 Dissolved Organic Carbon

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

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

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

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

Furthermore, Erickson *et al.* (1998) also found that the toxicity of silver ion to both organisms was much reduced when water from the St. Louis River was used in the test rather than normal laboratory water. The reduction in toxicity was some 60-fold for water fleas, although this is regarded as a more sensitive organism than the fathead minnow. The researchers surmised that the higher organic carbon content in the St. Louis River water was responsible for the reduced toxicity.

The data are shown in Table 3 below.

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

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

The greater protectiveness of DOC compared with that due to hardness, is seen as particularly important for regions of soft-water which contain much organic carbon.

Table 3: Acute toxicity of silver nitrate to juvenile fathead minnows and < 1-d-old Daphnia magna in laboratory water and St. Louis River water

Test Organism	Test Water	LC_{50}[1] (mg Ag/L)	95 % Confidence Limits
Pimphales promelas	Laboratory	10.4	8.6 – 12.5
	River	106	97 – 114
Daphnia magna	Laboratory	0.58	0.56 – 0.61
	River	35	32 - 39

[1]LC_{50} = median lethal concentration

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

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

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

5.3 Chloride Ion and other complexes

In their review, Hogstrand and Wood (1998) point out that the ability of native chloride and sulfide to significantly reduce the toxicity of silver by precipitating it out of solution in natural waters should not be overlooked. Silver ion forms complexes with chloride ion including $AgCl_2^-$, $AgCl_3^{2-}$ and $AgCl_4^{3-}$.

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

It has been suggested by some researchers that chloride levels >35 mg/L will affect silver solubility in fresh waters. However, as we now show lower concentrations can also be effective.

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

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

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

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

5.4 Sulfides and Sulfur Containing Ligands

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

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

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

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

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

In their study, Adams and Kramer (1998) showed (using X-Ray Diffraction) that dissolved silver ion in the presence of amorphous iron sulfide rapidly equilibrated, to give ultra-trace levels (~ 5 ng/L) of silver ion. This concentration is consistent with that calculated from the solubility product constant (see earlier). They also calculated that sulfur containing ligands, especially thiols, are more important than chloride until the total sulfur species is less than 10^{-13} M (~3.2×10^{-9} mg/L).

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

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

The procedure they used detected many colloidal sulfides, soluble sulfides and part of the polysulfides but not the thiols. Concentrations ranged from <1 nM to 570 nM. Interestingly, corresponding dissolved oxygen levels were between 6.8 to 10.2 mg/L with dissolved organic carbon levels of 3.2 to18.7 mg/L. They noted that, although all water samples were nearly saturated with respect to atmospheric oxygen, over half the samples had measurable AVS ranging from tens to hundreds of nM.

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

Hirsch (1998) looked at the toxicity of silver sulfide to the juvenile freshwater amphipod (*Hyalella azteca*), an epibenthic organism that burrows into the sediment surface. Using sediments from a non-contaminated source, spiked with varying amounts of silver sulfide, there was no difference found in survival rates between treatments and controls up to a level of silver of 753.3 mg Ag/kg sediment. The sediments had average AVS concentrations of 5.35 μmol/gm and total organic carbon values of the order of 1.5%. Hirsch noted that the concentration of AVS in the sediment would have favoured the formation of Ag_2S had any free silver ion been present. The relationship between acid volatile sulfides and metals is important in predicting bioaccumulation in benthic macroinvertebrates (Ankley 1996).

Call *et al.* (1999) showed that the capacity of river sediments to bind silver effectively occurs at relatively low levels of Total Organic Carbon ("TOC") and acid volatile sulfides. This capability is important in reducing silver bioavailability in pore waters to which benthic organisms would be exposed.

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

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

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

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

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

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

On the basis of their observations it was suggested (Rezan *et al.* 2000) that sulfur complexation might dramatically lower the acute toxicity of "b"-class metals including silver.

5.5 Hardness

Water hardness, principally in the form of calcium, was recognised by the USEPA (1980) (cited in CICAD 44) as having a critical role in reducing harm to aquatic organisms from acute silver toxicity.

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

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

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

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

Recent work by Bianchini and Wood (2008) identified both hardness and sulfides as being important in protecting against lethal acute effects as well as chronic silver toxicity in terms of mortality, whereas sulfide alone showed a protective effect against the sub-lethal chronic silver effects on growth and reproduction.

5.6 Colloids

The strong affinity of silver for suspended particulates in river and estuarine water was demonstrated in a study reported by Wen *et al.* (1997). In experiments to determine phase speciation, they used cross-flow ultrafiltration to separate water samples into particulate >0.45 µm or >0.1 µm, colloidal (0.1 – 0.45 µm), or truly dissolved (<0.1 µm) fractions. They were able to show that between 33-89% of the silver was bound to the particulate fraction.

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

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

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

Further support for the effectiveness of colloids in removing silver from water is provided by Shafer *et al.* (1998) and Benoit *et al.* (1994). They ex-

amined the removal of silver from influent water in Publicly Owned Treatment Works and found that more than 94% of the influent silver was removed during treatment. The percentage of filterable silver was directly related to DOC.

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

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

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

This report showed that, although there were detectable concentrations of silver in the lake sediments (average value 0.035 mg/kg), the silver level in the watershed averaged 6.7×10^{-12} g Ag/mL.

Importantly, no detectable free silver could be measured in leachates of the sediment samples at pH 5 showing that the silver in the sediments was tightly bound.

6. POTENTIAL ENVIRONMENTAL FATE

6.1 Uptake of Silver by Terrestrial Plants

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

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

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

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

The silver concentrations used in this study ranged from 0 to 1000 mg/L (ppm) which are significantly higher than expected for the SPERP. More importantly, they concluded that there would be little danger to stock grazing on pastures with these high levels of plant silver.

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

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

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

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

6.2 Bioaccumulation of Silver in Organisms

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

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

It is clear that BCFs appear to be correlated with the solubility of the silver compound.

In his review of bioaccumulation and toxicity of silver compounds, Ratte (1999) has tabulated the silver bioconcentration factors, the silver compound and the species studied.

The US EPA (1980) (cited in CICAD 44) has reported BCFs of 210 in diatoms, 240 in brown algae, 330 in mussels, 2300 in scallops and 18700 in oysters. In contrast, bluegills showed no significant accumulation when exposed to 0.5 µg/L silver (Coleman and Cearley, 1974).

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

Silver is a soft or "b"-class metal and would be expected to coordinate and complex strongly with soft bases which, in this context, are organic molecules containing sulfur (S) or nitrogen (N) atoms. Silver exhibits a great affinity for sulfur-containing ligands (organic compounds) (Frausto da Silva and Williams 1991).

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

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

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

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

Connell *et al.* (1991) found that incorporated silver was tightly bound to the cell membrane and was not released by mechanical disruption. They also observed that food-chain biomagnification was unlikely at concentrations normally found in the environment.

6.3 Bioaccumulation by Algae, Pelagic and Benthic Food Chains

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

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

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

In contrast, bivalves showed BCFs that corresponded to the daphnid BCF.

6.4 Bioaccumulation by Fish

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

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

Where bioavailability in the presence of these ameliorating factors has been considered, toxicity was shown to be reduced.

6.5 Bioaccumulation by Terrestrial Animals

Studies into the effects of silver ions on terrestrial species are limited. Exposure of earthworms to increasing concentrations of Ag_2S in artificial soil did not lead to an accumulation of silver, but there was evidence of reduced growth. The No Observed Effect Concentration ("NOEC") was given as 62 mg Ag/kg (Hirsch 1998).

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

Given the extremely low levels of bioavailable silver expected to arise from the trial, toxic effects and bioaccumulation for terrestrial species are considered unlikely.

7. SNOWY PRECIPITATION ENHANCEMENT RESEARCH PROJECT

The Act requires that the SPERP must only use silver iodide as the ice nucleating agent. This is dispensed through a network of 23 ground generators placed to the west of the main range of the Snowy Mountains.

When in operational mode, each generator burns a ~2% solution of silver iodide in acetone (w/w), at a rate of 1.25 litres per hour. Approximately 20g of silver iodide with an average particle size of 0.06μm is released from each generator for each hour of operation.

The average mass of silver iodide used each year (2004 through 2008) is 17.6 kg, dispensed from 13 separate locations across a target area of approximately 1000 square kilometres. A summary of reagent use statistics are shown in Table 4 below.

A good overview of the SPERP can be found in Heggli et al. (2005) and Huggins et al. (2008), although the reader should note that these papers pre-date the project expansion described in Section 1 above.

7.1 Preliminary Investigations

Given the location and environmental significance of the SPERP target area, an extensive assessment of the ameliorating factors described in Section 5 above was undertaken prior to the commencement of cloud seeding experiments. The factors examined are shown in Table 5.

Samples were collected from a large number of sites including proposed generator locations, and likely points of accumulation in the landscape. Background levels of total and bioavailable silver were also determined for all of these samples.

Table 4: SPERP AgI Use Statistics[3]

Year	Total mass of AgI dispensed (kg)
2004[4]	20.1
2005[5]	23.2
2006	6.8
2007	15.6
2008	20.1

[3] These statistics relate to the original target area of approximately 1000 km^2

[4] Twelve generators in operation during 2004

[5] Thirteen generators in operation for the period 2005 through 2008

In the following Sections we discuss the relevance of these factors to the SPERP.

7.2 Soil and Soil Organic Matter

Organic matter in soil will bind silver ions in the same way as dissolved organic matter in water binds silver ion, as discussed in detail earlier. As part of a recent study on the influence of aeolian dust deposits in the KNP, Johnston (2001) reported that the percentage of organic carbon in the ten centimetres of soil profiles from Mt. Clark and Mt. Twynam (within the KNP) to be 12.1% and 12.7% respectively. Concentrations of organic matter of this order would be expected to be very significant in immobilising silver in the ecosystem.
The pH of soils in the Kosciuszko alpine area, also reported by Johnston (2001), fall within the range (pH 4.5 – 4.8) levels found by Spark *et al.* (1997) to facilitate formation of metal-humate species due to increased dissolution of humic substances.

Costin (ISC 2002) has noted that the alpine humus soils in the KNP reflect an accumulation of soil colloids and nutrients in the surface soils. And, that the "soil building processes involve recycling by deep-rooted snow grasses and other major herbs (possibly in association with soil mycorrhiza), accretion of windblown dusts, and vigorous decomposition and redistribution of plant remains by soil organisms, particularly invertebrates...".

The role of groundwater in soils is controlling the spreading and filtering of catchment run-off before it enters streams was noted by Costin (ISC, 2002).

Silver also adsorbs to manganese dioxide, ferric compounds and clay minerals meaning that these compounds are involved in silver sequestration in soil and sediments.

Data reported by Johnston (2001) confirms a modest cation exchange capacity ("CEC") for soils in the KNP. This means that some binding of silver to clay minerals would be expected for the soils in the study area.

The relatively high organic nature of the soils in the SPERP target area (see Snowy Hydro Limited 2005 and others) suggests that DOC and soil organic matter will be one of the most significant factors regulating the bioavailability of silver ion. Concentrations of organic matter of this order would be expected to be very significant in immobilising silver in the ecosystem.

The significance and relevance of each of the ameliorating factors in regulating the bioavailability of silver ion in the present trial cannot be overstated.

7.3 Water chemistry

In the Independent Scientific Committee's ("ISC") report (ISC 2002) on the KNP, Marchant (Chapter 6) has noted that the water in the alpine lakes is very fresh, with extremely low salinities (< 3 ppm) and slightly acid with pH's ranging from 6.0 to 6.2. Furthermore, at least for Lake Albina and Blue Lake, significant amounts of decomposed leaves and twigs occurred in the bottom sediments.

Table 5: Assessment of Ameliorating Factors

Description	Acronym	Matrix Assessed
Chloride	Cl	Soil, Water
Specific Conductance	SPC	Water
Dissolved Organic Carbon	DOC	Water
Hardness	HD	Water
pH	pH	Soil, Water
Cation Exchange Capacity	CEC	Soil
Total Organic Carbon	TOC	Soil

Marchant also notes that "… it is well known that water quality problems (e.g. low water temperatures, low oxygen concentrations and high concentrations of toxins such as hydrogen sulfide) can occur below the deep dams that release bottom water". This indicates, qualitatively at least, that sulfur-containing ligands are present in the ecosystem.

The significance and relevance of each of these ameliorating factors in regulating the bioavailability of silver ion in the present trial cannot be overstated.

7.4 Silver Levels in Snow

Cloud seeding operations make very small additions of the insoluble silver iodide to the KNP. For silver iodide to mobilise in the environment, it must first dissolve and dissociate, leading to extremely low levels of silver ions. The silver ions produced will then be subject to the factors described below, which in turn act to ameliorate their bioavailability.

The proportion of this ultra-trace concentration of added silver ion that would become bioavailable will be determined by the relative importance of each of the ameliorating factors described in detail below. These factors affect the bioavailability of silver ions in both soil and water environments.

Warburton and co-workers (1985) have shown that if silver iodide aerosols are released at rates of 10^{13} to 10^{15} nuclei per second, the concentration of silver found in the precipitation is in the range 10^{-12} to 10^{-9} g/ml (corresponding to one part per trillion (ppt) to one part per billion (ppb) in snow). This concentration was similar to that found in a much earlier study by Warburton and Young (1972), where snow in seeded areas had a median concentration of the order of 5×10^{-9} M silver.

In separate studies associated with cloud seeding experiments around Lake Almanor (US), Warburton and co-workers (1995a, 1995b), found the amount of silver deposited in snow ranged from about 8×10^{-12} to 245×10^{-12} g/cm^2.

7.5 Other Relevant Factors Affecting the Fate of Silver

The study area has been subjected to extensive bushfires in the past, the most recent notable example having occurred in the summer of 2003. During the early planning stages for the SPERP, some stakeholders raised concerns with respect to likely environmental fate of any silver iodide as a result of bushfire.

It is reasonable to expect that any silver iodide associated with cloud seeding reaching the ground would be incorporated into the top organic-rich soil layer (in the first instance). The miniscule number of silver ions arising from dissociation of the solid silver iodide would then become bound to humic and other components as described above. While combustion would presumably destroy the organic matter to which the silver iodide is bound, the trace levels of silver iodide would remain in the ash or be volatilised depending on fire temperature.

The melting point of silver iodide is recorded as 558°C (Handbook of Chemistry and Physics) and its boiling point as 1506°C and it has a negligible vapour pressure (MSDS). At the levels this compound is being used in snow augmentation, it is difficult to see any environmental issue arising from the impact of fire. It is possible that at extremely high flame temperatures there could be some dissociation of silver iodide but the levels of iodine atoms formed would be insignificant.

8. MONITORING PROGRAM

8.1 Objectives

The specific objectives of the SPERP ecotoxicity monitoring program (Snowy Hydro Limited 2008b) are:

- To be able to detect any increases in the concentrations of silver in environmental matrices, compared to baseline concentrations and compared to natural variability;

- To be able to assess concentrations of silver against the relevant GTV for further investigation if required; and

- To provide an early warning of any adverse trend in silver concentration, allowing for timely and effective management intervention.

8.2 Overview of Monitoring

As described earlier in this paper, the following work was undertaken prior to commencement of the SPERP

- An assessment of factors known to ameliorate toxicity of silver ion; and

- Determination of background levels for total silver and bio-available silver.

This data was analysed to confirm that the presence of the ameliorating factors discussed earlier in this paper, and to verify that GTV for silver in each environmental matrix to be monitored was appropriate.

Annual monitoring of total silver concentrations in soils, sediments, potable water supplies and peat and moss is undertaken at a large number of locations across and downwind of the study area. These include:

- Generator sites (sites from which silver iodide is dispensed);

- Potential points of accumulation in the landscape (for example sediments in glacial alpine lakes, peat bogs, stream sediments);

- Potable water supplies; and

- Randomly selected locations across the study area.

Monitoring of potable water supplies is undertaken on a number of occasions throughout the winter, typically following significant snowfall and run-off events. Monitoring of other matrices commences following the cessation of cloud seeding operations for the season, usually in October each year (Snowy Hydro Limited 2008b).

8.3 Preliminary Interpretation of Results

A statistical analysis of the silver data for various environmental matrices being monitored was undertaken for the period 2004 through 2007. The data were compared to the relevant GTVs for each matrix, and also between periods and locations of sampling.

A statistical power analysis undertaken for generator sites (the locations from where silver iodide is dispensed, and the most likely to show any change) was used to assess the likelihood of being able to detect an increase in concentrations of silver before the GTV was reached (Snowy Hydro Limited 2008a).

The key outcomes of these investigations include the following:

- Measurable concentrations of silver occurred at all locations and in all matrices sampled prior to commencement of the cloud seeding trial. Importantly, there was a measurable baseline of silver present in the local environment prior to commencement of the SPERP;

- The sampling design had sufficient power to detect any statistically significant increase well before the GTV was reached. This provides an important level of confidence to stakeholders that management intervention could be implemented in a timely manner if ever required;

- The analysis of the silver data showed mean concentrations and upper 95% confidence limits of silver to all be well below the GTV in all matrices, and all locations and for all periods of sampling;

- Generally, mean concentrations of silver were less than 20% of the relevant GTV, and in many cases less than 10% of the GTV.

Detailed results and interpretations from the monitoring program for the period 2004 through 2009 (prior to expansion of the SPERP target area) are presently being prepared for publication.

9. CONCLUSIONS

The Act mandates that the SPERP must use silver iodide as the seeding agent. We consider the risk of an adverse ecotoxicological impact for the project to be negligibly small for the following reasons:

- Although silver ions from soluble silver salts have been shown to be toxic to aquatic species, this is not the case for the insoluble silver iodide;

- Since water solubility generally controls bioavailability, silver compounds that are not readily soluble or insoluble are of much less environmental concern;

- Where silver toxicity studies have been attempted using the insoluble silver salts, researchers have had to resort to indirect