DECEMBER 1, 2015

SILVER TOXICITY: A BRIEF OVERVIEW

LITERATURE REVIEW

JAMES FISHER, SHAWN BENNER, PATRICK GOLDEN, AND ROSS EDWARDS
PREPARED FOR: IDAHO POWER COMPANY
PREPARED BY: BOISE STATE UNIVERSITY AND HERITAGE ENVIRONMENTAL CONSULTANTS

Table of Contents

I Executive Summary

Silver is a rare metal present at concentrations averaging 50 ppb in the upper continental crust, 100-1,000 ppb in soil, and 0.002-0.03 ppb in freshwater environments. Localities exceeding these silver concentrations tend to be a result of anthropogenic releases, with exceptionally high sources from photographic industries, urban refuse combustion, and sewage treatment. Silver toxicity varies widely amongst different organisms and silver speciation. Many gilled aquatic organisms have been found to be highly sensitive to the free silver ion (Ag+).

Water quality parameters present in the environment such as Cl^-, Ca^+, pH, particulates/colloids, dissolved organic carbon (DOC), and sulfur-bearing species impact the equilibrium concentration of the silver ion and its biological uptake. Equilibrium concentrations of the silver ion are extremely difficult to measure in the aquatic environment. Numerical models have been used to estimate concentrations in place of real-time measurements. Equilibrium concentrations of the silver ion are highly dependent on aquatic chemistry and the presence of suspended solids such as colloids.

The free silver ion (Ag^+) is extremely toxic in aquatic environments. The most sensitive species that experience lethal effects (LC_{50}-96 hr) in waters amended with the free silver ion are the following: fathead minnows (5.3 ppb), juvenile rainbow trout (4.8 ppb), daphnids (5.0 ppb), and amphipods (1.9 ppb). Juvenile fish tend to experience toxic effects at lower concentrations than their adult counterpart. Free silver ion concentrations are fungicidal and bactericidal at 10 ppb. Algae have bioconcentration factors up to 2.1×10^6. Some species of algae experience a unique toxic response to both forms of dissolved silver; the free ion and complexed state. However, there is no evidence of a direct correlation between the amount of accumulated silver within an organism and toxicity.

The free silver ion is much less toxic to humans and terrestrial species relative to species in aquatic environments. Humans can ingest 10 grams of total recoverable silver in a lifetime without experiencing toxic effects or precursors to toxic effects. In excess of 10 grams the risk of developing argyria, a grey discoloration of the skin, increases. Data are sparse on silver ion toxicity to terrestrial animals; most studies examine the effects of the less toxic, insoluble silver species. The most sensitive animal to the free silver ion found were rats. Rats given water amended with soluble silver experienced sluggishness at 95 ppb after 125 days. Germinating plants experience toxic effects from the free silver ion at 750 ppb. Adult plants have a higher resilience to silver. Toxic silver concentrations in plants range from 14,000-120,000 ppb in soils amended with insoluble silver.

Water quality standards vary at the global, country, and local scales. Aquatic environment guidelines range from 0.05 ppb of the free silver ion and up to 3.4 ppb of total recoverable silver. The EPA and state governments typically assess silver toxicity as a function of hardness. Critical assessments of EPA standards highlight that more impactful variables on silver toxicity exist, such as DOC and chloride. The New South Wales (Australia) EPA set toxicity guidelines as a function of the free silver ion. There is little variability in drinking water standards. Standards set by the World Health Organization (WHO), EPA, and most state governments are fixed at 100 ppb of total recoverable silver.

Silver iodide (AgI) is an insoluble salt used in cloud seeding. AgI is present at trace concentrations in seeded snow and adjacent waterbodies (0.001 – 0.05 ppb) and does not dissociate readily in water ($K_{sp} = 9.2 \times 10^{-9}$ M). As a worst case scenario, AgI as an infinite solid species in solution, with unlimited time to react, assuming Ag^+ does not sorb/precipitate/complex, a solution of 0.984 ppb of the free

silver ion would result. This concentration is below every U.S. silver toxicity guideline. AgI primarily accumulates in the upper soil horizon or streambed sediments in solid form. Bioavailability depends on the bonding of the soluble silver fraction to the sediments and organics present. Environmental assessments of cloud seeding operations have found no detectable increase in total silver concentrations above background levels in soil, streams, or aquatic species in seeded areas. Likewise, there is currently no evidence supporting adverse effects to wildlife in natural settings. Using the worst case scenario, assuming 100% of the snowpack is seeded with AgI, all snow has 0.05 ppb silver, 100% of the AgI dissolves, and the dissolved fraction does not bind to any water constituents. This scenario would still result in free silver ion concentrations at least one order of magnitude lower than LC_{50}-96hr concentrations (acute toxicity) to known sensitive freshwater species.

II Terms

Absorption – Process in which a substance is some entity (in this case, silver) assumes the bulk phase of the adsorbing material. This entity is taken up by the *volume.*

Adsorption – Similar to absorption. This involves the adhesion of an entity (in this case, silver) to the surface of a bulk phase. This entity is taken up by the *surface*.

Acute Toxicity – Produces a significant effect within a short period of time, usually 96 hours or less. Acute toxicity may be a function of EC_{50} or LC_{50} (EPA Water Quality Handbook: Glossary, 2012). Typically, the concentration of a contaminant require to produce an acute response is much higher than that required to produce a chronic response (see chronic toxicity below).

Bioavailability – Bioavailability is the contaminant fraction available to cross an organism's cellular membrane. In other words, the fraction actively interacting with organisms are bioavailable (whether positive or negative). Fractions of the contaminant in the form of other chemical species inert to the organism of interest are not bioavailable.

Bioconcentration Factor (BCF) – Ratio of the contaminant concentration in an organism to the contaminant concentration in a medium of interest. Mediums used for this ratio are commonly water or air in the surrounding environment, or food commonly consumed. This is a measure of how much the contaminant accumulates within the organism.

Chronic Toxicity – This produces an effect that lingers for long periods of time after exposure, typically defined as 10% or more of the organism's lifespan. A few examples of chronic effects include reduced growth rates, mortality rates, or death (EPA Water Quality Handbook: Glossary, 2012). Typically, the concentration of a contaminant required to produce a chronic response is much lower than that required to produce an acute response (see acute toxicity above).

EC_{xx} – The Effect Concentration (EC) is often expressed as EC_{50}, but the quantile used may differ. This describes the concentration at which at least xx% of population at a specified exposure time experience a certain effect (for instance, stunted growth). Time of exposure times are also specified along with associated toxic concentration.

LC_{xx} – The Lethal Concentration (LC) is often expressed as LC_{50}, but the quantile used may differ. This is the same as EC_{xx} except the effect of interest is death. In other words, this describes the concentration where at least xx% of population at a specified exposure time experience death.

NOEC - "No Observed Effect Concentration". This is the highest concentration of a toxic substance that can be exposed to a species without exerting a statistically significant negative consequence.

NOAEL – "No Observed Adverse Effect Level". This is the highest concentration of a substance where there is no significant adverse effects or precursors to adverse effects relative to some control group (EPA Water Quality Handbook: Glossary, 2012).

LOEC - "Lowest Observed Effect Concentration". This is much the same as NOEC. This is the lowest concentration of a toxic species that exerts a statistically significant adverse consequence.

Total Recoverable Silver – Total amount of silver that can be solubilized by strong acid digestion. EPA standards of silver concentrations utilize this metric. The EPA also states the term "total [silver]"

and "total recoverable [silver]" are synonymous and can be used interchangeably as was listed on the EPA memorandum titled "Total vs. Total Recoverable Metals" on August 19, 1998.

III Unit Conversions

ppm (parts per million) = mg/kg (milligram per kilogram) = 10^{-6} g g^{-1} = mg/L (milligram/liter)*

ppb (parts per billion)= µg/kg (microgram per kilogram)= 10^{-9} g g^{-1} = µg/L (microgram/liter)*

ppt (parts per trillion)= ng/kg (nanogram per kilogram)= 10^{-12} g g^{-1} = ng/L (nanogram/liter)*

The units listed above are equivalent to the units in parenthesis assuming the density of water equals 1000 kg/m³. This is approximately true (w/in 3%) in typical ranges of temperatures and salinities of most natural waters.

1 Silver as an Element

1.1 Sources

The relative contributions of anthropogenic releases of silver to the environment are listed below in *Table 1*. These data were collected and analyzed in 1978, where an estimated 2.5 million kg of silver was released in the environment [1]. Distributions may have changed slightly since 1978 because it became economically viable for industries to recover trace amounts of silver and environmental regulations have become more stringent. Also, silver usage from the photography industry has decreased sharply since 1978 [2].

Table 1 shows most of the silver released due to anthropogenic practices. Silver in the natural environment is primarily found in sulfide minerals, typically in conjunction with lead, copper, iron, and gold. These sulfides are generally insoluble [1].

Silver sulfides are locally concentrated in ores. Many ore deposits in the Western United States are hydrothermal in nature. These ore deposits yield relatively high amounts of the following common silver minerals: argentite (Ag_2S), horn silver ($AgCl$), and stephanite (Ag_5S_4Sb) [3]. Outside of these locally concentrated ores, however, silver is present at trace amounts at shallow terrestrial depths. The upper continental crust (mostly sedimentary rocks) and bulk continental crust are generally 0.05 ppm and 0.08 ppm respectively [4].

Table 1: Global Releases of Silver in the Environment[a]

Reservoir	Source	Mass [metric tons]	Contribution [%]
Atmosphere	Metals production	30	1.2%
	Urban refuse combustion	10	0.4%
	Coal and petroleum combustion	9	0.4%
	Iron and steel production	7	0.3%
	Cloud seeding	3	0.1%
	Cement manufacture	2	0.1%
	Other	30	1.2%
	Total Atmosphere	*91*	*3.7%*
Aquatic	Soil erosion (natural)	428	17%
	Urban runoff	72	2.9%
	Sewage treatment plants	70	2.8%
	Photographic developing	65	2.6%
	Photographic manufacture	54	2.2%
	Other	6	0.2%
	Total Aquatic	695	28%
Terrestrial	Photographic industry	630	26%
	Urban refuse combustion	445	18%
	Sewage treatment	220	8.9%

Metals production	165	6.7%
Electrical contacts and conductors	150	6.1%
Alloys and solders	60	2.4%
Other	5	0.2%
Total Terrestrial	1675	68%

[a]Table modified from [1] based on data from 1978.

1.2 Typical Concentrations in the Environment

1.2.1 Crustal Abundances and Occurrences

The upper continental crust (mostly sedimentary rocks) and bulk continental crust are generally 0.05 ppm and 0.08 ppm respectively [4]. However, much higher, naturally occurring, silver concentrations are found in crustal material, especially in mineral ore bodies. Silver is often found in ore deposits associated with sulfide minerals, typically in conjunction with lead, copper, iron, and gold. Silver is also concentrated in some soils [5].

1.2.2 Soils

Silver concentrations in soils typically range between 0.1 to 1 ppm [6]. Organic soils usually range from 2 – 5 ppm [7]. Polluted soils (e.g. from excessive dry deposition or sewage sludge) are known to be several times higher than these ranges [7]. Note that these typical soil concentrations are at least one order of magnitude greater than the bulk continental crust., Silver is delivered to soils by wet and dry deposition of atmospheric silver and released from *in-situ* minerals by weathering. Soil serves as a large environmental sink of silver because it is generally immobile, and strongly associated with the solid phase [2].

1.2.3 Water

Silver is typically present in waters at very low concentrations, making it difficult to quantify using standard water analysis techniques. For this reason, silver concentrations in water measured prior to the 1990's should be interpreted with caution because levels of instrumental detection where often not sufficiently precise and sample collection did not commonly follow clean, ultra-trace techniques [8]. More recent studies utilizing ultra-trace techniques have found that common freshwater Ag concentrations are most commonly between 1 ppt and 30 ppt using unfiltered, total recoverable methods [3][9]. Concentrations in excess of 50 ppt are not uncommon in turbid environments. For instance, 0.05 grams of soil with 1 ppm Ag concentration suspended in a one liter water sample would result in a 50 ppt silver concentration (if unfiltered, total recoverable methods are employed). Riverine and entrained sediments commonly contain 0.2-1.7 ppm silver (same range as the shallow soil horizon) [3]. Hence, an important control of silver concentrations in aquatic systems is the amount of suspended sediment.

Because the turbidity of water has a large impact on the total recoverable silver in a water sample, selecting a proper filter size prior to chemical analysis is paramount. One study found passing river water samples through a 0.45 μm and 0.1 μm filter reduced silver concentrations by roughly 60% and 70% respectively in comparison to direct analysis methods [10]. Colloidal silver is primarily in the 0.25-0.40 μm size range [11]. In other words, the sample passing through 0.45 μm filters does not

account for the significant colloidal fraction of the water sample. Since there is uncertainty around what size filters result in "dissolved" silver, the filter size used on water samples should be disclosed in order to interpret reported silver concentrations in aqueous systems.

1.2.4 Air

Eisler (1996) reported on typical values of atmospheric loads of silver in the environment. Typical dust Ag concentrations were reported between 0.012-10.5 ng/m^3 in natural environments [1]. Since the average male breathes roughly 20 m^3 per day, about 0.2 µg of silver enters the lungs per day. Air samples taken right next to a smelter in Idaho resulted in dust concentrations as high as 36.5 ng/m^3 [1]. This is still considerably below acceptable standards set for the workplace. The Occupational Health and Safety Administration (OSHA) airborne limit for silver is 0.01 mg/m^3 based on an 8-hour work shift and 40-hour work weeks [12].

1.2.5 Riparian Sediments

Riparian sediments tend to be the same order of magnitude as silver concentrations in soil. Concentrations of these suspended particulates/sediments have been measured to average around 0.2 – 1.7 ppm [3].

1.2.6 Snow

Silver concentrations in snow in the Western United States typically have silver concentrations between 2-4 ppt [13][14][15][16] with a standard deviation of 1-2 ppt [13]. In Idaho, the mean concentration of background concentrations of silver is around 1 ppt based on results from the 1996 (Richard Stone IPC Report), 2004 [17], and 2015 [18] sampling campaign (AgI contaminated control site sampled in 2014, so no information on background concentrations are available [19]). Background Ag concentrations in Wyoming have been measured up to 15 ppt using clean techniques [3]. Snow samples containing more than 20 ppt were most likely caused by AgI or human contamination. For studies prior to 1990, contamination during collection or analysis likely limits validity.

1.3 Chemical Characteristics

1.3.1 Speciation

Silver mobility and toxicity are strongly influenced by chemical speciation and solid-aqueous partitioning. The most commonly occurring forms of Ag are reactive and tend to easily create bonds with other species in solution (complexes), with other elements to form mineral phases, and to reactive surfaces (adsorption).

1.3.2 Chemical Speciation

The silver element has four possible ionic states: 0, 1$^+$, 2$^+$, and 3$^+$, and 20 radioisotopes [20]. However, the most common oxidation state in the natural environment is either uncharged (Ag^0) or the monovalent silver ion (Ag$^+$, also known as the argentous ion) [1]. Silver is also available in 20 radioisotopes but none occur naturally in the environment [20]. Speciation strongly controls silver

toxicity (*described below*); the free, non-complexed, silver ion (Ag⁺) is by far the most toxic species [1][20][21]. Hereafter, monovalent silver ion will be referred to as the "silver ion[1]".

1.3.3   Complexation and Adsorption

The silver ion (Ag+) has a strong affinity to create aqueous complexes and bind to adsorption sites. Aqueous complexes are dissolved compounds that are typically composed of an anion and cation. The anion ligand, or adsorption site to which silver will bind to, depends on the environment in which silver resides; Ag behaves differently in oxidizing and reducing environments. Examples of oxic environments include rainwater and snow, rivers, and lakes. The most common species the silver ion bonds to in oxic environments involve chloride (Cl^-) and dissolved organic carbon (DOC). In addition to the $AgCl_{(aq)}$ complex and $AgCl_{(s)}$ solid phase, silver can also form similar compounds with bromide and iodide [20]. Examples of reducing (or anoxic) environments are swamps, peat, and deep groundwater reservoirs. Reduced silver sulfur (sulfide) species (either as a solid or complexed) and the dissolved silver concentrations can be higher in these environments [1].

Silver speciation can also change when exposed to light. Many silver salts, such as AgCl and AgBr, photolytically decompose when exposed to ultraviolet light. In this reaction, the Ag+ is reduced to Ag^0 and the anion is released to the solution. This technology is harnessed in photography but is a hindrance for chemical analysis of water samples, as this will under-estimate the total recoverable silver concentration. Photolytic reduction is partially suppressed if samples are treated with nitric acid [22].

1.3.4   Ag mineral solubility

Silver forms more insoluble mineral phases (often referred to as 'salts' when artificially made) than any other trace metal [22]. Silver nitrate ($AgNO_3$) is the only silver mineral phase considered soluble). The solubility product (K_{sp}), expressed in terms of molarity of some of the most common silver salts, are listed in ***Table 2***. The maximum dissolved silver concentrations provided in ***Table 2*** assumes the silver species had an unlimited amount of time to react (estimated for calculations, not observed in the environment) and does not re-precipitate with other species in solution. However, these concentrations do not specify what dissolved species will result (toxic or non-toxic), under what conditions the maximum amount of salt dissolves

Table 2: Solubility Product of Common Silver Minerals (salts) in Terms of Molarity[a]

Silver Salt	Solubility Product (K_{sp}) [M]	Maximum Dissolved Silver Concentration [$^0/_{00}$]
Silver nitrate ($AgNO_3$)	11	1.2×10^3
Silver chloride (AgCl)	8.3×10^{-6}	8.9×10^{-4}
Silver iodide (AgI)	9.2×10^{-9}	9.9×10^{-7}
Silver sulfide (Ag_2S)	2.6×10^{-17}	5.6×10^{-15}

[a]Table modified from Williams [2].

---

[1] In literature, this is called the argentous ion, free silver, free silver ion, or the monovalent silver ion. For simplicity, the toxic Ag⁺ ion will be called the silver ion in this paper (not to be confused with dissolved silver, which contains the free silver ion, complexed dissolved silver, and in some cases colloids).

1.3.5 Implications for Assessing Silver Concentrations

The strong bonding tendency of silver influences how observed silver concentrations are collected and assessed. Natural waters generally contain both dissolved and suspended fractions. Because silver tends to be associated with the solid phase, a bulk water sample analysis will produce silver concentrations that are dominated by the solid phase fraction. To determine the dissolved fraction the sample must be filtered prior to analysis. The filter size traditionally used is 0.45 µm. However, this size allows small, colloidal sized, particles to pass through into the sample to be analyzed, which will result in exaggerated dissolved Ag concentrations. Therefore, a 0.1 µm filter must be employed to eliminate silver associated with small solid particles and colloids. In some instances, it is of value to use unfiltered samples; this provides a silver concentration inclusive of the suspended and dissolved phase (total recoverable) fractions.

A second practical consideration is the influence of complex formation. It is important to note that the total dissolved concentration of Ag is not equal to the concentration of the most toxic free silver ion (Ag^+) [23]. In laboratory environments where the highly soluble silver nitrate is used, free silver (Ag^+) concentrations can be quite high. However, these laboratory conditions produce silver ion concentrations not commonly observed in natural environments. In natural environments, dissolved silver is mostly complexed into a much less toxic form, such as a silver-chloride or silver-thiosulfate complex [24]. To determine the 'free' silver ion concentration in solution, geochemical modeling (using programs like MINTEQ+) have been used [21]. Of course, input data for this assessment should be produced with filtered samples.

In practice, the dissolved silver ion concentration will generally be below 0.2 ppb, but this is highly dependent on the environmental conditions [25]. All else equal, dissolved silver ion concentrations will be higher under conditions of lower anion concentrations, lower levels of reactive sulfides and/or sulfur, lower amounts of suspended sediments, lower pH, and lower dissolved organic carbon [2].

1.4 Fate of Silver in the Environment

Silver distribution and transport is dominated by sorption/precipitation processes in freshwater systems (both groundwater and surface water) [20]. Dissolved and colloidal silver will tend to adsorb to particulates or form insoluble mineral phases and partition into the soils or sediment fraction.

Because gases and sub-micron sized particles can travel thousands of kilometers from their source, the primary source of trace metals in many remote environments (such as ice sheets, lakes, and peat) is from atmospheric transport [26]. Silver, like many trace metals, is largely immobilized in the soil column by either precipitating into an insoluble salt, reacting to form complex molecules, or adsorbing on reactive surfaces associated with organic matter, clays, and manganese and iron oxides in the soil [20].

Industrial wastewaters, from photographic industries for example, first complex their potentially toxic silver into silver into silver thiosulfate. Next, silver is converted into one of the most insoluble

silver salts; silver sulfide. Silver that is not economically recoverable can be mixed with sewage sledges and amended to agricultural soils. Approximately 80,000 kg of silver was amended in agricultural soils in 1978 [1]. Silver sulfides do not adversely affect crops at the concentrations found in amended soils (*Section 2.3.3*) nor does it increase the likelihood of toxic forms of silver bioaccumulating in species consuming these crops (*Section 2.3.2*).

2 Silver Toxicity

2.1 Silver Toxicity in Aquatic Environments

2.1.1 Overview: Bioavailability

There are several water quality parameters that dictate the toxicity of the silver ion; the most impactful being dissolved organic carbon (DOC) and chloride in freshwater systems [24]. The subsequent subsections will highlight factors inhibiting a linear relationship between the silver ion and toxicity. These subsections are largely a summary of Williams (2009) [2] and Eisler (1996) [1].

Recent studies assessing silver toxicity do not focus on total recoverable silver because there is not a direct correlation to toxicity (*Figure 2.1*). The Biotic Ligand Model was developed for this reason. In order to determine the potential toxicity to a species, the Biotic Ligand Model estimates the proportions of silver species between dissolved and solid, what fractions of dissolved Ag are complexed[2], and what fraction will be present as the toxic silver ion. This model does have limitations in assessing silver toxicity. First, it is primarily suited for gilled fish. Second, it does not account for the ameliorating effects of sulfide, a known parameter to reduce silver toxicity [3].

Recent studies have shown the silver ion complexed with DOC may be toxic [27]. Additions of DOC always results in higher total recoverable silver concentrations (reducing bioavilability to aquatic life). However, recent geochemical modeling studies suggest silver complexed with DOC may be toxic, but at least several times less toxic than the silver ion.

2.1.2 Overview: Toxicity

The toxicity of silver depends on many factors. This includes, but is not limited to the species and form of silver, environment silver is present (atmosphere, soil, or water body), and if aqueous, the chemical characteristics of the water.

Silver forms insoluble salts with several other species, including arsenate, arsenite, bromide, chloride, iodide, carbonate, chromate, cyanide, iodate, oxalate, oxide, sulfate, sulfide, tartrate, and thiocyanide, in aqueous media alone [22]. The free silver ion is therefore not as abundant in natural environments as once thought.

The silver ion is extremely toxic, but solid or complexed forms of silver are much less toxic. For example, $AgCl$, Ag_2S, and $Ag_2O_3S_2$ are 300, 15,000, and 17,500 times less toxic than the silver ion respectively [1].

---

[2] A complex has an ion at the center (commonly a metal ion) bonded to one or more ligands. Complexes can be of any charge, including neutral, and tend to exude both dissolved and solid behaviors in solution.
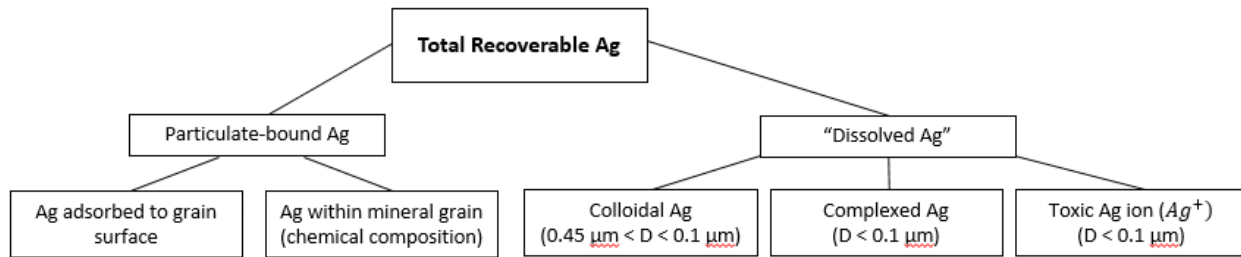
Figure 2.1: The form of silver is important when assessing toxicity. Quantifying total recoverable silver does not adequately address the threat of that silver level to the environment. The most toxic silver species, the silver ion, is essentially the non-complexed quantity of silver passed through a 0.1 μm filter (to eliminate colloids). D is the maximum diameter of the silver bearing species. D < 0.1 μg are silver species smaller than colloids (loosely defined as particulates sizes between 0.45 μg and 0.10 μg).

2.1.3 Dissolved Organic Carbon (DOC)

The World Health Organization states DOC has the highest protective effects of any other water quality parameter on silver toxicity [20]. Erickson's 1998 study showed how important dissolved organic carbon (DOC) was on controlling silver toxicity. This study compared lab water and water from the St. Louis River with similar Cl, sulfur-containing species, and was void of visible suspended sediment. Erickson stated the major difference between lab water and St. Louis River water was the concentration of DOC. The results showed fish (*Daphnia Magna*) in the St. Louis River water had LC_{50} values 60 times higher than in lab water. In other words, controlling all of the other water quality parameters, *Daphnia Manga* were able to withstand Ag concentrations 60 times more concentrated by using water more representative of environmental conditions. Wood (1999) demonstrated that DOC complexes may be toxic to both fathead minnows and rainbow trout, but noted total recoverable silver LC_{50} values were raised the most (reducing toxicity) with increases in DOC.

DOC concentrations change significantly in the watershed through time. Boyer (2000) showed DOC spikes in streams 2-4 weeks prior to peak streamflow in a Rocky Mountain catchment in Colorado. DOC concentrations quadrupled relative the rest of the year because shallow groundwater interacted with the upper-most soil horizon during this time. The longer residence times of water ("quickflow" snowmelt) has in the upper vadose zone, the more time organic carbon has to dissolve and later be discharged in the stream [28]. It should be noted that DOC concentrations are very complex and these trends do not apply to every watershed.

2.1.4 Influence of Chloride Ion (Cl⁻)

Adding the same amount of dissolved silver to freshwater environments is more toxic than when added to saltwater environments. First, there are more cations (namely, Na^+) to compete for organic ligand binding sites in saltwater, preventing the silver ion from interfering with osmoregulatory processes or bioaccumulation. Second, saltwater ameliorates silver ion toxicity effects by forming silver-chloro complexes and precipitates (only in brackish waters are Cl⁻ concentrations high enough to precipitate AgCl) [1]. Studies have shown Cl⁻ to have stronger ameliorating effects compared to hardness by binding to the silver ion to form silver-chloro complexes. Silver-chloro complexes commonly formed are $AgCl_2^-$, $AgCl_3^{2-}$, and $AgCl_4^{3-}$ [2]. In fact, one study modeled the ratio of the toxic

silver ion to the total recoverable silver reducing from 100% to about 8% with an addition of 5 $^o/_{oo}$ (parts per thousand) Cl^- [29].

High concentration spikes of the silver ion can still be toxic to fish in brackish environments. Strangely, this is true even when the silver ion concentrations are negligible in brackish waters (i.e. nearly all the silver is in some silver-chloro complex). However, the mechanism causing toxicity in salt-water species differs. In fish for instance, higher silver ion spikes will result in increased Na^+ and Cl^- concentrations in the blood plasma under waters of high salinity (as opposed to reduced Na^+ and Cl^- in plasma in freshwater species). In this case, dehydration is the ultimate cause of death of the fish in saltier conditions. In contrast, death in freshwater is more likely to be suffocation [20].

2.1.5 Influence of Sulfides and Sulfates

Silver forms the strongest complexes with sulfides in reducing environments. Silver has the highest affinity thiols[3], however, these are not common in natural environments. Silver thiosulfate ($Ag_2O_3S_2$) tends to only be the dominant species in industrial wastewater effluents [1]. In the United States, silver concentrations in these effluents are generally in decline as recovery of silver in these waste products are becoming more economically viable and efficient [20].

WHO (2002) found that in environments not anthropogenically altered, silver sulfhydrate (AgHS) or simple sulfur polymer species (HS-Ag-S-Ag-SH) dominate. At higher concentrations, colloidal silver sulfide or silver polysulfide complexes dominate [20]. Under reducing conditions, the silver ion is sometimes released from the sulfur bearing species. Because concentrations of the silver ion is typically extremely low in natural environments relative to the available binding sites of sulfur, the silver ions are quickly combined with other sulfur complexes. Both scenarios result in essentially non-toxic forms of silver [20].

2.1.6 Influence of Hardness

Hardness is also a significant control on Ag toxicity. However, it is not the largest control on toxicity as once thought [30]. Below are the data used to create the Environmental Protection Agency (EPA) Ag toxicity equation as a function of hardness, re-evaluated by Hogstrand (1996) [29]. Clearly, chloride ion concentrations have a much higher correlation on Ag toxicity than hardness, yet the EPA standard was based on the data in the right plot in ***Figure 2.2***.

---

[3] Thiols have similar molecular structures and chemical makeup as alcohols (hence the suffix "ol"). The main difference is the sulfur in thiols take the place of hydrogen in alcohols. Thiols give gasoline its characteristic odor.
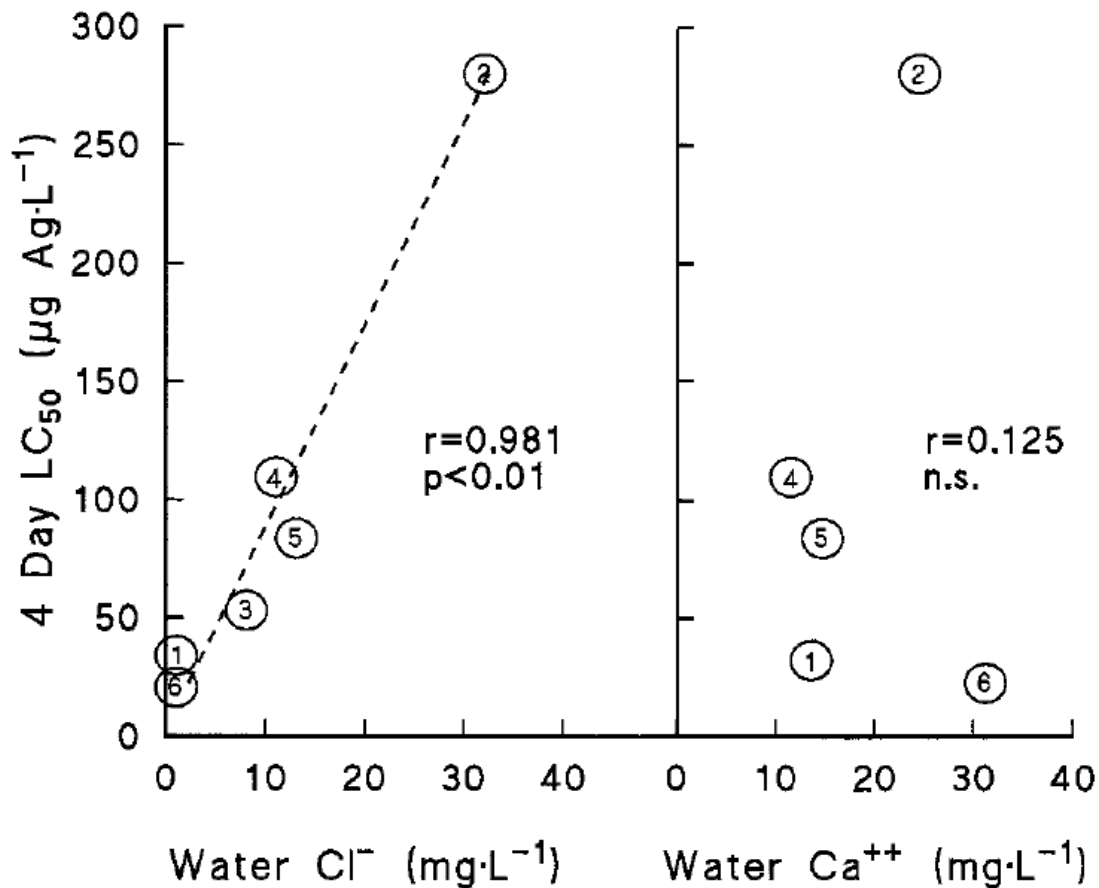
Figure 2.2: **This figure and caption are from Hogstrand (1996) [29]. Plot of data published by Lemke [31] on the toxicity of $AgNO_3$ to juvenile rainbow trout, indicating the close correlation between toxicity and water [Cl^-], and the lack of importance of water [Ca^+] in modifying 96-hour LC50. Numbers refer to the coded laboratories in the original report [of the inter-laboratory comparison].**

While there does remain a correlation between toxicity and water hardness, it is not as impactful as DOC, Cl^-, or sulfates. In fact, Erickson (1998) found that over the range of hardness values between 50 ppm and 250 ppm, Ag toxicity was only reduced by a factor of 2.5 [32]. This same trend was affirmed by several other publications [2][30]. EPA assesses toxicity of total recoverable silver concentrations as a function of hardness. Critical assessments regarding the toxicity of silver in relation to hardness (*Section 3.1*) interpret the EPA silver toxicity relationship to be under-protective and under-protective at lower and higher hardness values respectively [2]. In other words, low buffering capacity of lab waters (low ionic strength) over-estimate the toxicity of silver when applied to natural environments. Conversely, the increasing hardness will not buffer the silver ion toxicity as much as previously thought.

The mechanism by which hardness decreases toxicity is identical to that of DOC and sulfate. Cations (mainly calcium) compete with toxic silver ions at the binding sites of fish gills [32].

2.1.7 Colloids and Larger Particulates

Most available silver is adsorbed to the particulate fraction in stream networks. The fraction of silver adsorbed in the particulate increases as a function of turbidity. One recent study estimated 33-89% of total recoverable silver was present on a particulate phase (anything that could not pass through a 0.1 μm filter) [10] whereas some studies have shown 98% of total recoverable silver bound to particulates [2]. The high affinity of silver to sediments is most clearly seen in the nearly 6-orders of magnitude reduction of silver concentration in sediments and river water. River water samples rarely exceed 30 ppt of silver (when passed through a 0.45 μm filter) while river sediments typically range between 200,000 ppt and 1,700,000 ppt [10].

2.1.8 pH

Generally, as pH decreases, silver toxicity increases. One study showed silver toxicity decreasing by a factor of 3 when increasing the pH from 7.17 to 8.58 when testing juvenile fathead minnows [32]. However, increasing concentrations of humic acid[4] have been shown to decrease silver toxicity [2]. The two competing effects tend to result in a net bioavailability reduction with increased pH.

The precise mechanism of how pH influences silver toxicity is less obvious and more research is needed in this area [32]. Decreasing pH would increase the competition of H^+ ions and the silver ion at gill sites; reducing toxicity. Increasing pH within realistic environmental values are not sufficient to result in significant silver speciation with the hydroxide ion. On the other hand, decreasing pH releases the adsorbed silver in soils or particulates, increasing the amount of dissolved silver and making the silver ion more bioavailable. These observations may suggest that the two effects cancel out and result in a net decrease in toxicity with increased pH.

2.2 Toxicity to Aquatic Species

2.2.1 Overview: Early Research

The validity of results from prior to the 1990's may have been compromised by a number of factors[7]. First, the importance of ultra-clean lab methods were not globally implemented. Thus, samples containing extremely low silver concentrations were reported with higher values either because of anthropogenic contamination in the field or lab, or because samples were at or below instrument detection limits. Second, laboratory conditions did not realistically simulate the natural environment. Laboratory water was often used instead of natural waters for aquatic toxicity tests [32]. Laboratory waters often lack natural concentrations of DOC, sulfides, pH, trace metals, and suspended sediments. Many studies did not report these other water quality metrics, making their applicability to standards questionable [32]. Likewise, the most bioavailable form of silver was used in laboratory procedures instead of silver compounds common in the environment. For instance, silver nitrate ($AgNO_3$) was used in many studies. This is by far the most soluble silver compound and can produce environmentally irrelevant silver ion concentrations (especially when laboratory waters lack natural toxicity buffers) [29]. $AgNO_3$ is rarely found in the natural environment. Recent research is focused on more common silver species in the environment, such as silver salts formed with bromide, iodide, and chloride, which are much less soluble and produce lower free Ag ion concentrations [1].

---

[4] Humic acid is produced from decomposition of organics, often abundant in soils.

Much of the historical (pre-clean techniques), as well as recent studies, were plotted in ***Figure 2.3*** in the 2002 WHO literature review [20]. The lethal concentrations vary by 2 orders of magnitude or more when replicating toxicity tests. This is likely a product of not normalizing for the toxicity buffers and lack of clean techniques.
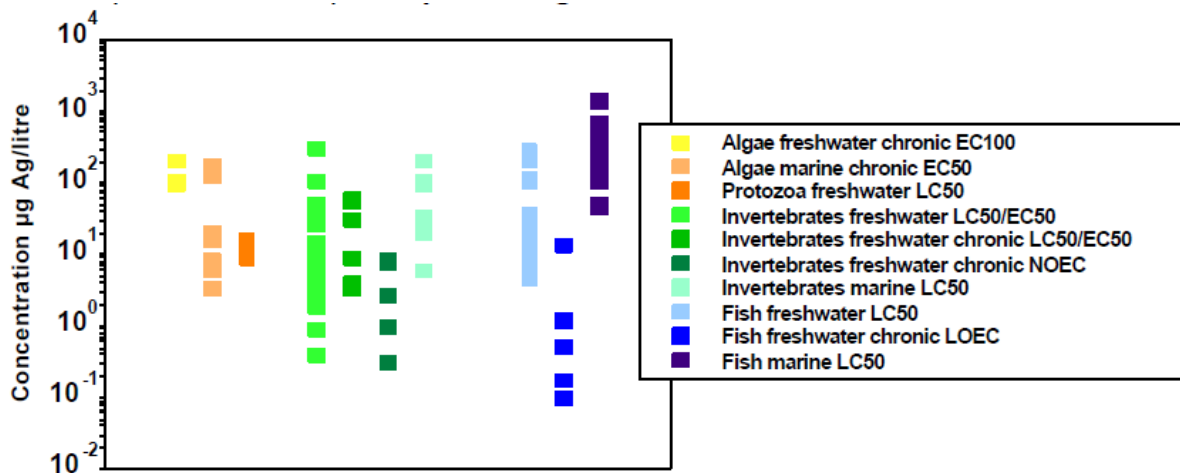

Figure 2.3: "Plotted values are from studies where silver was added to the medium as silver nitrate and the silver was likely to be present as the free ion (a scenario unlikely in the environment)." [20].

2.2.2 Toxicity to Fish

The silver ion is especially toxic to fish because Ag^+ disrupts the gas exchanges and acid-base regulatory functions. This inhibited ability to maintain a state of homeostasis can result in a number of fatal consequences as seen in ***Figure 2.4*** [29]. Fortunately, mitigating silver toxicity in fish is reversible because it is mostly caused from water interaction at the gill surface. Additions of ameliorating factors in water (*Sections 2.1.3 - 2.1.8*) lower the concentration of the silver ion and immediately restore the ability for fish to osmoregulate normally [1]. Frogs respond differently to lethal concentrations of the silver ion. Silver concentrations (primarily as silver nitrate) in excess of 10 ppb interfered with frogs' calcium metabolism [1].

Importantly, the reason silver is toxic is not because of accumulations in internal organs, but because of the disruptive gas exchanges at the gill surfaces of fish and respiratory processes of other aquatic species. This was verified in several studies. Wood (1996) compared 10 ppb silver nitrate solution (yielding relatively high amounts of the silver ion) and 30,000 ppb of silver thiosulfate (negligible silver ion concentrations). The silver thiosulfate solution caused accumulations in the plasma and internal organs to be more than 3 times greater than the rainbow trout in the silver nitrate solution. The rainbow trout exposed to the silver thiosulfate solution did not experience any of the osmoregulatory stresses while the rainbow trout in the silver nitrate solution experienced lethal effects, despite silver nitrate additions resulted in total recoverable silver concentrations 3,000 times less than the silver thiosulfate group. Bioaccumulation factors of silver in the blood plasma were higher in the fish exposed to silver thiosulfate, but only the fish exposed to silver nitrates experienced toxic effects [33].
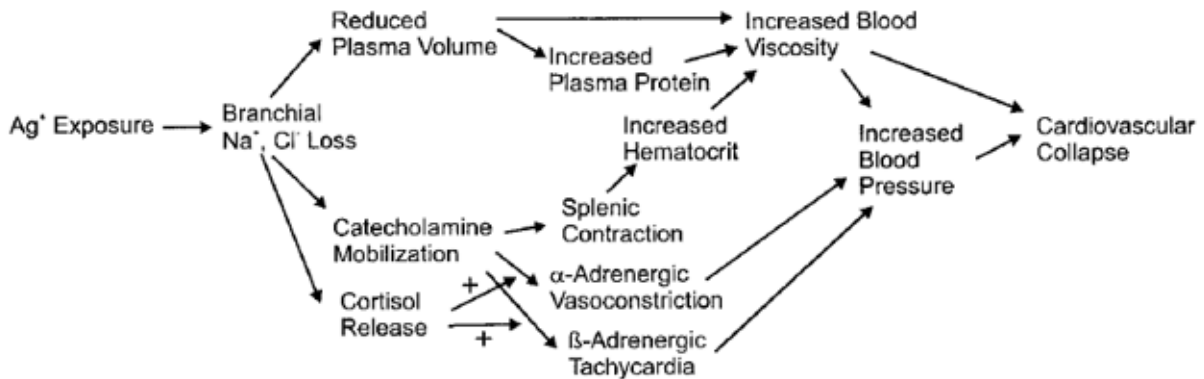
Figure 2.4: "Suggested etiology of acute silver toxicity in freshwater fish. Exposure to the free silver ion, Ag^+, results in a net loss of Na^+ and Cl^- from the blood plasma. This osmolyte loss causes a sequence of events that eventually leads to a fatally increased blood viscosity and blood pressure. Cardiovascular collapse is likely to be the final cause of death". Figure and caption directly from [29].

There are several fish species that are especially sensitive to silver nitrate toxicity tests. Four of the most sensitive are fathead minnows (5.3 ppb Ag), speckled dace (4.9 ppb Ag), mottled sculpin (5.3 ppb Ag), and rainbow trout (4.8 and 10.2 ppb Ag for juvenile and adult fish respectively). All metrics for toxicity were 96-hour LC_{50} tests [20]. These values and values reported in subsequent toxicity sections cannot be compared directly because lab waters spiked with silver nitrate have differing amounts of hardness, pH, DOC, salinity, and alkalinity. Therefore, it is difficult to determine the single most sensitive species.

Juvenile fish are the most sensitive to the silver ion (Ag^+). Developing trout and phytoplankton experience adverse toxic effects at concentrations as low as 170 ppt. Lowest Observed Effect Concentrations (tests usually 60 days) for larvae and embryos have been measured as low as 100 ppt of the silver ion; experiencing stunted growth [20].

2.2.3   Microorganisms and Invertebrates

Ionic silver is fungicidal, algicidal, and bactericidal at concentrations as low as 10 ppb [2]. The silver ion is still occasionally used as an antibiotic today. The most sensitive microorganism (besides algae) is the protozoan (8.8 ppb Ag). This test used silver nitrate as well but the test was a 24 hour LC_{50} test.

The most sensitive invertebrate species studies were mayflies (6.8 ppb Ag), daphnids (5 ppb Ag), and amphipods (1.9 ppb Ag). All of the following were 96 hour LC_{50} tests using silver nitrate as the environmental stressor [20].

Hirsch (1998) investigated how extremely high total recoverable silver concentrations would affect perhaps the most sensitive invertebrate, the amphipod. These amphipods were subjected to extremely high concentrations of 753 ppm Ag spiked natural stream sediments using Ag_2S (one of the most insoluble silver salts). The study showed no adverse effects over the 10 day period even though amphipods burrow in these sediments [34]. This reinforces the necessity of quantifying toxic species of silver and not just total recoverable silver. Field data alone does not adequately address toxicity. To fully address toxicity, field data should be input data into a model estimating silver

speciation. The precise mechanism causing silver toxicity should be interpreted based on these speciation values.

2.2.4   Algae and Clams

There are two ways silver can accumulate in high, and potentially toxic, concentrations within a species relative to the surrounding environment. The first is bioconcentration, where uptake, adsorption or absorption rate of a toxic species is higher than the excretion rate. The bioconcentration factor is the ratio of concentrations of the chemical species within an organism to the surrounding environment. The second is biomagnification, where silver is accumulated from an organism's diet. The sum of bioconcentration and biomagnifications is called bioaccumulation [23].

Bioaccumulation factors are highest in algae and clams than any other studied freshwater species, especially algae. Marine and freshwater algae accumulate Ag from adsorption rather than uptake, so bioaccumulation factors as high as 66,000 have been recorded [1]. Lee (2005) suggested some types of algae accumulate via intracellular accumulation, meaning even silver-chloro complexes could be toxic to algae [35]. Other marine species with notably high bioaccumulation rates are diatoms (210), brown algae (240), mussels (330), 2,300 (scallops), and oysters (18,700). Freshwater species studies have much lower bioconcentration factors than marine organisms, ranging from negligible (in bluegills) to 60 (in daphnids) [1].

Green algae have bioconcentration factors as high as 2.5×10^6, the highest recorded of any other algae in published literature reviews. However, bioconcentration factors are rarely this high in nature. This is because bioconcentration factors are again correlated most to the toxic silver ion [23].

Another toxicity concern was raised if the algae with high bioaccumulations were consumed by higher order species in the food chain. This effect has not been witnessed in literature either [23]. The silver absorbed to the algae remains in the absorbed (virtually non-toxic) state even when pH is reduced to 2, when the cell walls of the algae break down, and when digestive enzymes react with algae [23]. Therefore, biomagnification to other species is unlikely.

Some forms of algae showed signs of acute toxicity at silver ion concentrations as low as 0.3 – 0.6 ppb, and caused blue-green algal mats to disappear from an experimental ecosystem at Ag concentrations between 2- 7 ppb [20].

2.3   Terrestrial Species

2.3.1   Humans

Silver is generally considered non-toxic to humans and animals. Humans are exposed to large amounts of silver every day. Silver is abundant in our tooth fillings, silverware, jewelry, and many electronics [36]. In addition, humans consume an estimated 70-88 µg of silver per day [37], mostly through water. More recent estimates of total silver intake by humans is 7.1 µg per day [38]. Humans can consume up to 10 grams of silver throughout their lifetime without any adverse effects or precursors to adverse effects [38]. Assuming the high estimate of 88 µg per day for 70 years, total human intake of Ag would only be 2.2 grams.

The EPA standard of 100 ppb (total recoverable silver) is a secondary maximum contaminant level. This means it is not toxic at this concentration, it is developed to reduce nuisance conditions. This

value is based on historical (accidental) exposures of humans to silver. Doctors prescribed nasal sprays containing extremely high concentrations of silver in the 1930's; 4% silver iodide [7]. There were no reported physiological adverse effects. However, prolonged ingestion of high concentrations of either colloidal silver or the silver ion leads to a skin condition known as argyria. Like animals, there are no adverse effects known but a graying discoloration of the skin [39].

2.3.2 Animals

There are few studies looking at the toxicity of silver to mammals. This is because there is little evidence of silver toxicity in natural aquatic systems, which accumulate silver via bioconcentration (Ag via body surface uptake) and biomagnification (Ag via food). Animals can only accumulate silver through the latter mechanism while aquatic organisms accumulate silver through both [23]. The few studies on silver toxicity studies pertaining to mammals reveal biomagnification is unlikely. However, high silver concentrations in the liver will inhibit the absorption of vitamin E, copper and selenium [1]. Toxic effects in animals often manifest themselves in vitamin deficiency symptoms.

Once the silver ion is ingested or inserted in the bloodstream, most is removed by the gastrointestinal tract and the liver [40]. The silver ion binds to RNA, DNA, or proteins, subsequently accumulating in the liver [23].

In one study turkeys were fed a diet of 900 ppm silver nitrate for 4 weeks – roughly 1,000 times the concentration typically found in soil. Turkeys experienced growth depression, enlarged heart, increased mortality, and a copper deficiency. The enlarged heart and mortality levels were corrected once turkeys were fed copper supplements in addition to the silver spiked food [37]. The copper supplements ameliorated the deficiency related symptoms in turkeys.

A few studies pertaining to rats and silver nitrate have been conducted as well. Lethal concentrations of silver nitrate for rats are 13.9 ppm silver to body weight. Rats experienced lethal effects via drinking water with 1586 ppm Ag for 37 weeks. Rats also experienced sluggishness when drinking water was 95 ppb and kidney failure when drinking water was 400 ppb for 100 and 125 days respectively [20].

To evaluate the effects of cloud seeding on livestock, 1-year old sheep were fed up to 10 mg silver iodide per kilogram of body weight per day[5]. After 86 days, none of the health metrics recorded differed significantly from control group, despite accumulating silver in the liver at concentrations of 17 ppm [41].

2.3.3 Plants

There have been a few studies performed concerning the effect of insoluble silver compounds on crops. One study was performed for wastewater treatment sludge applications to crops. This study evaluated whether high silver amounts from photo-processing facilities would adversely affect plants. This study investigated corn, lettuce, oats, turnips, lettuce, spinach, and Chinese cabbage. Sewage sludges were added to one set of crops (mean Ag = 13.5 ppm) while the other set was spiked with silver up to 155 ppm. The results showed that no crops, except for lettuce, showed large increases of silver in edible crop portions. Soybeans subjected to concentrations above about 100 ppm experienced decreased yield. Lettuce, Chinese cabbage, and spinach experienced decreased

---

[5] 1-year old sheep are typically 60 kg. This would result in 600 g of AgI per sheep per day. 1,000 generator hours from cloud seeding (typical of a given winter season) would release 23 kg of AgI, resulting in ~10 g of AgI deposited per km^2.

yield at 14 ppm soils and toxicity threshold values at 26 ppm and 43 ppm for lettuce and Chinese cabbage respectively [42]. Because most natural soils have silver concentrations between 0.1 and 1 ppm, toxicity threats to plants is unlikely.

This study also showed that silver concentrations increased roughly 0.25 ppm (dry weight) in control plants. In both sets of crops, the lower stem, upper stem, and leaf portions (except for lettuce) accumulated trace amounts of silver from the silver-spiked soils [42].

Ratte (1999) showed two species of plants that have significant bioaccumulation potential. First, mushrooms have bioconcentration factors up to 150 when grown on silver enhanced sewage [23]. Silver was concentrated in the stalk and stem, with bioconcentration factors of up to 230. There was no impairment in growth or fruit given these bioconcentration factors. No conclusion was drawn on the bonding of silver to the mushrooms or the potential susceptibility to biomagnifications. The second species listed was a type of grass grown on an Ontario silver mine tailing pile. Bioconcentration factors of grass blades relative to water in the tailings were up to 124,000 [23]. Strangely, the highest bioconcentration factor of grass roots was only 3 even though the roots had higher Ag concentrations than the grass blades.

It is also worth noting that, as with animals and fish, species are much more susceptible to silver toxicity in the very early stages of life [1]. The most sensitive phase of a plant is during germination. Concentrations of just 750 ppb from soluble silver nitrate induced negative effects on some plant species [20].

3 Standards

The environmental standards for evaluating silver concentrations vary with the application (human vs. aquatic species impact) and between jurisdictions (state, federal, international).

Because silver is considered essentially non-toxic to humans, the EPA lists silver in the "secondary drinking water standards" for potable water. These standards are in terms of total recoverable silver (how much silver is dissolved after strong acid digestion) and is set orders of magnitude higher than normally present in natural conditions. WHO, U.S. EPA, and the Australian EPA have established drinking water standards at 100 ppb. Two states, Arizona and Hawaii, have set more stringent standards on drinking water at 50 ppb [43].

These agencies are aware that the silver ion is the primary control to toxicity of aquatic species, but differ in how they estimate the concentration of the silver ion. State and federal agencies enforce acute silver toxicity standards in terms of dissolved silver concentrations, estimated empirically as a function of total recoverable silver. The Australian EPA on the other hand, regulates the toxic silver ion specifically, as seen in *Table 3*.

Table 3: Drinking Water and Freshwater Standards/Guidelines

Standard	Potable Water Total Recoverable Ag [ppb]	Acute Toxicity of Dissolved Ag in Freshwater [ppb]	Source
Arizona DEQ	50	1+ [a,b,d]	[44]
Hawaii DEQ	50	3.2[b,d]	[45]
Idaho DEQ	100	3.4[b,c]	[46]
Wyoming DEQ	100	1.7[b,c]	[47]
U.S. EPA	100	3.2[b,d]	[37]
Australian EPA	100	0.05[e]	[48]
WHO	100	No standard	[38]

a) 1 ppb is the minimum standard, standard increases with increased water hardness **b)** These standards are based on hardness values and Water Effective Ratios. Hardness is assumed 100 ppm for regulatory purposes; **c)** Coefficient multiplying total recoverable silver, used to estimate dissolved silver: water–effect ratio (WER) equals 1; **d)** Coefficient multiplying total recoverable silver, used to estimate dissolved silver: water–effect ratio (WER) equals 0.85; **e)** This standard is the 95% species protection level. This concentration is just the silver ion.

3.1 U.S. EPA Standards

The EPA has two water quality standards for toxic substances: Criteria Maximum Concentration (CMC) and Criterion Continuous Concentrations (CCC). The EPA did not establish a CCC standard for silver, there is only a CMC standard. The EPA defines CMC standards as "an estimate of the highest

concentration of a material surface to which an aquatic community can be exposed briefly without resulting in an unacceptable effect" [49]. The EPA derived these standards using empirical equations estimating the percent dissolved silver (includes complexed silver, ionic silver, and sometimes colloidal silver depending on definition of "dissolved") and its effect on aquatic species in a laboratory setting. Standards and equations are based off of total recoverable silver measurements.

It is important to understand how these standards were calculated in order to interpret the toxicity of silver values in the environment relative to these standards. The EPA is aware that silver speciation is the largest control on toxicity, but is also aware that water quality tests generally quantify total recoverable silver instead of the concentration of the silver ion in solution [50]. Therefore, the EPA created two empirical formulas to estimate toxicity given the water hardness and total recoverable silver concentrations. The first empirical equation calculates permissible total recoverable silver concentrations in freshwater environments as a function of hardness. To create this formula, six laboratories conducted both static and flow-through tests of silver toxicity; resulting in relationships of LC_{50}-96 hour and hardness values at various concentrations for the following sensitive aquatic species: *Daphnia magna*, rainbow trout, and fathead minnows [31]. The relationships for these 3 species EPA were averaged to compute *Equation 1* below [37]; and is plotted against hardness in **Figure 2.5**.

[1] $Ag = (WER) * e^{(1.72*\ln(hardness))-6.59}$
        Ag = Concentration of total recoverable silver [ppb]
        hardness = Concentration of calcium and magnesium salts [ppm]
        WER = water-effect ratio, fixed at 0.85 [unitless]

Equation 1 has been critically discussed in literature [30] [29][27]. Williams (2009) stated *Equation 1* is under-protective at high hardness and over-protective at low hardness [2]. In other words, the relationship between hardness and Ag toxicity does not possess as much curvature in this relationship as **Figure 2.2** shows and may have a more linear trend (*Section 2.1.6*). Hogstrand (1998) stated "The U.S. EPA hardness equation currently used for regulating acute toxicity is faulty, and research is urgently needed to replace it with a relationship that includes... ...more important geochemical modifying factors" [25]. The influential geochemical modifying factors referenced here are explained in greater detail in *Section 2.1*.

Erickson (1998) criticized the data used for the EPA Ag toxicity equation in not standardizing water quality variables constant (such as pH and alkalinity) when measuring the effect of hardness and silver toxicity. Erickson accounted for those variables and found hardness to be 10 times less impactful than the EPA data when methods were replicated. In this same study, when total organic carbon (not specifically DOC, which is the impactful variable in total organic carbon) was increased by 17 ppm, toxicity values decreased by factors ranging between 10 and 60 [32].

The water-effect ratio (WER) is another coefficient developed by the EPA to estimate the proportion of dissolved silver to total recoverable silver (again, this includes complexed silver, the silver ion, and in some cases colloidal silver) [51]. WER was calculated based on three studies mentioned in the

1993 EPA memorandum, which revealed the primary control on toxicity was the silver ion, not total recoverable silver [50]. The studies used in designing the WER are listed in the *Table 4* below (Table modified from 1993 EPA memorandum). Every study was a static water test. The CMC toxicity concentrations were adjusted using the WER coefficient, fixed at 0.85 based on the results from *Table 4*, apply to both freshwater and saltwater standards. After 1993, CMC toxicity values were calculated as an empirical function of "dissolved" using *Equation 1* multiplied the WER of 0.85.

The WER was established so the EPA could give states discretion to adjust standard values to more site-specific conditions. The EPA is aware that many factors ameliorate silver toxicity, so states are given the right to adjust the WER in order to estimate the concentration of the toxic silver ion (relative to the total recoverable fraction) likely present in that environment.

Table 4 EPA Data Used to Derive the Water Effect Ratio (WER)

Concentration Ag (ppb)	Dissolved[a] Fraction (%)	Species[b]	Food[c]	Hardness [ppm]	Alkalinity [ppm]	Reference
0.19	74	DM	NO	47	37	[52]
9.98	13	DM	YES	47	37	[52]
4	41	DM	NO	36	25	[53]
4	11	DM	YES	36	25	[53]
3	79	FM	NO	51	49	[54]
2-54	79	FM	YES	49	49	[54]
2-32	73	FM	NO	50	49	[54]
4-32	91	FM	NO	48	49	[54]
5-89	90	FM	NO	120	49	[54]
6-401	93	FM	NO	249	49	[54]

a: "Dissolved" was defined as whatever passed through a 45 μm filter.
b: Two species were analyzed. DM = daphnia magna, FM = fathead minnow.
c: The EPA memorandum stated the studies that included food probably reflected more realistic toxicity values.
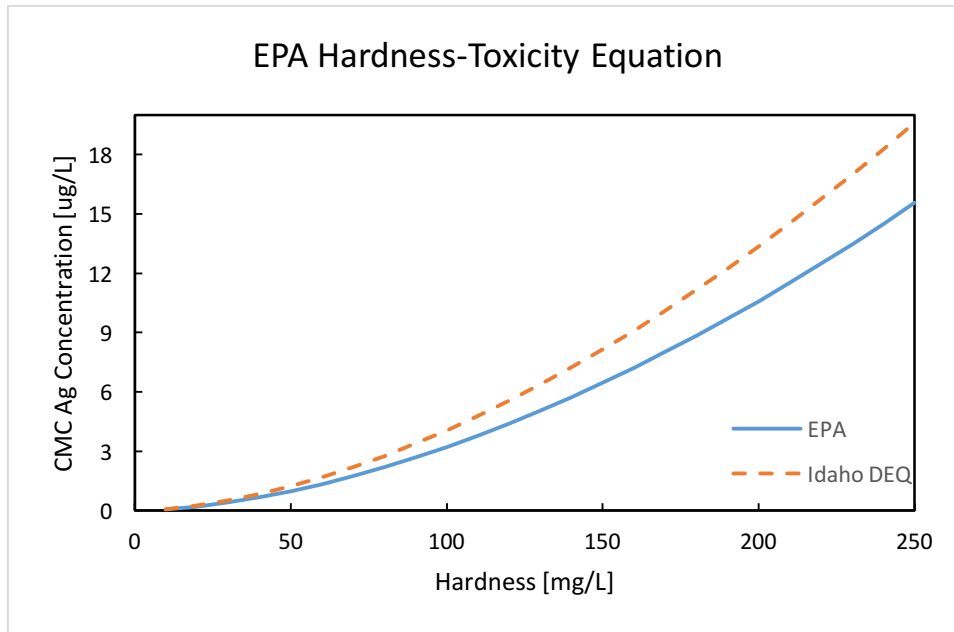
Figure 2.5: **EPA standards applied as a function of hardness. Generally, hardness values in natural environments in Idaho typically reside between 60 and 120 ppm** [55]**. Idaho DEQ standards are slightly less stringent.**

3.2 Idaho Department of Environmental Quality Standards

The Idaho Department of Environmental Quality utilizes the same formula for the EPA except the two coefficients are altered slightly. First, the Y-intercept is changed from -6.59 to -6.52. Second, the WER is fixed at 1 (assuming total recoverable silver is equal to total dissolved silver) and hardness is assumed to be 100 if actual hardness measurements are unavailable. Idaho's adjustments to the calculation increase the contaminant threshold level. This allows a wider range of permissible total recoverable silver concentrations, especially at high hardness values (*Figure 2.5*). Associated tables in descriptions are available in IDAPA 58, section 210 [56]. Expressed mathematically:

$$[2] \quad Ag = (WER) * e^{(1.72*\ln(hardness))-6.52} \; = \; (1) * e^{(1.72*\ln(100))-6.52} \; = \; 3.4 \, ppb$$

3.3 Australian EPA Standards

Australia utilizes guidelines called 'trigger values', and have a different definition compared to the EPA standards in the United States. Trigger values are generally not fixed, but are permissible values relative to natural background concentrations. Generally, local guideline levels are established to be most applicable to the region of study. However, if no background information is available, the conservative value in *Table 3* is assigned to the region. Silver ion concentrations of 0.05 ppb are trigger values in highly protected environments. Should sources go above this trigger value, environmental authorities are to investigate the sources of the contaminants and discern whether these values are tolerable/typical in the local setting and what proportion of these values are anthropogenic [48]. In other words, these are not "pass or fail" standards, but rather guidelines revealing where research and/or mitigation efforts should be focused.

3.4 World Health Organization (WHO) Standards

WHO ceased to provide world-wide standards of toxic chemicals starting in 1982. Instead, WHO establishes water quality 'guidelines'. Guidelines allow each nation to judge the water quality criteria based on their circumstances and culture. WHO found essentially no risk of silver toxicity to humans due to the low natural levels of silver present in drinking water relative to safe lifetime oral intake of silver. A human can safely intake up to 10 grams of silver orally in their lifetime based on the no-observed-acute-effect-level (NOAEL) and experience no adverse effects or precursors to adverse effects [38]. In other words, a person would have to drink 4 L of water with 100 ppb Ag for 70 years to obtain this value. Even in polluted areas, silver concentrations are generally at least 2 orders of magnitude less concentrated than the 100 ppb WHO drinking water guideline.

4   Concerns of AgI Cloud Seeding and the Environment

4.1   AgI Effects of Cloud Seeding

The effects of cloud seeding on the environment has been studied extensively; especially with respect to freshwater ecosystems [2] [3][15][57]. All studies found sub-ppb total recoverable silver enrichments in precipitation silver due to cloud seeding. These concentrations are low because the total silver flux from cloud seeding can be considered small; it comprises 0.1% of the total silver released to the environment globally [1]. The enriched silver is largely immobilized in soil or absorbs/complexes to aqueous chemical species [7].

Table 5: Recent Freshwater Samples Collected at AgI Seeded Areas

Project Location	Highest Ag (Mean Ag) [ppt]	Samples Collected	Date(s) Sampled	Source
Wyoming (pre-seeded)	192 (21)	40	October (23-25)-2005	[3]
Wyoming (seeded)	2 (< 1)	39	July (20-21)-2010	[15]
Idaho (2010-2012, seeded)	32 (9)	112	August 2010 – June 2012 (Highest sample collected June 24-2011)	2012 IPC Freshwater Sampling Report
Idaho (2015)[6]	45 (7)	24	March 20-2015	2015 IPC Freshwater Sampling Data Sheet

More publications on the potential effects of AgI seeding on soils, streams, and organisms are anticipated to be published from the Snowy Hydro Limited cloud seeding project in Australia. Snowy Hydro collected nearly 7,000 samples of stream sediments, stream water, moss, peat, and soils. Results will be expected to be published soon. However, preliminary statements regarding these data note no significant changes in silver concentrations and "mean concentrations for all locations and sample types are well below relevant environmental guidelines" [58].

4.2   AgI Abundance in Snowpack

AgI is present in trace amounts in snow because AgI ice nuclei are small. Between 10^{14} - 10^{16} ice nuclei are produced by combusting one gram of silver iodide, yielding 0.06 μm diameter AgI nuclei.

---

[6] Unlike other campaigns listed in this table, all samples were collected in one basin on the same day. Therefore, these data cannot offer insight on seasonal variations in flow rates known to modify the sediment loading – the speculated primary source of total recoverable silver in these samples.

Cooler temperatures (up to -15°C) and higher wind speeds generally produce more AgI nuclei per gram [59]. Due to the small size of these nuclei, generators burn roughly 21 grams per hour to seed a storm. The average release of AgI via ground generators from 2003-2012 is 18.6 kg. These nuclei are dispersed throughout the 2,400 km² Payette Basin per snow season[7].

This results in part per trillion enhancements in seeded snow above background concentrations. These concentrations have considerable spatial variability because seeding rates do not have a linear relationship with total recoverable silver concentration in snow. For example, a seeded snowflake may accrete more water during fallout and secondary ice forming processes such as ice multiplication produce snowflakes void of AgI. These scenarios would both reduce the silver concentrations in the snow.

Field studies in the Western United States investigating silver concentrations in snow Ag from seeding are likely range from 2-20 ppt, rarely exceed 25 ppt [60], and almost never exceed 50 ppt [3]. The layer(s) containing these elevated concentrations tend to occupy a thin layer (1-10 cm scale) in the snowpack. In most instances, vertical sampling at the 1-5 cm scale across multiple sites in a seeded snowpack will produce AgI seeding signatures in roughly 20% of the samples [61][15][62][8][18] with two exception having roughly 80% [63][71].

4.3 Cloud Seeding Byproducts

The potential impact of other chemicals used to create ice nuclei through AgI combustion have also been assessed. Aircraft AgI flares are composed of ammonium perchlorate, zinc powder, aluminum powder, silver iodide, and copper iodide. None of these chemicals are listed as hazardous materials by the EPA. Flares burn 150 g of silver iodide in conjunction with the rest of these compounds [64]. These flares likely disperse 200 km down-wind [65], so concentrations will be at trace levels in snow. Additionally, there is a limited fire risk from aircraft seeding activities because it is conducted at high altitude under snow covered conditions. Also, ground generators are at limited risk because at least a 9.1 m (30 ft) radius of trees is cleared surrounding ground generators [64].

4.4 AgI Toxicity

4.4.1   Overview

AgI is extremely insoluble (only a small fraction of the solid is dissolved before the solution becomes saturated and no longer dissolves the solid). This means the maximum dissolved Ag concentration, assuming unlimited AgI, is approximately 1 ppb. However, a large fraction of this dissolved Ag would adsorb to particulate matter such as manganese and iron compounds or clay particulates [7]. Once

---

[7] Source: http://www.idwr.idaho.gov/waterboard/Meetings_Minutes/agenda/pdf/2013/03mar/5-13/IdahoPowerCSProgram_IWRB_032013.pdf

[8] Huggins' 2009 study in the Snowy Mountains study arbitrarily displayed statistics of % of samples greater than 1 ppt. This study stated ~50% of samples from a seeded storm had Ag concentrations greater than 1 ppt. This is not a useful statistic because background Ag concentrations were predicted around 3 ppt here.

absorbed to particulates, Ag^+ is no longer bioavailable (toxic) to alter the osmoregulatory processes of fish and related species.

A number of studies demonstrated that the total Ag loading from AgI cloud seeding is low in soils, water bodies, and the atmosphere. The Australian EPA found no significant difference in silver concentrations in aquatic, soil, stream sediments, and sensitive aquatic species that bioaccumulate trace metals with the area targeted for cloud seeding [66]. Huggins (2009) found that the average Ag concentrations in seeded snowpack were actually lower in seeded than unseeded years. This was attributed to the relatively large fluctuations of background concentrations year to year, varying from 3 to 9 ppt [62]. These large fluctuations are attributed primarily to dry deposition of aluminosilicate dust. Lastly, stream samples taken from the Wyoming Weather Modification Pilot Program did not find a correlation between AgI seeded watersheds and stream Ag concentrations. The largest control on Ag concentrations in these streams were suspended sediments [3].

4.4.2 Nano-Silver (Ag^0)

Nano-silver particles are manufactured for use as an antimicrobial agent in consumer products (i.e. long underwear, paint, plastics, and paper). These products are specifically designed to release the silver ion [11]. "Nano-silver species" are defined as being smaller than 100 nm in its longest dimension [36]. Nano-silver has not been well understood until recent years and has been the subject of many recent toxicity studies. The silver ion is toxic not only to bacteria, but every other aquatic species at small concentrations. Nano-silver has an extremely high surface area/volume ratio, increasing the risk of the solid particles being dissolved in solution. Finally, these consumer products tend to be manufactured to prevent bonding of these nano-silver particles [11]. Again, this encourages anti-microbial activity and resists natural processes that would otherwise mitigate Ag toxicity (via DOC, agglomeration, chloride, sorption, etc.).

An AgI nucleus is usually 60 nm in its widest dimension [59] and is classified as a nano-silver particle. However, AgI is not an engineered nano-particle (it is formed by combustion) and it is highly insoluble [36]. Likewise, AgI nuclei are not manufactured to resist bonding, so AgI tends to accumulate in the upper 2 cm of the soil horizon via adsorption [67]. AgI was not identified as a serious source of concern in the EPA's 2010 literature review of nano-silver [11].

Reidy (2013) distinguishes between how the silver ion and nano-silver are bioavailable, and thus toxic to aquatic species. The silver ion enters organisms via diffusion across some biologic membrane (gill, skin cell, etc). Silver ion concentrations tend fluctuate in an organism until some equilibrium is reached. The silver ion has essentially no surface area and reacts primarily with organics, mineral surfaces, and forms complexes. Nano-silver, on the other hand, is actively taken up by an organism. The nano-silver particle then dissociates within the organism resulting in very high, local concentrations of dissolved silver. Nano-silver particles dissociate readily within the species due to their extremely high surface area-to-volume ratio. Nano-silver tends to bind to biomolecules [68].

Newton (2011) investigated the difference in toxicity of nano-silver particles and ionic silver to *Dapnia magna*. Results showed nano-silver toxicity were a function of dissolution into the toxic silver ion, implying nano-silver had no effect in solid form to *Daphnia magna*. Therefore, the toxicity of

nano-silver can be estimated in the Biotic Ligand model once dissolution estimates become reliable [69].

4.4.3   An Assessment of Cloud Seeding-Derived AgI Toxicity to Freshwater Environments

We present here a 'worst case scenario' calculation for assessing the impact of cloud seeding. In this calculation we make assumptions about the amount of Ag delivered to the snowpack, the behavior of that Ag once deposited, and the delivery of that Ag to a water body. A summary of these calculations and discussion are presented by Edwards (2006) [3]. **Table 6** shows two classes of assumptions, maximum and likely.

Table 6: Hypothetical Scenario Evaluating Environmental Impacts due to Cloud Seeding

Primary Controls on Toxicity	Hypothetical (maximum) Values	Likely Values
% AgI dissolving into Ag^+	100%	<<1% (K_{sp} = 9.2x10^{-9}M) [2]
% increase in precipitation due to AgI	15%	3-15% [70]
Concentration of seeded snow	50 ppt	3-48 ppt [15][62] [18][b]
% of AgI in snow reaching water bodies	100%[a]	Variable, but <100%

a: This assumes no sorption to soil particles in the upper horizon or uptake by vegetation.
b: 1 sample out of 1,300 had a concentration exceeding 48 ppt Ag.

If 15% of the snowpack contained the enriched Ag concentrations of 50 ppt, then cloud seeding would raise the average silver concentration of the snowpack from the 2 ppt Ag background concentration to 9.2 ppt. This AgI enhancement is still within typical concentrations in natural freshwaters of 1-30 ppt Ag. The trace amounts of dissolved silver will likely complex or will not be bioavailable to aquatic species due sorption processes, where the majority of naturally occurring silver is already present. Wen (2002) found river sediments typically have between 0.2 to 1 ppm of silver, almost 6 orders of magnitude higher than the overlying water [10]. Therefore, the majority of the AgI will become immobilized in a non-toxic form at ultra-trace amounts in stream sediments.

One final hypothetical scenario was proposed by Edwards (2006). If 100% of the snow was at 50 ppt and all other assumptions from **Table 5** remained the same. The resulting total recoverable silver concentrations in snowmelt entering the stream would still be more than 10 times lower than the LC_{50} concentration (from Biotic Ligand Model) of the most sensitive aquatic species studied [3]. The LC_{50} values were computed by the EPA using silver nitrate ($AgNO_3$) (*Section 2.1.1)*. AgI is approximately 10,000 times less toxic than the $AgNO_3$ salts used in many other toxicity studies [23]. The LC_{50} concentration would be even higher using AgI alone versus the $AgNO_3$ used to derive the standard. Therefore, AgI based LC_{50} values would likely allow much higher total recoverable silver concentrations before these sensitive species experience toxic effects.

4.4.4   AgI Accumulation in Soils

A variable, but significant, contribution of AgI released from cloud seeding is expected to accumulate in the shallow soils where it is deposited. Two studies have been conducted to evaluate if that accumulation results in significant increase in Ag concentrations in the soil.

One study in Greece collected 2,500 samples after 13 years of hail suppression cloud seeding. More than 800 kg of AgI was burned over the two target areas during that time period. They found no difference in silver concentrations between soils in the 2 target areas and the 3 control sites. In fact, one of those control sites had an average Ag concentration roughly 20% higher than the highest average target area concentration [6].

In another study, 1,464 soils samples were collected in the upper 2 cm in 200 m intervals from a ground generator. Samples were collected the year before cloud seeding began and every subsequent year where cloud seeding was practiced. The results showed no soils exceeded 1 ppm of Ag except for one site, which had equally high concentrations in pre-seeding conditions. There was also no statistically significant increase of silver between target/control sites and no observed accumulation of silver through time [67].

There was no correlation between increases in silver concentration in soil strata and cloud seeding activities practiced by Snowy Hydro Limited. Stromsoe (2011) estimated annual 19-fold increase in AgI usage (assuming every AgI particle landed in target zone) in order to produce a statistically significant silver increase [26].

4.4.5   Iodine Concentrations from AgI

The iodine associated with AgI could be considered another potential impact. However, the iodine contribution from cloud seeding is negligible compared to its naturally occurring abundance. Total recoverable iodine concentrations in precipitation are typically between 0.1 and 15 ppb [71]; at least 1 order of magnitude higher than the iodine present from AgI in rain water. Cooper [40] elaborated on this point, calculating 130 gallons of cloud seeded rainwater is necessary to obtain as much total recoverable iodine as one serving of iodized table salt.

5 Conclusions

The toxicity of silver depends primarily on concentration, speciation, and bioavailability. Natural silver compounds and complexes are not soluble or bioavailable. The silver ion (Ag+) is the bioavailable (and thus toxic) form of silver. The silver ion was typically the dominant species in laboratory toxicity studies quantifying the toxicity of silver. For the gilled organisms, toxicity is related to Ag+ gill interactions leading to an osmotic imbalance. This is seldom the case in the natural environment. Silver can accumulate in organisms several orders of magnitude higher than its surrounding environment without experiencing adverse effects. Currently, there are no direct correlations between accumulated silver and toxic effects in all species studied except algae. Likewise, silver compounds do not dissociate in the digestive systems of organism studied, so silver toxicity to terrestrial species is also highly unlikely.

Silver iodide has been used in weather modification programs for over sixty years. In modern programs extremely small amounts of AgI are dispersed in the atmosphere over relatively large areas. It is insoluble with a low bioavailbility. As a result toxic effects are highly unlikely. Environmental sampling has found no evidence of adverse effects on wildlife or silver accumulating at detectable levels above background in soils, streams, or aquatic species in seeded areas. There are no documented cases of silver toxicity in the environment from any source of anthropogenic silver release.

6 Recommended Readings

For more in depth analysis of silver toxicity, the following literature reviews are extremely helpful in providing an overall sense of silver toxicity.

1. Eisler (1996) [1]
2. Williams (2009) [2]
3. Ratte (1999) [23]
4. Cardno ENTRIX (2009) [7]
5. WHO (2002) [20]

7 References

[1]   Eisler, Ronald, "Silver hazards to fish, wildlife, and invertebrates: A synoptic review," Environmental Protection Agency, Laurel, MD, Contaminant Hazard Biological Report 32, 1996.

[2]   Williams, Bruce D. and Denholm, John A., "An Assessment of the Environmental Toxicity of Silver Iodide - With Reference to a Cloud Seeding Trial in the Snowy Mountains of Australia," *J. Weather Modif.*, vol. 41, no. 1, pp. 75–96, Apr. 2009.

[3]   Edwards, Ross and Simeral, David, "Baseline Silver Concentrations in Freshwater and Snow in the Wyoming Weather Modification Project Target Area." Desert Research Institute, 2006.

[4]   Taylor, Stuart R. and Scott M. McLennan, "The geochemical evolution of the continental crust," *Rev. Geophys.*, vol. 33, pp. 241–265, 1995.

[5]   Purcell, Thomas W. and Peters, Jennifer J., "Sources of Silver in the Environment," *Environ. Toxicol. Chem.*, vol. 17, no. 4, pp. 539–546, 1998.

[6]   Tsiouris, S.E, Aravanopoulous, F.A, Papadoyannis, I.N, Sofoniou, M.K., Polyzopoulos, N, Christodoulou, M, Samanidou, V.F, Zachariadis, G.A, and H.-I.A Constantinidou, "Soil Silver Content of Agricultural Areas Subjected to Cloud Seeding with Silver Iodide," *Fresenius Environ. Bull.*, vol. 11, pp. 697–702, 2002.

[7]   Cardno ENTRIX, "Geochemistry and Impacts of Silver Iodide Use in Cloud Seeding." 2011.

[8]   Boutron, Claude, "A clean laboratory for ultralow concentration heavy metal analysis," *Fresenius J. Anal. Chem.*, vol. 337, no. 5, pp. 482–491, 1990.

[9]   Gill, G.A, Wen, L-S, Tang, D, and P Santschi, "Silver in Colorado watersheds." Transport, fate, and effects of silver in the environment. Proceedings of teh 5th international conference., 1997.

[10]   Wen, Liang-Saw, Santschi, Peter H., Gill, Gary A., and Tang, Degui, "Silver Concentrations in Colorado, USA, Watersheds using Improved Methodology," *Environ. Toxicol. Chem.*, vol. 21, no. 10, pp. 2040–2051, 2002.

[11]   EPA, "State of the Science Literature Review: Everything Nanosilver and More," Environmental Protection Agency, Washington, D.C., Task Order 95, 2010.

[12]   US Department of Labor, "Limits for Air Contaminants," Occupational Safety and Health Standards, Washington, D.C., Toxic and Hazardous Substances 1910.1000, Table Z-1, 2006.

[13]   J. A. Warburton, S. K. Chai, R. H. Stone, and L. G. Young, "The Assessment of Snowpack Enhancement by Silver Iodide Cloud-Seeding using the Physics and Chemistry of the Snowfall," *J. Weather Modif.*, vol. 28, no. 1, pp. 19–28, 1996.

[14]   Huggins, A. W, Kenyon, S. L., Warren, L., Peace, A. D., Billish, S. P., and Manton, M. J., "The Snowy Precipitation Enhancement Research Project: A Description and Preliminary Results," *Jounal Weather Modif.*, vol. 40, pp. 28–53, 2008.

[15]   Huggins, Arlen W., "Trace Chemical Monitoring for the Wyoming Weather Modification Pilot Project: Tasks for the 2010 Field Project." Desert Research Institute, 2010.

[16]   WMA, "Weather Modification Association (WMA) Position Statement on the Environmental Impact of Using Silver Iodide as a Cloud Seeding Agent," 2009.

[17]   Edwards, Ross, Huggins, Arlen, and Joseph McConnell, "Trace Chemistry Evaluation of the IPCo 2003-3004 Cloud Seeding Program." Desert Research Institute, 2004.

[18]   Fisher, James F., Golden, Patrick, Benner, Shawn G., and Marion Lytle, "Trace chemical evaluation of cloud seeding in the Payette Basin," Denver, CO, 2015.

[19]   Benner, Shawn, Kohn, Matthew, and Golden, Patrick, "Payette Basin Exploratory Snow Sampling: Final Report." Heritage Environmental Consultants, 2014.

[20]   WHO, "Silver and silver compounds: environmental aspects by P.D Howe and S. Dobson," World Health Organization, Geneva, Switzerland, CICAD 44, 2002.

[21] N. R. Bury, J. C. McGeer, and C. M. Wood, "Effects of altering freshwater chemistry on physiological responses of rainbow trout to silver exposure," *Environ. Toxicol. Chem.*, vol. 18, no. 1, pp. 49–55, Jan. 1999.

[22] Gaines, P., "Chemical Stability: Silver." Inorganic Ventures, Christiansburg, VA, 2014.

[23] Ratte, Hans T., "Bioaccumulation and toxicity of silver compounds: a review," *Environ. Toxicol. Chem.*, vol. 18, no. 1, pp. 89–108, 1999.

[24] Wood, C.M, Playle, R.C., and C. Hogstrand, "Physiology and modeling of mechanism of silver uptake and toxicity in fish," *Environ. Toxicol. Chem.*, vol. 18, pp. 71–83, 1999.

[25] Hogstrand, C. and Wood, C.M., "Toward a Better Understanding of the Bioavailability, Physiology, and Toxicity of Silver in Fish: Implications for Water Quality Criteria," *Environ. Toxicol. Chem.*, vol. 17, pp. 547–561, 1998.

[26] Stromsoe, N., Callow, J.N., McGowan, H.A., and S.A. Marx, "Attribution of sources to metal accumulation in an alpine tarn, Snowy Mountains, Australia," *Environ. Pollut.*, vol. 181, pp. 133–143, 2013.

[27] Karen, D, Ownby, D, Forsythe, B, Bills, T, La Point, T.W, Cobb, G, and S. Klaine, "Influence of water quality on silver toxicity to rainbow trout (oncorhynchus mykiss), fathead minnows (pimephales promelas), and water fleas (daphnia magna)," *Environ. Toxicol. Chem.*, vol. 18, pp. 63–70, 1999.

[28] Boyer, E.W., Hornberger, G.M., Bencala, K.E., and D.M. McKnight, "Effects of asynchronous snowmelt on flushing of dissolved organic carbon: a mixing model approach," *Hydrol. Process.*, vol. 14, pp. 3291–3308, 2000.

[29] Hogstrand, C., Galvez, F., and Wood, C.M, "Toxicity, silver accumulation, and metallothionein induction in freshwater rainbow trout during exposure to different silver salts," *Environ. Toxicol. Chem.*, vol. 15, pp. 1102–1108, 1996.

[30] N. R. Bury, F. Galvez, and C. M. Wood, "Effects of chloride, calcium, and dissolved organic carbon on silver toxicity: Comparison between rainbow trout and fathead minnows," *Environ. Toxicol. Chem.*, vol. 18, no. 1, pp. 56–62, Jan. 1999.

[31] EPA, "Interlaboratory comparison: Acute testing set by A.E. Lemke," Environmental Protection Agency, Washington, D.C., EPA 600/3-81-005, 1981.

[32] Erickson, R.J., Brooke, L.T., Kahl, M.D., Venter, F.V., Harting, S.L., Markee, T.P., and R.L. Spehar, "Effects of laboratory test conditions on teh toxicity of silver to aquatic organisms," *Environ. Toxicol. Chem.*, vol. 17, pp. 572–578, 1998.

[33] Wood, C.M., Hogstrand, C., Galvez, F., and R.S. Munger, "The physiology of waterborne silver toxicity in freshwater rainbow trout (Oncorhynchus mykiss) 2. The effects of silver thiosulfate," *Aquat. Toxicol.*, vol. 35, pp. 111–125, 1996.

[34] Hirsch, Marianne P., "Toxicity of silver sulfide-spiked sediments to the freshwater amphipod (hyalella azteca)," *Environ. Toxicol. Chem.*, vol. 17, pp. 601–604, 1998.

[35] Lee, D-Y, Fortine, C, and P. Campbell, "Contrasting effects of chloride on the toxicity of silver to two green algae, Pseudokirchneriella subcapitata and Chlamydomonas reinhardtii," *Aquat. Toxicol.*, vol. 75, pp. 127–135, 2005.

[36] Pacific Gas & Electric, "Responses to Questions Regarding Cloud Seeding in teh Lake Almanor Basin," Pacific Gas and Electric, San Francisco, CA, Document, 2011.

[37] EPA, "Ambient Water Quality Criteria for Silver," EPA, Washington, D.C., 440/5-80-071, 1980.

[38] WHO, "Silver in Drinking-water," World Health Organization, Geneva, Switzerland, 2003.

[39] US Public Health Service, "Toxicological profile for silver," Agency for Toxic Services and Disease Registry TP*90-24, 1990.

[40] Cooper, C.F and W.C Jolly, "Ecological Effects of Silver Iodide and Other Weather Modification Agents: A Review," *Water Resour. Res.*, vol. 6, no. 1, pp. 88–98, 1970.

[41] Younger, R.L. and Crookshank, H.R., "Chronic exposure of sheep to silver iodide," *Water. Air. Soil Pollut.*, vol. 9, pp. 281–287, 1977.

[42] Hirsch, Marianne P., "Availability of sludge-bornde silver to agricultural crops," *Environ. Toxicol. Chem.*, vol. 17, pp. 610–616, 1998.

[43] EPA, "Drinking water standards and health advisories table," Environmental Protection Agency, San Francisco, CA, 2007.

[44] Arizona DEQ, "Title 18 Environmental Quality. Chapter 11. Department of Environmental Quality. Article 1. Water quality standards for surface waters.," Arizona DEQ, Arizona, 2009.

[45] Hawaii Department of Health, "Title 11: Hawaii Administrative Rules. Chapter 54: Water Quality Standards." 2013.

[46] Idaho DEQ, "Title 01. Chapter 02. IDAPA 58: Water Quality Standards.," Idaho Department of Environmental Quality, Boise, ID, 58.01.02.

[47] NSW EPA, "Using the ANZECC Guidelines and Water Quality Objectives in NSW." NSW Environmental Protection Authorities, 2013.

[48] EPA, "National Recommended Water Quality Criteria." Environmental Protection Agency, 2015.

[49] EPA, "Office of Water Policy and Techical Guidance on interpretation and implementation of aquatic life metals criteria by Martha Prothro," Environmental Protection Agency, Washington, D.C., Memorandum to water management division managers, Oct 1., 1993.

[50] EPA, "Interim Guidance on Determination and Use of Water-Effect Ratios for Metals," Environmental Protection Agency, Washington, D.C., EPA-823-B-94-001, 1994.

[51] Chapman, G.A., "Memorandum to C. Stephan June. 4.," 1993.

[52] Nebaker, A.V, McAulittle, R., Mshar, R., and D.G. Stevens, "Toxicity of Silver to Steelhead and Rainbow Trout, Fathead Minnows, and Daphnia magna," *Environ. Toxicol. Chem.*, vol. 2, pp. 95–104, 1983.

[53] UWS, "Preliminary data from work assignment 1-10," University of Winsconsin - Superior, Contract 68-C1-0034, 1993.

[54] Briggs, J.C. and J.F. Ficke, "Quality of Rivers of the United States, 1975 Water Year -- Based on the National Stream Quality Accounting Network (NASQAN)," U.S. Geological Survey, Open-File Report 78-200, 1977.

[55] IDEQ, "Water Quality Standards," Rules of the Department of Environmental Quality: IDAPA 58.01.02, 2007.

[56] USBR, "Environmental Assessment for the Walker River Basin Cloud Seeding Project," United States Bureau of Reclamation, Westminster, CO, 2010.

[57] Snowy Hydro Limited, "Cloud Seeding Program: Environmental Management." Cooma, NSW, 2013.

[58] D. M. Garvey, "Testing of Cloud Seeding Materials at the Cloud Simulation and Aerosol Laboratory, 1971–1973," *J. Appl. Meteorol.*, vol. 14, no. 5, pp. 883–890, Aug. 1975.

[59] Huggins, Arlen W., "Brief summary of findings related to trace chemical monitoring for the Wyoming Weather Modification Pilot Project (WWMPP)," 2013.

[60] J. A. Warburton, R. H. Stone, and B. Marler, "How the Transport and Dispersion of AgI Aerosols May Affect Detectability of Seeding Effects by Statistical-Methods," *J. Appl. Meteorol.*, vol. 34, no. 9, pp. 1929–1941, Sep. 1995.

[61] Huggins, Arlen W., "Summary of studies that document the effectiveness of cloud seeding for snowfall augmentation," *J. Weather Modif.*, vol. 41, pp. 127–134, 2009.

[62] Warburton, J. A., Young, L.G., and R.H. Stone, "Assessment of seeding effects in the snowpack augmentation programs: ice nucleation and scavenging of seeding aerosols," *J. Appl. Meteorol.*, vol. 34, pp. 121–130, 1995.

[63] NSW EPA, "Review of the Snowy Hydro Limited Cloud Seeding Program 2013 Annual Compliance Report," NSW Environmental Protection Authority, AUS, 2013.

[64] Gibbs, Dennis and Fayram, Thomas, "Santa Barbara County and Twitchell Reservoir Cloud Seeding Program: CEQA Final Mitigated Negative Declaration," County of Santa Barbara, Report 13NGD-00000-00011, 2013.

[65] DeFelice, T.P, Golden, J, Griffith, D, Woodley, W, Rosenfeld, D, Breed, D, Solak, M, and B. Boe, "Extra area effects of cloud seeding - An updated assessment," *Atmospheric Res.*, vol. 135–136, pp. 193–203, 2014.

[66] Lincoln-Smith, M, Dye, A, Kemsley, K, and J. Denholm, "Environmental monitoring and assessment: A statistical analysis on concentrations of silver and indium at generator locations," *J. Weather Modif.*, vol. 43, pp. 1–8, 2011.

[67] Reidy, B., Haase, A, Luch, A, Dawson, K, and I. Lynch, "Mechanisms of silver nanoparticle release, transformation and toxicity: A critical review of current knowledge and recommendations for future studies and applications," *Materials*, vol. 6, pp. 2295–2350, 2013.

[68] Newton, K, "The influence of dissolved organic carbon and surface chemistry on the toxicity of silver nanoparticles in daphnia magna," *Clemson Univ.*, vol. Thesis, 2011.

[69] WWMPP, "The Wyoming Weather Modification Pilot Project: Level II Study. Executive Draft Summary." 2014.

[70] J. Risher and L. S. Keith, *Iodine and Inorganic Iodides: Human Health Aspects.* World Health Organization, 2009.

[71] McGurty, Brian M. "Turning Silver into Gold: Measuring the Benefits of Cloud Seeding". *Hydro Review*, vol. 6. pp. 53-57. 1999.