

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 non-toxic 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 non-toxic (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.

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 water 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 $\mu\text{g/L}$ were found, while for urban and industrialised areas the levels were typically 0.01 to 0.1 $\mu\text{g/L}$.

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 (1.07×10^{-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 $\mu\text{g}/\text{kg}$, compared with the concentrations in the control areas which ranged from 30.4 to 6.7 $\mu\text{g}/\text{kg}$.

Contamination by silver in aquatic environments has been reviewed by Flegel *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 $\mu\text{g}/\text{m}^3$ 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 $\mu\text{g}/\text{m}^3$) and the US (0.01–0.02 $\mu\text{g}/\text{m}^3$). 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 (5×10^{-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 $\mu\text{g/L}$) 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 $\mu\text{g/L}$ 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 $\mu\text{g/L}$ 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 $\mu\text{g/L}$.

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 $\mu\text{g/L}$. 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 $\mu\text{g/L}$ 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 $\mu\text{g/L}$ silver ion. The most sensitive fish species are even less tolerant with LC_{50} 's between 2.5 and 10 $\mu\text{g/L}$.

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 $\mu\text{g/L}$ 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 BIOAVAILABILITY 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 sulfhydrylate (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 $\text{Ag}_2(\text{S}_2\text{O}_3)$ 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 $> 100 \mu\text{g/L}$ (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 than 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 (*Oncorhynchus 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 $\log K \sim 9$ 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
<i>Pimphales promelas</i>	Laboratory	10.4	8.6 – 12.5
	River	106	97 – 114
<i>Daphnia magna</i>	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 $\text{Ag}(\text{S}_2\text{O}_3)^{2-}$ 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 to 18.7 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 μ m) 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 μ mol/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 Ag₂S 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 μ mol/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 μ mol/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:

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

More recently however, it has become clear that this expression is under-protective at high hardness levels, and is overly conservative where waters have low hardness (Galvez and Wood, 1997). In the study reported by Galvez and Wood (1997), they found that the protective effect of chloride is much more significant than that due to calcium. CICAD 44 notes that silver is less toxic to fathead minnows when water hardness increased from 50 to 250 mg CaCO₃/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 sulphhydryl 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 $\mu\text{g Ag/L}$ and died at concentrations greater than 130 $\mu\text{g Ag/L}$ (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 gastrointestinal 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 (monocarboxylic 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 Ag₂S 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 gen-

erators 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 Statistics³

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 km²

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 be-

fore 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/cm².

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

- methods to achieve the desired concentration of silver ion;
- The majority of studies into acute and chronic effects of silver ion have used soluble silver nitrate;
 - A number of studies have shown that the toxicity of silver ion in water is significantly ameliorated by the presence in water of chloride ion, carbonate ion, sulfide ion (reactive and other forms) and dissolved organic carbon. In addition, silver is strongly adsorbed onto particulate matter in water. Findings from recent studies point to the fact that silver ion concentrations in natural waters are negligibly small;
 - The study by Johnston (2001) has shown that many of these factors exist in the KNP and, as a result, the bioavailability of silver would be expected to be of the order of current background levels;
 - The research results reported by Johnston have been validated by extensive additional sampling and analyses for the relevant parameters;
 - Background levels of silver occurring in snow in the KNP are generally less than 2×10^{-9} g/L, while background level of silver in stream runoff was below the detection limit of 1x10 g/L for silver. This level is several orders of magnitude below the chronic toxicity level;
 - The Snowy Hydro Limited (2005) assessment of background levels also showed silver to be present in the environment at concentrations ranging from 0.47 mg kg⁻¹ in soil at generator sites to 0.09 mg kg⁻¹ in alpine humus in the target area;
 - The average mass of silver iodide used each year is 17.6 kg, dispensed from 13 separate locations across a target area of approximately 1000 square kilometres. The likelihood of any environmental impact, even in potential zones of accumulation is minimal because of the small quantities and because silver iodide is not water soluble and not readily bioavailable. Hence no acute or chronic toxic effects are expected;

- The SPERP monitoring program has a high probability of detecting any adverse trend in silver concentration well before the GTV is reached. A statistical power analysis of the SPERP monitoring data for generator sites has shown the monitoring design to have sufficient power to detect any statistically significant change in silver concentrations; and
- Mean silver concentrations have all been shown to be well below the GTV for all matrices, at all locations and for periods of sampling during the SPERP.

The conclusion of this review of the literature, assessment of ameliorating factors and interpretation of results to date provides compelling evidence that the use of silver iodide for the SPERP will not result in an adverse ecotoxicological impact on the environment of the study area.

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