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The toxicology of silver iodide in relation to its use as a cloud seeding agent

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A CLOUD SEEDING AGENT

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ABSTRACT

The toxicology of the cloud seeding agent silver iodide (AgI) was reviewed in the light of background levels of silver and iodine occurring in the environment. The extreme dilution of added AgI in resultant precipitation, together with the inherent insolubility of AgI makes the possibility of poisoning highly unlikely. It is concluded that there is no danger of either silver or iodide toxicity in the use of AgI as a cloud seeding agent.

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INTRODUCTION

The purpose of this report is to review the toxicology of silver iodide (AgI), and to enable a rational decision to be reached regarding possible danger involved in the use of AgI as a cloud seeding agent.

It has been claimed that:

(i)   Seven metric tons (7 t) of AgI was released in a cloud seeding experiment during the past 6 years. The AgI may pose a serious threat of toxicity to man.

(ii) The iodide released may be dangerous to pregnant women, cause thyroid disease and mental retardation.

(iii) The amount of AgI used in South Africa was 20 to 30 times greater than that used for the highest seeding in America.

(iv) Since no one knows the exact fate of silver or iodine in human metabolism it cannot be said that AgI as used in cloud seeding is not toxic.

CHEMISTRY OF SILVER IODIDE

Silver iodide is an ionic solid practically insoluble in water. Silver iodide is made up of positive silver ions (Ag^+) and negative iodide ions (I^-). On solution in water, the silver and iodide ions behave independently:

$$AgI \text{ (solid)} \xleftarrow[\text{in water}]{\text{solution}} Ag^+ + I^-$$
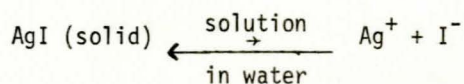
The soluble Ag^+ and I^- ions must be considered for possible toxicity. To facilitate the dis= cussion, the toxicology of the silver and iodide parts of AgI will be considered separately.

TOXICOLOGY OF SILVER

The toxicity of silver is dependent on the chemical form in which it is present, as well as the species (man, animal or plant) exposed to silver. Insoluble forms of silver such as silver sulphide, silver iodide, and silver metal itself have a low toxicity potential, and are unlikely to produce toxic effects. Soluble forms of silver, such as silver nitrate ($AgNO_3$) have a high toxic potential.

Toxicity to man

Soluble silver salts are only toxic to man in high concentrations. The acute lethal dose of silver nitrate crystals to man is assumed 10 g, and its lethality is due to the caustic nature of the silver nitrate salt, rather than direct toxicity of silver (Cooper and Jolly, 1970). Soluble silver salts in low concentration are not toxic to man. Chronic administration of silver to man results in darkening of the skin (argyria), caused by deposition of a fraction of the ingested silver in the skin. Argyria is merely cosmetically undesirable, and there are no other symptoms of toxicity (Lawrence and Block, 1968). The quantity of silver necessary to cause argyria is approximately 1 g. The limit of silver in drinking water of 50 $\mu g.dm^{-3}$ commonly used in drinking water standards, is based on its skin discolouring properties and not on actual toxicity (McKee and Wolf, 1963).

Insoluble forms of silver are not toxic to man. For instance silver metal, as used in cutlery, would hardly be regarded as poisonous. Silver iodide, the form of silver used for cloud seeding, is insoluble for all practical purposes. The maximum amount of silver iodide (AgI) which can dissolve in water is 1,6 parts in a thousand million, i.e. 1,6 $\mu g.dm^{-3}$ AgI, which corresponds to a silver ion concentration of 0,7 $\mu g.dm^{-3}$ Ag^+ (Weast, 1975). Such a low concentration of dissolved silver is completely harmless to man. Man naturally ingests silver in his diet, as silver is found in grains and cereals up to 900 $\mu g.dm^{-3}$ and in very much higher concentrations in mushrooms (Browning, 1961).

Toxicity to animals

Terrestrial animals also have a low susceptibility to silver toxicity. Direct toxicity tests with silver iodide have been done on animals : Sheep fed with forage containing 1 300 $\mu g.kg^{-1}$ AgI for 3 months showed no evidence of silver toxicity or accumulation of silver in the tissues (Younger and Crookshank, 1978). The chronic intake of food containing 1 000 $\mu g.kg^{-1}$ AgI by goats or rabbits was without any detectable toxicity or accumulation of Ag (Roy and Bailey, 1974; Jones and Bailey, 1974).

Toxicity to plants

Soluble silver is not toxic to land plants in the $\mu g.dm^{-3}$ range. Soluble silver levels of around 1 000 $\mu g.dm^{-3}$ are required to damage land plants (Clark, 1899). Except for mushrooms and ferns, plants do not concentrate silver to any appreciable extent (Cooper and Jolly, 1970).

Toxicity to fish

Soluble silver (as e.g. $AgNO_3$) is highly toxic to fish in low concentrations. Concentrations

of soluble silver of as little as 0,2 μg.dm^{-3} have been reported to be fatal to rainbow trout (Davies, Goettl, Sinley, 1978). The toxicity tests on fish are somewhat artificial, as the tests were done in aquaria. In nature silver nitrate is very rapidly immobilized and rendered insoluble by clay minerals in suspension in the water and by decaying organic matter and detritus (Cooper and Jolly, 1970).

Toxicity to micro-organisms

Soluble silver is highly toxic to micro-organisms such as bacteria, protozoa, algae etc. and was at one time used for disinfecting drinking water. Low concentrations of soluble silver temporarily inhibit the growth of micro-organisms (Cooper and Jolly, 1970). The mechanism of the inhibition is a reversible binding with sulphide groups of proteins (Snodgrass, Vallee and Hoch, 1960).

As the binding of silver to micro-organisms is reversible (Chambers, Proctor and Kabler, 1962), the effect of added soluble silver to the environment will be transient. The end path of Ag in the environment is as a highly insoluble silver sulphide, whose solubility is 0,08 pg.dm^{-3} (Weast, 1975). Naturally occurring silver sulphide (Ag$_2$S, Argentite) is the main primary silver mineral (Dana and Ford, 1932). The strong tendency that silver shows to return to the highly insoluble sulphide is exemplified by the ease with which silver cutlery tarnishes, the tarnish coating being silver sulphide. Silver compounds added to the environment can be expected to be rapidly converted to the non toxic, highly insoluble sulphide.

CONCENTRATION OF SILVER IN THE ENVIRONMENT

Background levels

Dust contains appreciable amounts of silver. The average level of Ag in the surface soil of North America is 70 μg.kg^{-1} Ag (Mason, 1966). The natural background of silver in rain or snow can consequently be expected to be related to the amount of dust in the air. The background level of Ag in snow in the USA is 0,05 μg.dm^{-3} Ag for the centre of the continent and 0,005 μg.dm^{-3} Ag for the coastal areas (Warburton and Young, 1972). The higher value for inland areas is believed to be due to the greater amount of dust present in the atmosphere over the centre of the continent.

Background silver concentrations in precipitation for various parts of the world are shown in Table 1.

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TABLE 1

Background levels for Ag in precipitation*

Place	Ag in precipitation
Nebraska	0,09 μg.dm^{-3}
St. Louis	0,05 "
Germany	0,07 "
Colorado	0,008 "
Australia	0,005 "

*(Sheaffer, Mulvey and Skogerboe, 1978; Streumpler, 1976; Warburton, 1963).

The background concentration of Ag in precipitation is between 0,005 μg.dm^{-3} and 0,1 μg.dm^{-3} (Table 1). The concentration of Ag in precipitation is only one seven hundredth of the value for Ag in the surface soil of 70 μg.kg^{-1} (Mason, 1966). By contrast the concentration of silver in sea water is reported to be 0,2 μg.dm^{-3} (Cooper and Jolly, 1970).

Seeded levels

Cloud seeding is reported to increase the silver concentration in precipitation by between 2 and 50 times above the background level. The median concentration for seeded precipitation is around 0,2 μg.dm^{-3} Ag (Warburton, 1963; Warburton and Young, 1972).

The maximum concentration observed in cloud seeding projects in the United States was 20 μg.dm^{-3} Ag (Warburton and Young, 1972). This maximum is still less than the limit for drinking water standards of 50 μg.dm^{-3} Ag.

South African values

Silver concentrations found in rain from cloud seeded areas in South Africa are given in Table 2.

The silver concentrations in the rain samples are of the same order as found in the USA. The average Ag concentration found in Pretoria rain samples during the 1978/1979 rain season was 0,13 μg.dm^{-3} Ag, with a range of <0,01 to 1,0 μg.dm^{-3} Ag (Hydrological Research Institute, 1979). River samples taken during March 1979 from the seeded areas showed silver concentrations varying between 0,1 and 11 μg.dm^{-3} Ag. The relatively high values found in the river samples are due to the high suspended particulate load of the rivers (i.e. muddy rivers). The Ag analyses include the insoluble silver fractions. The dissolved silver will be less than this amount.

TABLE 2

Silver in rain samples from seeded areas in South Africa

Date	Ag
Dec 1978	0,1 $\mu g.dm^{-3}$
Jan 1979	<0,01
Feb 1979	<0,01
Feb 1979	<0,01
March 1979	<0,01
March 1979	<0,01
March 1979	0,01
April 1979	1,0

DISCUSSION AND CONCLUSION REGARDING SILVER TOXICITY

Cloud seeding increases the silver concentration in precipitation from its background level of between 0,005 and 0,1 $\mu g.dm^{-3}$ to a median value of 0,2 $\mu g.dm^{-3}$ Ag. Maximum concentrations of up to 20 $\mu g.dm^{-3}$ Ag have been observed but this is still less than the drinking water standard of 50 $\mu g.dm^{-3}$.

The insolubility of AgI precludes the possibility of toxicity to any organisms except the most sensitive, viz fish and micro-organisms, and even here, toxicity from seeded rain is unlikely, as silver is rapidly immobilized to its highly insoluble sulphide by organic matter and soil.

There does not appear to be any danger of silver poisoning following the use of silver iodide as a cloud seeding agent.

TOXICOLOGY OF IODIDE

Isotopes of iodine

All the iodine found in nature (in rocks, soil, water, etc.) is the non radioactive isotope I^{127}. The iodine in AgI is also entirely the I^{127} isotope (Weast, 1975). The natural non radioactive isotope I^{127} is an essential element for human nutrition; the minimum daily requirement for an adult is 100 μg (Wintrobe, Thorn, Adams, Bennett, Braunwald, Isselbacher and Petersdorf, 1970).

Radioactive isotopes of iodine such as I^{131} and I^{125} are not found in nature, but are made in small quantities in atomic reactors for medical and research purposes and are also produced in atomic explosions. The radioactive isotopes of iodine are highly toxic even in the most minute quantities (McKee and Wolf, 1963; Wintrobe et al., 1970). The toxicity of the radioactive isotopes will not be discussed further here, as the iodide used in weather modification is the naturally occurring non radioactive isotope I^{127}.

Natural occurrence of iodine in the environment

Iodine is found naturally throughout the earths crust (300 µg.kg^{-1} I), in the oceans (50 µg.dm^{-3} I), and in the soil at a concentration of between 600 and 8 000 µg.kg^{-1} (Bear, 1964). Using an average figure for the natural abundance of iodine in ground of 4 000 µg.kg^{-1}, and a specific gravity for sand of 2,6; the total quantity of iodine naturally present in the upper 400 mm surface soil of a plot of ground of area 1 km^2 is 4 t.

An area of ground of 10 km^2 thus contains around 400 t of iodine in the upper 400 mm of the soil. Most of the iodine naturally present in soil is readily soluble (Bear, 1964).

Quantity of iodide released in cloud seeding

The total quantity of silver iodide released over an experimental cloud seeding area over the past 6 years is alleged to be around 7 t. As iodide makes up 54% of the mass of the AgI molecule, the amount of iodide released amounts to 4 t. This 4 t of iodide was released over an area far in excess of 1 km^2 and over a period of 6 years. Consequently the total amount of iodide released was less than that already present in the soil. Natural iodide input from unseeded precipitation, dust and leaf litter to soil can be much as 6 t.km^{-2}/a (Aston and Brazier, 1979).

Concentration of iodide in rainwater

Of four rain samples from a seeded area analyzed for Ag in April 1979, the highest concentration of Ag found was 1 µg.dm^{-3} (Table 2); and as AgI is 54% I by mass, the iodide concentration from AgI must also have been around 1 µg.dm^{-3}.

The maximum concentration of Ag from AgI seeding found in rainwater in the United States was 20 µg.dm^{-3} Ag (Warburton and Young, 1972). The corresponding maximum iodide concentration from the AgI would then be 23 µg.dm^{-3} I. This level of iodine is of the same order as that found naturally in ground water, of 10 to 20 µg.dm^{-3} I (Höll, Peter and Lüdemann, 1972).

Even if we assume that 20 to 30 times more AgI has been used in the experimental cloud seeding area in South Africa than in analagous projects in America, then the maximum iodide contribution of AgI to the rainwater would be 600 $\mu g.dm^{-3}$ I. This is less than the iodine concentration for emergency disinfection of drinking water of 8 000 $\mu g.dm^{-3}$ I (Holden, 1970). Water containing up to 10 000 $\mu g.dm^{-3}$ I can be safely consumed without danger (Dawson, 1974; McKee and Wolf, 1963).

Physiological requirements for iodine

Iodine is essential for normal health as it is an integral part of the thyroid hormones (Wintrobe *et al.*, 1970). The minimum daily requirement (MDR) of iodide is given in Table 3.

TABLE 3

Minimum daily requirement (MDR) of iodide as μg iodide per day*

Age	MDR
child (0 - 1 year)	40
" (1 - 10 years)	80
male (10 - 18 years)	135
female (10 - 18 years)	115
adult male	130
adult female	100
pregnancy	125
lactation	150

*Taken from Harrison's principles of internal medicine, p 391, (Wintrobe *et al.*, 1970).

Note that the iodine requirement increases during pregnancy. Iodide deficiency has been and still is a major cause of goitre, i.e., enlargement of the thyroid and gland (Aston and Brazier, 1979; Wintrobe *et al.*, 1970).

It is common practice in many countries throughout the world to augment the daily intake of iodides as a prophylactic against goitre. During the earlier part of this century iodide was added to drinking water, but this proved too costly, and instead it is now usually added to table salt up to levels of 1 part in 50 000, i.e. 20 $mg.kg^{-1}$ I. It has been shown that a per= son would need to drink 600 dm^3 of rain from a storm seeded with AgI to obtain as much iodine as is present in an egg seasoned with iodized salt (Douglas, 1968). Iodization of drinking water or salt has been proved to markedly reduce the incidence of goitre, and its beneficial

effects far outweigh the possibility of isolated adverse reactions (McKee and Wolf, 1963; Cantarow and Schepartz, 1957; Zoeteman, 1972; Wintrobe *et al.*, 1970).

Iodide ingested in excess of the daily requirement is readily excreted in the urine and is not accumulated, except when large quantities are ingested for long periods, e.g. from expectorants; and even in the latter case the accumulation is only temporary (Cantarow and Schepartz, 1957; Goodman and Gilman, 1966; Wintrobe *et al.*, 1970). Silver iodide is in any case insoluble in water and the iodide is unlikely to be absorbed in the first instance.

Goodman and Gilman (1966) state that it is a popular fallacy that iodine is highly toxic. This is substantiated by the fact that no legal standard for iodide in drinking water has been promulgated. The problem throughout the world is that there is too little iodide in drinking water, not too much.

Medicinal uses of iodine

The <u>non</u> radioactive natural isotope of iodine is widely used in medicine. Iodine compounds are used in expectorants (cough mixtures), in radiological contrast media, as antiseptics, and for the emergency disinfection of drinking water (Goodman and Gilman, 1966). Iodine has also been used for the disinfection of swimming baths (Holden, 1970). Tincture of iodine for instance contain 37 g.dm^{-3} I, while expectorants contain around 14 g.dm^{-3} I (Goodman and Gilman, 1966). These iodine concentrations are about <u>one million times greater</u> than the iodide concentration which AgI contributes to rain water (Cooper and Jolly, 1970). The instances of iodine toxicity or allergy which have been described following the medicinal uses of iodine (Goodman and Gilman, 1966) are <u>extremely unlikely</u> to arise from the iodide used for cloud seeding, as the concentra= tions involved are negligible.

DISCUSSION

(i) The 7 t of AgI, containing 4 t of iodide is only a small fraction of the amount of iodide already naturally present in the soil in the seeded area. The 400 mm surface soil of an area of ground 10 km^2 contains naturally several hundred tons of iodide. The amount of iodide used poses no threat of toxicity to man. Iodide in small concen= trations is not a toxin; it is an essential element for normal health. There is like= wise no danger of silver toxicity to man as silver iodide is practically insoluble, and the little that does dissolve is rapidly immobilized into harmless silver sulphide (Ag$_2$S) in the environment.

(ii) An increase in the background level of non radioactive I^{127}, far from causing thyroid disease, will help to decrease the incidence of goitre (Goodman and Gilman, 1966). An increase in the I^{127} levels in the environment from cloud seeding also serves to help protect against the effects of radioactive fallout containing I^{131} and I^{125}.

The iodide released in cloud seeding could not possibly cause mental retardation or be a danger to pregnant women.

(iii) Even if the allegation is true that 30 times more iodide was used for seeding in South Africa, than in America, the amount of iodide released is still a small fraction of the iodide naturally present in the environment. Such an increase in the amount used would not cause any danger of silver toxicity, due to the ease with which silver is immobilized in nature as silver sulphide (Ag_2S).

(iv) The world medical literature has proved beyond doubt that a moderate increase in iodide intake is beneficial, and serves to protect against thyroid disorders. As far as silver is concerned, insoluble silver compounds such as AgI have a low toxic potential.

Although it is true that the full bio-pathways of neither iodide nor silver are known, the present world knowledge indicates that the use of silver iodide as a cloud seeding agent poses no immediate conceivable danger to health.

RECOMMENDATION

There is no immediate danger from the use of AgI as a cloud seeding agent.

It is however recommended that for continued cloud seeding a full and accurate record of the total mass of AgI used each year be kept, and that the total area over which this mass of AgI was distributed be reported.

A rational decision can only be reached if the full amount of AgI used each season is known.

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UNITS AND SYMBOLS

The following units and symbols are used in this report:-

ELEMENT SYMBOLS

Ag	=	silver
I^{127} (abbreviated as I)	=	natural non-radioactive iodine
AgI^{127} (abbreviated as AgI)	=	silver iodide
I^{125}; I^{131}	=	radioactive iodine isotopes.

MASS

1 metric ton (1 t) = 1 000 kg

1 microgram (µg) = one millionth of a gram (10^{-6} g).

CONCENTRATION IN WATER SOLUTION

$pg.dm^{-3}$ = one picogram per cubic decimetre equals one part in a million million parts of water (1 x 10^{-12}).

$µg.dm^{-3}$ = one microgram per cubic decimetre equals one part in a thousand million parts of water (1 x 10^{-9}).

$g.dm^{-3}$ = one gram per cubic decimetre equals one part in a thousand parts of water (1 x 10^{-3}).

CONCENTRATION IN SOLIDS

$µg.kg^{-1}$ = one microgram per kilogram equals one part in a thousand million parts (1 x 10^{-9}).

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