

## Assessment of Seeding Effects in Snowpack Augmentation Programs: Ice Nucleation and Scavenging of Seeding Aerosols

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### ABSTRACT

Trace chemical analysis techniques have been used in a series of cloud-seeding experiments in the central Sierra Nevada with the ultimate purpose of distinguishing whether the submicron-sized aerosol particles used for seeding are removed by nucleation or by scavenging in snowfall. The research programs used submicron-sized seeding aerosols with different nucleating characteristics.

When winter storms were seeded with silver iodide in the Lake Tahoe and Lake Almanor watersheds, positive correlations were observed between silver concentrations and precipitation amounts in both catchment areas. This is considered to be evidence that the AgI aerosols are not being removed in the snowfall entirely by scavenging processes.

When two separate aerosols of silver iodide and indium sesquioxide were released simultaneously from the same ground locations during winter snowstorms in the Lake Almanor watershed, it was found that considerably more of the ice-nucleating aerosol particles (AgI) were removed by the snowfall than the non-ice-nucleating ones ( $\text{In}_2\text{O}_3$ ). Under the experimental conditions employed, scavenging alone of the two aerosols would lead to a chemical ratio of Ag:In in the snowfall of 0.83:1. Ratios as high as 17.2:1 were observed, the mean ratio being 4:1. These results are considered to be evidence of the removal of substantial numbers of the AgI aerosol particles through direct nucleation of ice crystals.

### 1. Introduction

Measurements have been made of seeding chemicals in precipitation in weather modification field experiments for more than three decades. The first known work of this kind was conducted by Gubeli (1959) in Switzerland, Isono (1961) in Japan, and Warburton (1963) in Australia. Gubeli extracted silver, originating as silver iodide, from 50-L rainwater samples by evaporation and chemical reduction methods. Neither Isono nor Warburton physically measured the actual silver or iodine in the precipitation, but both used the colloidal property of silver iodide (the most commonly used seeding chemical), its extremely low solubility in water, and its ice-nucleating characteristics to detect the presence of this chemical compound in the precipitation and to assess, by inference, its concentration. Although the analysis procedures were somewhat complex, as well as being slow and labor intensive, they did provide relatively reliable methods for estimating the amounts of seeding material in the precipitation falling in designated target areas of large-scale weather modification projects.

With the advent of high thermal neutron flux nuclear research reactors and later the development of flameless

atomic absorption spectrophotometers, the cost and time for analyzing precipitation samples for their trace chemical constituents were greatly reduced. More importantly, the sensitivity of detection and measurement of many of the elements of interest were improved to the point where direct analysis of liquid water samples having concentrations of specific trace chemicals as low as a few parts per trillion were able to be achieved.

Because of the almost universal use of silver iodide in cloud-seeding experiments, a substantial number of investigations of the silver content of precipitation have been conducted throughout the world. In addition, measurements of silver and silver iodide have been made on individual or groups of cloud particulates. Koenig (1960) demonstrated how individual AgI particles could be identified in ice crystals. Knight (1969) demonstrated how this could be achieved by a crystal growth method.

When silver iodide aerosols are released at rates of  $10^{13}$ – $10^{15}$  nuclei per second (common dispensing rates), the concentrations of this released silver in the precipitation are usually found to be in the range of  $1 \times 10^{-12}$  g mL<sup>-1</sup> (1 ppt) to  $1 \times 10^{-9}$  g mL<sup>-1</sup> (1 ppb). Silver, being a heavy metal and having a high thermal neutron cross section, made it a prime candidate for analysis at these concentration levels by neutron activation. The short half-life (24 s) radioisotope of silver was used by Warburton and Young (1968, 1972) to

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measure this element at concentrations down to  $10^{-11}$  M after preconcentration of the silver by ion exchange. Several researchers have now reported measurements of the silver from silver iodide in precipitation at these concentrations by both flame and flameless atomic absorption methods, including Parungo and Robertson (1969), Warburton (1969), Lacaux (1970), Wisniewski and Sax (1979). Other methods used included isotope dilution and anodic stripping voltammetry; see, for example, Eisner and Marx (1970). The reproducibility of results using these trace analytical methods is usually within  $\pm 20\%$  for concentrations near  $10^{-2}$  ppb.

With the improvement in sensitivity of analysis, weather modification researchers began to use other chemical aerosols, the elements of which could also be measured accurately at these extremely low concentration levels. In order to be used in conjunction with silver iodide in atmospheric tracer studies, the choice of element should preferably satisfy three general requirements: that it can be dispensed in the form of submicron-sized aerosol particles; that its natural background concentration level in precipitation is at most less than 10 ppt; and that the sensitivity of measurement by the available techniques is in the range of a few parts per trillion. These considerations have led to the use, in particular, of the trace metal indium in a number of atmospheric modification tracer experiments in the central Sierra Nevada. Results from these studies are also presented here.

## 2. Tracking seeding aerosols from source to receptor

Experimental attempts to study the transport, dispersion, and removal of submicron-sized aerosol particles either with aircraft or ground-based monitoring systems have been limited (see, e.g., Fookes et al. 1962; Smith et al. 1966; Marwitz and Stewart 1981; Stith et al. 1985).

The work described in this paper does not attempt to follow the chain of events from aerosol release through nucleation or scavenging to arrival at the surface in the precipitation. Instead, a source-receptor approach has been used.

Knowing the locations of the aerosol sources and their chemical and physical characteristics, it is feasible to sample the air or precipitation with appropriate equipment at downwind sites, measure the source materials deposited, and therefore estimate their geographical and temporal distributions. If the experimental design requires knowledge of the capture processes that the aerosols have undergone, it may be possible to deduce this somewhat by judicious choices of the source materials that, because of their physical dimensions and chemical nature, may interact differently with the cloud hydrometeors and precipitation elements.

## 3. Discussion of the processes of capture of seeding and tracer aerosols

Cleansing of the lower atmosphere of its chemical impurities is regularly achieved by dry deposition and by cloud and precipitation scavenging and nucleation processes. There have been many observations of this, the timescale varying from hours to months depending upon the chemical and physical nature of the impurity. Because atmospheric impurities are finite in amount, their concentrations in wet deposition usually decrease with increase in precipitation rate or amount (Junge 1963). This is true for radon and its daughter products, sodium, potassium, calcium, nitrate, chloride and sulfate, to name a few of the more common substances. However, when ice-forming nuclei are present that can affect the principal precipitation forming processes, some of the reported results do not follow this normal trend. Vali (1970) reported a direct relation between the rate of rainfall and the freezing nucleus content of that rain. In experiments where submicron-sized aerosols of ice-nucleating silver iodide have been continually dispensed into cloud systems during storms, some of the reported results discussed below followed the norm but others did not.

### a. Observations of scavenging of submicron-sized silver iodide aerosols

The principal precipitation scavenging mechanisms for atmospheric aerosols are known to be Brownian motion, phoretic processes, electrostatic attraction, and impaction. All are functions of the radius, volume, or surface area of the precipitation particulates, which are capturing the aerosol particles, as well as of the sizes and concentrations of the particles themselves. For the case of submicron-sized AgI particles that have been injected into clouds from cloud-seeding generators, one would therefore expect to observe silver concentrations that are correlated negatively with, or are directly proportional to, precipitation amount if the particles are being removed entirely by these scavenging mechanisms. Both constant and negative correlations have been observed by Warburton et al. (1982) in some of the silver iodide seeded cases in the National Hail Research Experiment (NHRE). In those studies, the silver iodide aerosols were released into the cloud systems from aircraft. Similar results were also reported by Lacaux and Warburton (1982) and Lacaux et al. (1985) for some of the seeded convective storms in the Swiss Grossversuch IV hail suppression experiments. Those results also showed that substantial proportions of the silver iodide aerosols that had been injected by rockets into the storms were scavenged quite quickly and that it would not have been possible for those aerosols to have affected the precipitation formation processes significantly as was intended.

The silver iodide aerosols used in seeding programs typically have mean particle radii around  $0.03 \mu\text{m}$ ,

(Mossop and Tuck-Lee 1969). Also, if the seeding generators producing the AgI aerosols use a mixture of silver iodide and ammonium iodide in acetone, the particles are extremely insoluble (solubility 2 parts in  $10^9$  water) and are also nonhygroscopic. Hence, most, if not all, of the scavenging of these particles would be caused by Brownian capture, diffusio-phoresis, and thermophoresis, the particles being too small for capture by inertial impaction or by turbulent diffusion. However, it is also worth noting that the mean particle radius is in the size range where the collection efficiencies for the phoretic processes are near their minima in the "Greenfield gap" (Greenfield 1957).

If the cloud conditions are such that water droplets are growing, Brownian capture will be the dominant process for particles less than  $0.1\text{-}\mu\text{m}$  radius, with thermophoresis the next most important, whereas if the droplets are evaporating, both of the phoretic processes tend to dominate over Brownian capture for particles larger than  $0.05\text{-}\mu\text{m}$  radius (Young 1974). Since most of the AgI particles are smaller than this, however, Brownian motion capture will dominate. As stated earlier, all of these scavenging processes relate directly to the sizes of the cloud hydrometeors and should lead to constant or negative correlations between silver (iodide) concentrations and precipitation rates and amounts.

Additionally, very few, if any, of these particles would be expected to be removed as cloud condensation nuclei (CCN). This is because the smallest radius nonhygroscopic particle capable of acting as a CCN is, by the Gibbs-Thompson relationship,

$$r = \frac{1.1 \times 10^{-5}}{\sigma} \quad (\text{cm}),$$

where  $\sigma$  is the supersaturation over water. It would be necessary for supersaturations in the cloud to exceed 1.4% for even the largest of the AgI particles produced by cloud-seeding generators to behave as CCN.

In clouds where the ice phase exists, submicron-sized silver iodide particles can also be scavenged by vapor pressure gradient transport (Facy effect) to ice particle surfaces growing in conditions where the cloud is supersaturated with respect to ice.

#### *b. Observations of removal of silver iodide aerosols by ice nucleation*

The principal mechanisms responsible for removal of submicron-sized aerosols by ice nucleation are condensation freezing, sublimation, and contact. Condensation freezing requires the ice-nucleating particle to act first as a cloud condensation nucleus and subsequently to cause the droplet to freeze at a warmer temperature than would have occurred without its presence in the droplet (Vali 1971). Sublimation is the process by which supercooled water vapor diffuses directly onto the ice nucleus, producing an ice embryo that subse-

quently grows by the Bergeron-Findeisen process; contact nucleation occurs when the ice-nucleating particle is transported to the surface of a supercooled droplet. Such transport can occur by the same Brownian motion or phoretic processes described earlier.

Any of these processes that have led to the production of new ice particles could lead to positive correlations between silver concentration and precipitation amount. Such positive correlations have been observed in some of the National Hail Research Experiment seeded storms by Warburton et al. (1982) and in Grossversuch IV by Lacaux et al. (1985). Those positive correlations occurred in convective clouds in which some of the silver iodide aerosols released had sufficient time to function as ice-forming nuclei at temperatures colder than  $-5^\circ\text{C}$ , the threshold nucleation temperature.

#### **4. Winter snowfall studies of scavenging and nucleation of seeding aerosols**

Field programs for studying the capture and removal of submicron-sized AgI aerosols by snowfall have been conducted in both the Truckee-Tahoe and Lake Almanor (Mooney and Lunn 1968) watersheds of the Sierra Nevada, and the results of these investigations are now discussed. The watersheds are shown in Figs. 1 and 3. Elevations in both areas range from 4600 to 10 500 ft MSL.

It is extremely important to emphasize at this point that the snow sample studies that follow are *not* analyses of individual ice crystals or snowflakes that may contain a particular size or type of particle but are of integrated samples of snowfall containing as many as  $10^6\text{--}10^7$  crystals, which have occurred over periods of at least 1–2 h and sometimes longer periods. Because of this, the aerosol material deposited in these precipitation samples is not expected to be differentiated by particle size but are considered to consist of statistically representative samples of the entire particle size spectra that have been released at the generator sites.

##### *a. Positive correlations between silver concentration and snowfall amount*

The Lake Tahoe-Truckee River watershed was seeded with ground-based generators located either on the western side or on the Sierra Nevada crest for two successive winter seasons. The snowfall was sampled in the target area following seeding operations. Figure 2 shows the snowfall water mass deposited in grams per square centimeter as a function of observed silver concentrations above the background of  $2 \times 10^{-12}$  g  $\text{mL}^{-1}$  (2 ppt). These data are from 16 sampling sites in this target area, and the line of best fit has a slope of 0.8. The Lake Almanor watershed was also seeded for two successive winters with AgI using the generator locations shown in Fig. 3. Figure 4 shows the water

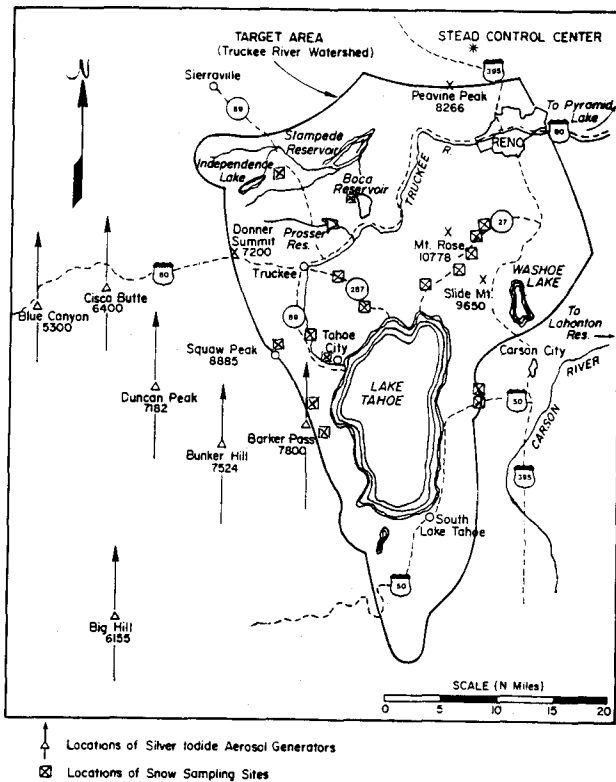


FIG. 1. The watershed of Lake Tahoe and the Truckee River in the central Sierra Nevada. Specific geographical features are shown. The Stead Control Center is the site of the DRI Atmospheric Sciences Laboratories. Also shown are the sites of silver iodide aerosol generators and snow sampling equipment.

mass deposited in grams per square centimeter as a function of silver concentrations above the background for 52 profiles of snowfall sampled in that watershed. The line of best fit has a slope of 0.9, very close to that for the Truckee-Tahoe area. Although there is significant scatter among the points, Figs. 2 and 4 show essentially the same relationship, indicating that an increase of 10-ppt silver concentration in the snow is associated with an increase of 8–9 g cm<sup>2</sup> mass of snow deposited. To explain this positive correlation, Warburton et al. (1986) proposed a mechanism in which some of the ice-nucleating AgI aerosol particles initiated new ice crystal growth, and this was followed by aggregation of these crystals into snowflakes rather than having the particulates growing to precipitable sizes by diffusional or accretional capture of supercooled water substance. These results do not necessarily imply that the overall precipitation amounts coming from the seeded clouds have been changed but are considered to be evidence that some of the AgI aerosol is carrying out the nucleation function intended.

*b. Distinguishing between ice nucleation and scavenging of submicron-sized seeding aerosols*

The positive relationships between silver concentrations and snowfall amounts suggested the feasibility of

distinguishing between the silver iodide being removed in the snowfall by “active” ice nucleation and that being “passively” scavenged. In order to determine if such a distinction could be made, experiments were planned in which two submicron-sized aerosols having similar size distributions would be released at somewhat similar known rates into supercooled clouds simultaneously from the same locations. Silver iodide would be used as the ice nucleator and indium sesquioxide as the non-ice-nucleating aerosol. The insoluble, nonhygroscopic silver iodide aerosol would be produced by burning a mixture of silver iodide and ammonium iodide dissolved in acetone in a propane flame. The indium sesquioxide aerosol would be produced in a similar manner by burning a solution of indium nitrate dissolved in ethyl alcohol in a propane flame. The indium sesquioxide particles formed are also nonhygroscopic and very insoluble in water. Also, they do not nucleate ice-particle formation. This was tested by collecting samples of the aerosol in a large syringe (2-L volume) and injecting them into the DRI cloud chamber (volume 6.7 m<sup>3</sup>) at a temperature of –20°C. No ice crystals were nucleated during 20 such tests. The indium nitrate mixture that was burned produces a submicron-sized aerosol with the particle size distribution shown in Fig. 5. This distribution and that of the silver iodide shown in Fig. 6 were determined from samples collected on electron microscope grids held in the aerosol plumes at a distance of 10 m from the generator nozzles. The

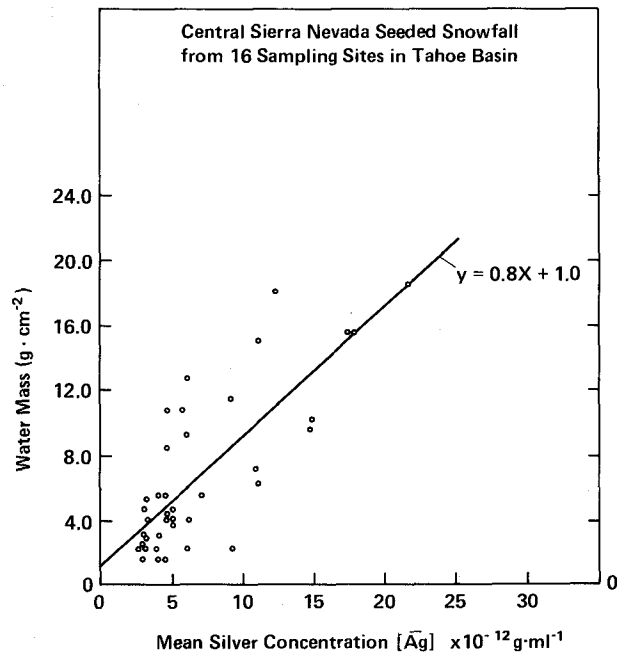


FIG. 2. Water mass deposited (g cm<sup>-2</sup>) as a function of concentrations of silver above the background of  $2.0 \times 10^{-12}$  g mL<sup>-1</sup> in the snowfall. Data from 16 sampling sites in the Lake Tahoe-Truckee River watershed after seeding with silver iodide aerosols. Line of best fit:  $Y = 0.8X + 1.0$ .

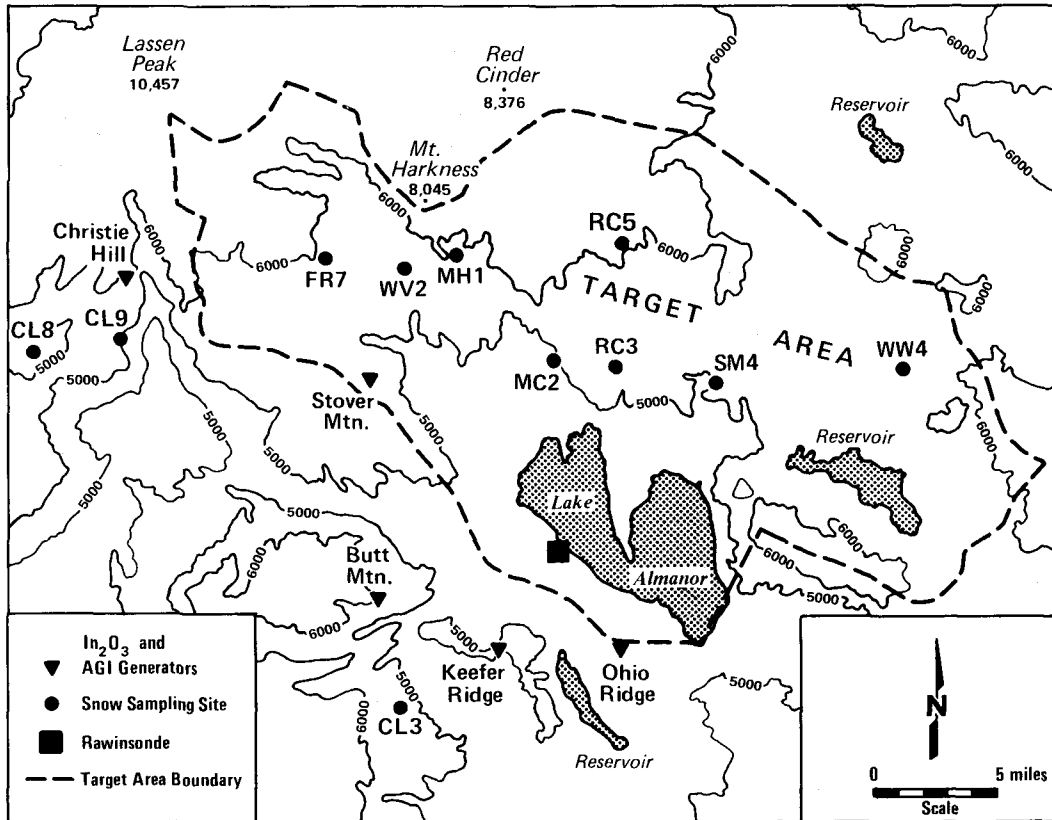


FIG. 3. Lake Almanor watershed in the central Sierra Nevada showing specific geographical features. Also shown are the release sites for both AgI and  $\text{In}_2\text{O}_3$  aerosols, sites used for snow sampling, and sites for rawinsonde releases.

mean particle radius for indium sesquioxide was calculated to be  $0.033 \mu\text{m}$  and that for silver iodide was  $0.030 \mu\text{m}$ .

**5. Further field studies in the Lake Almanor watershed**

The field program to study the distinctions between scavenging and ice nucleation of seeding aerosols was conducted in the Lake Almanor watershed because there was far less chance of contamination from other seeding projects in the central Sierra Nevada. There were no silver iodide seeding experiments or operations being conducted within a radius of 160 km of the Almanor target area during the experimental study period. The nearest project (160 km distant) was in the Tahoe-Truckee watershed located southeast, and therefore not upwind of the Almanor watershed during storms with a westerly component.

The seeding and tracer aerosols were released from 10 ground-based generators arranged in pairs, one for silver iodide, the other for indium sesquioxide. The two generators of each pair were set about 50 m apart to minimize or eliminate coagulation effects between the plumes near their sources. The locations of these five pairs of aerosol generators, the boundary of the

target area, and the eight sites where the snow sampling occurred are shown in Fig. 3.

*a. Targeting of the silver iodide and indium sesquioxide aerosols*

Several successive winter storms were seeded simultaneously with the silver iodide and indium sesquioxide aerosols. The snowfall was sampled by collecting vertical profiles (cores) of the snowpack at the eight sites directly following these major winter storm events. The profiles were subdivided vertically into 2-cm-depth increments. Each increment analyzed for its silver and indium contents and its density measured. The total number of snow increments collected was 683. The mean density of these 683 increments was 0.172 (standard error 0.003).

The natural background concentrations of silver  $B_S$  and of indium  $B_I$  in precipitation in this region had already been measured by Warburton et al. (1989) as 2.0 ppt ( $\sigma = 1.0$  ppt) and 1.5 ppt ( $\sigma = 1.0$  ppt), respectively. This silver value was determined from analyses of 870 snow samples collected during a complete unseeded winter season in 1983, and the indium value was from 220 separate snow analyses.

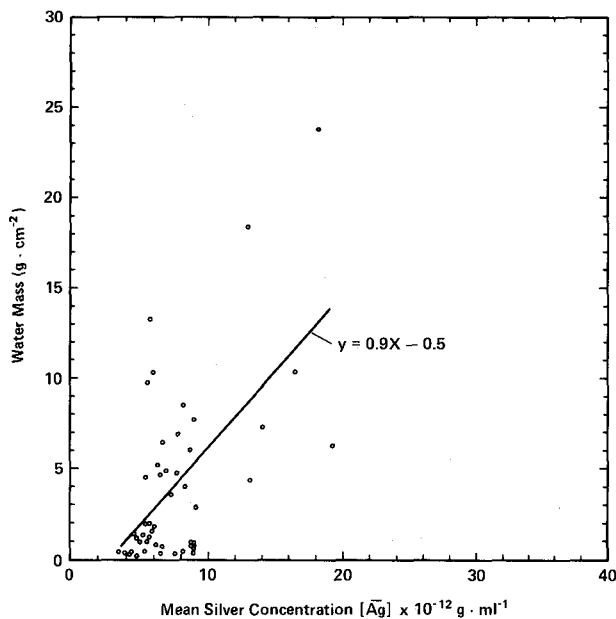


FIG. 4. Water mass deposited ( $\text{g cm}^{-2}$ ) as a function of concentrations of silver above the background of  $2.0 \times 10^{-12} \text{ g mL}^{-1}$  in the snowfall. Data from 52 vertical profiles (cores) collected after seeding with silver iodide in the Lake Almanor watershed. Line of best fit:  $Y = 0.9X - 0.5$ .

To be sure that the chemical signals during the seeding events are significantly above the background values of  $B_S$  and  $B_I$  "threshold" values of 4.0 ppt were used for both elements ( $B + 2\sigma$ ). All core increments containing both elements in concentrations greater than these threshold values form the database for analysis. Of the 683 profile elements analyzed, 98 contained indium and 177 contained silver above these threshold values. This indicated that the targeting effectiveness of the seeding activity was around 18% compared with the 15% reported by Warburton et al. (1979) for the Lake Tahoe watershed using 2.0 ppt as the background. These low targeting figures are almost certainly due to inadequate dispersion of the seeding aerosols over the target areas.

Figure 7 shows an example of the results obtained in the study. It is the silver-indium vertical profile for snow that fell during the storm that was seeded during the afternoon and late evening hours of 8 February 1985. Silver and indium concentrations are shown on the  $x$  axis for each 2-cm increment of snow on the  $y$  axis. The horizontal bars shown at the extreme right of each concentration value are the standard deviations for those values, each concentration and its error having been determined from at least five and up to ten separate measurements on snow taken from each 2-cm-depth increment. The mass of water in each 2-cm-depth increment is measured and the masses of silver and indium determined in the whole profile. For this particular profile, the silver mass was calculated to be 26.5

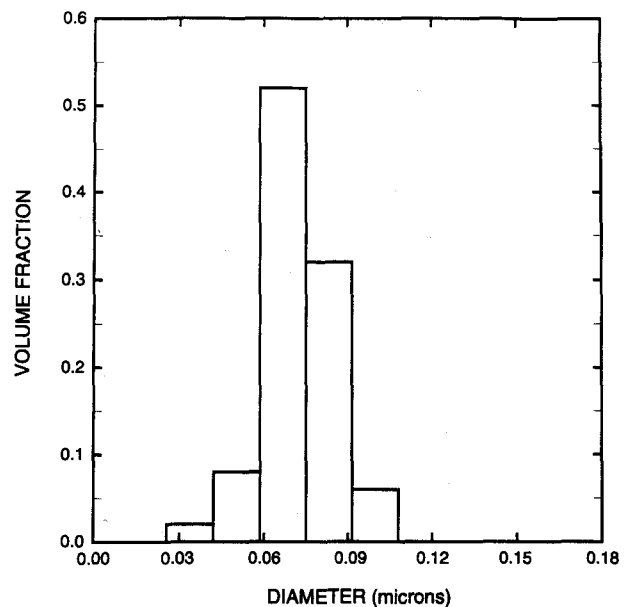


FIG. 5. Particle size distribution of indium sesquioxide aerosols used in Lake Almanor project area during the two-aerosol seeding experiments. Mean particle diameter,  $0.065 \mu\text{m}$ .

$\times 10^{-9} \text{ g}$  and that of indium to be  $6.6 \times 10^{-9} \text{ g}$ , giving a ratio  $\text{Ag}:\text{In} = 4.0$ . A total of 32 profiles were collected from the eight sites. Of these, 27 contained increments with silver and indium above the threshold levels described earlier, while five did not. These results are now discussed.

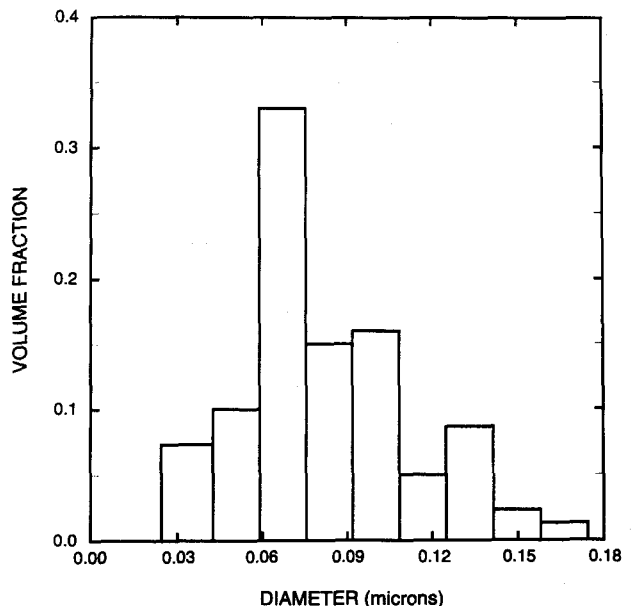


FIG. 6. Particle size distribution of silver iodide aerosols used in Lake Almanor project area during the two-aerosol seeding experiments. Mean particle diameter is  $0.060 \mu\text{m}$ .

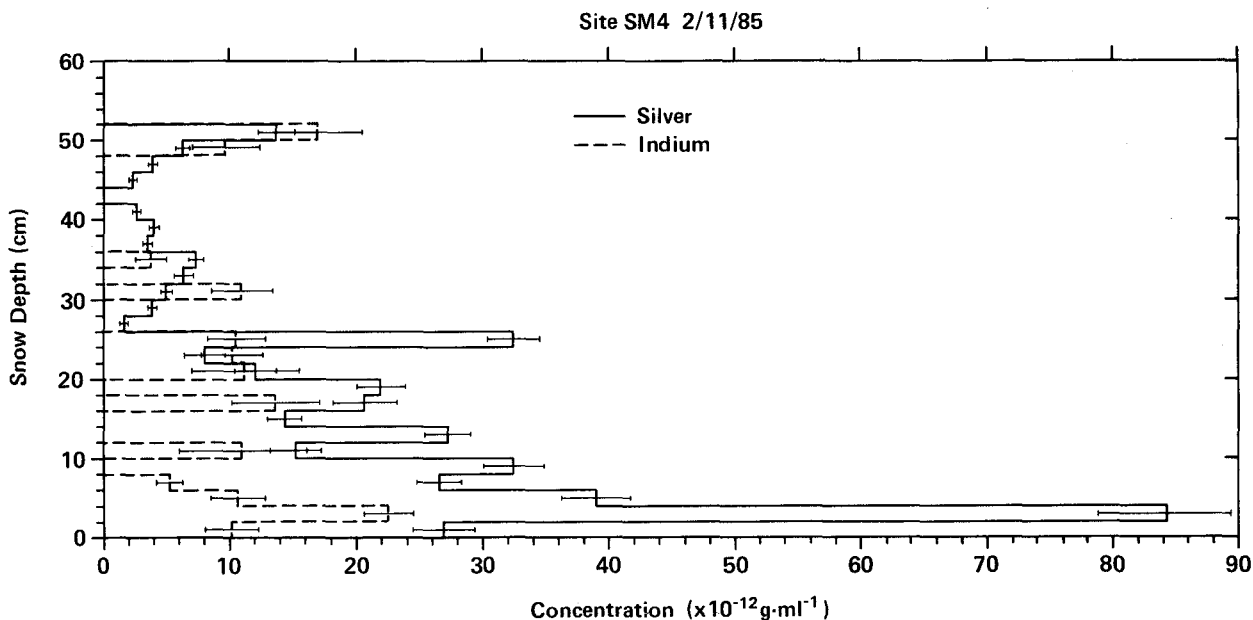


FIG. 7. Concurrently detected concentrations of silver and indium in 2-cm-depth increments of snow core collected at Swain Mountain, Lake Almanor project area. Measurements made following a two-aerosol seeding experiment on 20 December 1984.

*b. The observed indium deposition-precipitation amount relationship*

The plexiglass profilers used in the sampling program have a cross-sectional area of 200 cm<sup>2</sup>. Using this collection area, the total mass of indium per square centimeter deposited in each 2-cm-deep snow increment has been calculated from the mass of snowmelt in that increment and its indium concentration above the threshold value. It was found that the indium concentrations were relatively constant. The sum of these masses for the whole profile was then determined and this quantity plotted against the depth of water-equivalent precipitation in which this indium was detected. The results from the 27 profiles are displayed in Fig. 8.

Because the indium sesquioxide particles do not nucleate ice growth, are nonhygroscopic, and had particle sizes ranging from 0.015- to 0.055- $\mu\text{m}$  radius, their removal in the precipitation is considered to be entirely due to Brownian motion and thermophoretic and diffusiophoretic scavenging by water droplets and ice crystals, with no CCN or ice-nucleation removal. The experimental accuracy of the atomic absorption chemical analysis measurements is  $\pm 15\%$ , and the linear relationship ( $r = 0.96$ ) supports the view that removal was directly proportional to the volume of the precipitation hydrometeors.

*c. The observed silver deposition-precipitation amount relationship*

The same 27 snowpack profiles that contained silver above the threshold value gave quite different results.

Figure 9 displays the mass of silver per square centimeter deposited in these snow profiles. The indium data is included also in Fig. 9 to illustrate the differences. Note that the silver and indium values are paired, having come from the same snow increments in the profiles. For each silver mass per square centimeter there is a corresponding indium mass per square centimeter for the same profile depth (cm) and its water equivalent (mm). Clearly, most of the silver values are significantly higher than their paired indium values, which is caused by much higher concentrations but with considerable variability from profile to profile.

**6. The silver mass-indium mass ratios in the snowfall**

*a. "Expected" silver mass-indium mass ratios from scavenging alone*

Table 1 presents the physical parameters that enable the determination of the ratio of silver mass to indium mass deposition "expected" in the precipitation, if scavenging alone were responsible for the removal of the two submicron-sized aerosols. It assumes that the ratio of silver iodide to indium sesquioxide aerosol particle numbers remains the same as it was at the source origins throughout their trajectories to the surface in the precipitation.

Hence, for the release rates used in the experiment, the expected ratio of Ag mass/In mass in the snow would be 0.83:1 if both aerosols were scavenged with equal efficiencies. Note that if more AgI is removed along its path than In<sub>2</sub>O<sub>3</sub> because of additional pro-

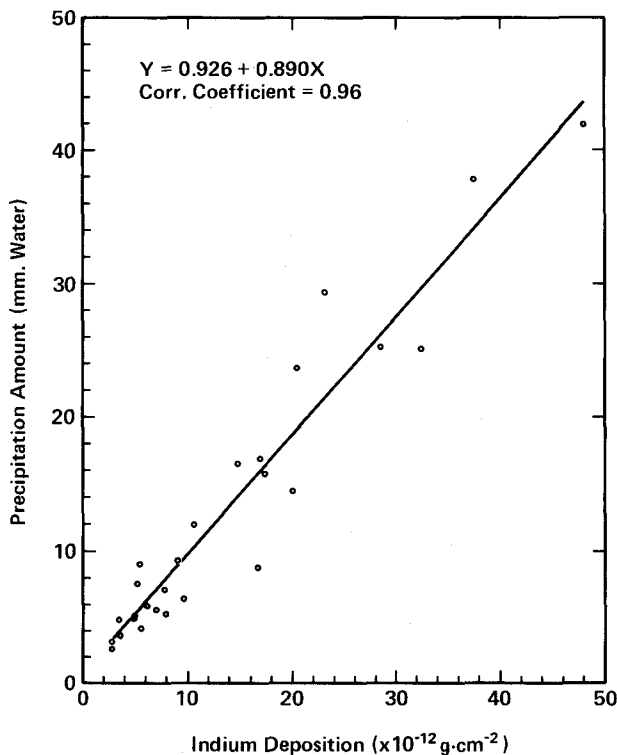


FIG. 8. Precipitation amount as a function of indium deposition ( $\text{g cm}^{-2}$ ) in the Lake Almanor project two-aerosol seeding experiments. Line of best fit,  $Y = 0.926X + 0.890$ .

cesses such as ice nucleation, ratios less than 0.83:1 can occur.

b. "Observed" silver mass-indium mass ratios in Lake Almanor project snowfall

The ratios of silver mass per square centimeter to indium mass per square centimeter for the entire set of 27 profiles from the two winter seasons used for the study ranged from 0.6 to 17.2. These observed ratios are presented in Table 2, in which the sites have been arranged from west to east across the target area (see Fig. 3).

In Table 2 it can be seen that the four storms that were seeded with both aerosols and that produced snowfall in the target area were either "cold westerly" or "cold southerly" types. These are defined as follows:

- cold westerly: mean wind directions could range from  $235^\circ$  to  $305^\circ$ , and the height of the  $-5^\circ\text{C}$  isotherm can be at or lower than the 2300-m level;
- cold southerly: mean wind directions could range from  $145^\circ$  to  $234^\circ$ , and the height of the  $-5^\circ\text{C}$  isotherm can be at or lower than the 2300-m level.

Rawinsondes were released at regular intervals in the Almanor project, and these provided the wind directions and upper air temperatures for storm classification and seeding decision making.

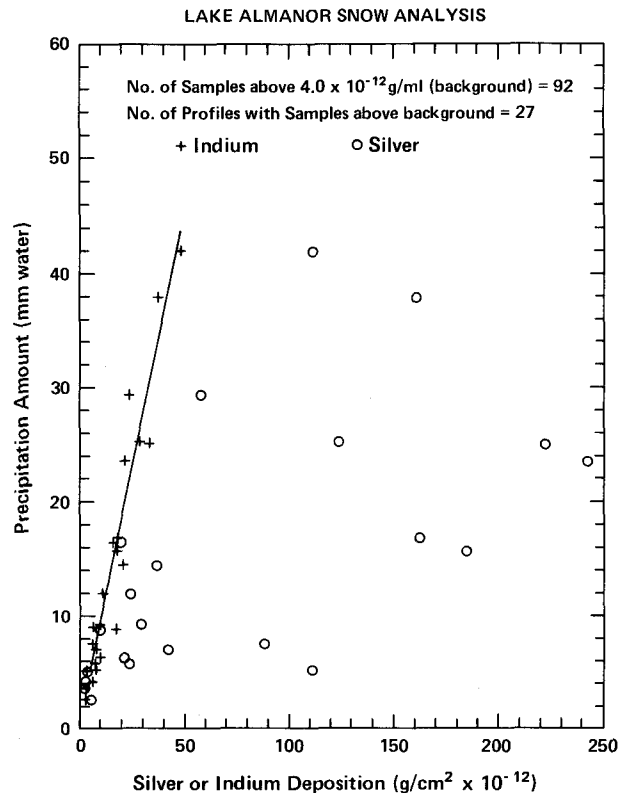


FIG. 9. Precipitation amount as functions of silver and indium deposition ( $\text{g cm}^{-2}$ ) in the Lake Almanor project two-aerosol seeding experiments. Line of best fit for indium,  $Y = 0.926X + 0.890$ . Values of silver and indium above threshold values of  $4.0 \times 10^{-12} \text{ g mL}^{-1}$  ( $B_{Ag}$  and  $B_{In} + 2\sigma$ ).

Because the experimental ranges of variability in the measured concentrations of silver and indium are  $\pm 15\%$ , this could result in experimental standard deviations of 0.2 from the mean silver mass-to-indium

TABLE 1. "Expected Ag/In (mass per square centimeter) ratio in Lake Almanor project snowfall.

Quantity	Silver iodide	Indium sesquioxide
Mean particle diameter:	0.060 $\mu\text{m}$	0.065 $\mu\text{m}$
Mean particle volume:	$1.08 \times 10^{-16} \text{ mL}$	$1.37 \times 10^{-16} \text{ mL}$
Density:	$5.67 \text{ g mL}^{-1}$	$7.18 \text{ g mL}^{-1}$
Molecular weight:	$234.8 \text{ g mol}^{-1}$	$277.6 \text{ g mol}^{-1}$
Mean mass of element per particle:	$2.81 \times 10^{-16} \text{ g}$	$6.41 \times 10^{-16} \text{ g}$
Ratio: indium/silver, masses per particle:	2.28:1	
Experimental release rates:	$18.75 \text{ g h}^{-1}$	$12.50 \text{ g h}^{-1}$
Ratio: $\text{AgI}/\text{In}_2\text{O}_3$ release rates:	1.5:1	
Release rates, particles per hour:	$3.07 \times 10^{16}$	$1.61 \times 10^{16}$
Ratio: $\text{AgI}/\text{In}_2\text{O}_3$ , particles release rates:	1.9:1	
"Expected observed ratio of masses deposited in precipitation by scavenging alone: Ag/In:	0.83:1	



TABLE 2. Silver/indium (mass per square centimeter) ratios observed in profiles at eight Lake Almanor snow sampling sites.

Storm type and date	Site code							
	FR-7	WV-2	MH-1	MC-2	RC-3	RC-5	SM-4	WW-4
CW—16 December 1984	9.6	2.4	1.8	0.6	1.3	4.4	6.9	5.4
CW—8 February 1985	0.6	1.3	4.3	0.7	1.4	1.2	4.0	2.5
CS—6 March 1985	17.2	2.2	14.2	2.0	0.5	ND	0.5	ND
CW—26 March 1985	4.0	11.9	ND	ND	3.3	ND	1.1	10.7

ND—silver and indium not detected above threshold values.

CW—cold westerly storm.

CS—cold southerly storm.

mass ratio of 0.83:1. Using this criterion, there is a 95% confidence level that ratios greater than 1.4 provide evidence of removal processes for silver iodide other than scavenging. As shown in Table 2, 17 of the 27 profiles fall into this category, the values ranging from 1.5 to 17.2. The only process known to the authors that would produce this result is ice nucleation, and it is concluded that these observed major differences between AgI and  $\text{In}_2\text{O}_3$  removal have been caused in this way.

## 7. Discussion and conclusions

It has been shown that it is possible, with the development of accurate trace chemical analytical methods, to use ice-nucleating and non-ice-nucleating aerosols to investigate effects of seeding supercooled clouds. The elements of silver and indium, released in submicron-sized aerosol form, have been used for this purpose in a series of experiments in winter orographic storms in the central Sierra Nevada. It has been determined that

- the natural background concentrations of silver and indium are 2.0 ( $\sigma = 1.0$ ) and 1.5 ( $\sigma = 1.0$ ) ppt, respectively;

- the concentration of seeding silver above this background in the snowfall is often positively correlated with precipitation amount; this could occur if some of the silver iodide had nucleated new ice crystals and these crystals had aggregated with other nucleated or naturally occurring crystals to form snowflakes;

- separate submicron-sized aerosols of silver iodide and indium sesquioxide follow the same general trajectories when released from approximately the same locations at the ground; this was based on the detection of both silver and indium in the same precipitation samples at several receptor sites in the designated seeding project target area;

- when the two submicron-sized aerosols were released simultaneously into winter orographic clouds, the mass ratios of the ice-nucleating to the non-ice-nucleating chemical in the snow, on many occasions, far exceeded the ratio expected if scavenging of the two aerosols alone were occurring;

- when the “expected” scavenging ratio of the chemical masses deposited was  $0.83 \pm 0.20$ , ratios up to 17.2:1 were observed in the snow profiles; such significant departures from “scavenged” values are considered to be attributable to the participation of silver iodide aerosol particles in the precipitation initiation processes.

These results alone were not able to quantify whether such participation by the silver iodide aerosol particles had produced changes in precipitation amounts. Additional concurrent information is needed to do this, and this aspect of the seeding assessment problem needs to be addressed.

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## REFERENCES

- Eisner, U., and H. B. Mark, Jr., 1970: The anodic stripping voltammetry of trace silver solutions employing graphite electrodes: Application to silver analysis of rain and snow samples from silver iodide seeded clouds. *Electroanalytical Chemistry and Interfacial Electrochemistry. J. Electroanal. Chem.*, **24**, 345–355.
- Fookes, R. A., J. A. Warburton, and J. S. Watt, 1962: A radioisotope technique for tracing air movements in clear air and clouds. *Nature*, **196**, No. 4852, 328.
- Greenfield, S. M., 1957: Rain scavenging of radioactive particulate matter from the atmosphere. *J. Meteor.*, **14**, 115–125.
- Gubeli, V. O., 1959: Zur Bestimmung von Ultraspuren von Silberjodid in Regenwasser. *Z. Angewandte Math. Phys. (ZAMP)*, **10**, 310–314.
- Henderson, T. J., (Ed.), 1991: Cloud seeding in California: Weather modification projects operating in California during 1990–91. *J. Weat. Mod.*, **23**, No. 1, 104.

- Isono, K., 1961: Some results of cloud seeding experiments with use of silver iodide ground generators. *Proc., International Cloud Physics Conf.*, Australia, CSIRO, 75–76.
- Junge, C. E., 1963: *Air Chemistry and Radioactivity*. Academic Press, New York.
- Knight, C. A., 1969: Small particle detection and identification by crystal growth: Preliminary work on AgI particle detection. *J. Appl. Meteor.*, **17**, 705–707.
- Koenig, L. R., 1960: The chemical identification of silver iodide ice nuclei: A laboratory and preliminary field study. *J. Meteor.*, **17**, 426–434.
- Lacaux, J. P., 1970: Dosage de l'argent dans les précipitations par spectrométrie d'absorption atomique sans flamme. *J. Rech. Atmos.*, **6**, 329–333.
- , and J. A. Warburton, 1982: Precipitation scavenging of sub-micron particles released by rockets into convective clouds. *Proc., 4th Int. Symp. on Scavenging, Dry Deposition, and Resuspension*, Santa Monica, CA, Amer. Meteor. Soc., 303–314.
- , J. Fournet-Fayard, J. A. Warburton, and P. Waldteufel, 1985: The disposition of silver released from Soviet OBLAKO rockets in precipitation during the hail suppression experiment Grossversuch IV. Part II. Case studies of seeded cells. *J. Climate Appl. Meteor.*, **24**, 977–992.
- Marwitz, J. D., and R. E. Stewart, 1981: Some seeding signatures in Sierra storms. *J. Appl. Meteor.*, **20**, 1129–1144.
- Mooney, M. L., and G. W. Lunn, 1968: The area of maximum effect resulting from the Lake Almanor randomized cloud seeding experiment. *J. Appl. Meteor.*, **8**, 68–74.
- Mossop, S. C., and C. Tuck-Lee, 1969: The composition and size distribution of aerosols produced by burning solutions of AgI and NaI in acetone. *J. Appl. Meteor.*, **7**, 234–240.
- Parungo, F. P., and C. E. Robertson, 1969: Silver analysis of seeded snow by atomic absorption spectrophotometry. *J. Appl. Meteor.*, **8**, 315–321.
- Smith, E. J., J. A. Warburton, K. J. Heffernan, and W. J. Thompson, 1966: Performance measurements of AgI smoke generators on aircraft. *J. Appl. Meteor.*, **5**, 292–295.
- Stith, J. L., D. A. Griffith, R. L. Rose, J. A. Flueck, J. R. Miller, Jr., and P. L. Smith, 1985: A study of transport, diffusion, and ice activation in cumulus clouds using an atmospheric tracer. *J. Climate Appl. Meteor.*, **25**, 1959–1970.
- Vali, G., 1970: Entry of freezing nuclei into precipitation. *Proc. Symp. on Precipitation Scavenging*, Richland, Washington, U.S. Atomic Energy Commission, 49–68.
- , 1971: Quantitative evaluation of experimental results on the heterogeneous freezing nucleation of supercooled liquids. *J. Atmos. Sci.*, **28**, 402–409.
- Warburton, J. A., 1963: The detection of silver in rainwater from cloudseeding Experiments in Australia. *J. Appl. Meteor.*, **2**, 569–573.
- , 1969: Trace silver detection in precipitation by atomic absorption spectrophotometry. *J. Appl. Meteor.*, **8**, 464–466.
- , and L. G. Young, 1968: Neutron activation procedures for silver analysis in precipitation. *J. Appl. Meteor.*, **7**, 433–443.
- , and —, 1972: Determination of silver in precipitation down to  $10^{-11}$  M concentration by ion exchange and neutron activation analysis. *Anal. Chem.*, **44**, 2043–2045.
- , G. O. Linkletter, and R. H. Stone, 1982: The use of trace chemistry to estimate seeding effects in the northeast Colorado hail-suppression experiment. *J. Appl. Meteor.*, **21**, 1089–1110.
- , L. G. Young, M. S. Owens, and R. H. Stone, 1986: The capture of ice-nucleating and non ice-nucleating aerosols by ice-phase precipitation. *J. Rech. Atmos.*, **19**, 249–255.
- , R. H. Stone, and L. G. Young, 1989: A new scientific method employing ice-nucleating and non ice-nucleating aerosols simultaneously for assessing the effects of cloud seeding on precipitation. *Proc. Fifth WMO Scientific Conf. on Weather Modification and Applied Cloud Physics*, Beijing, China, 191–194.
- Wisniewski, J., and R. I. Sax, 1979: Silver concentration in rainwater from seeded and non-seeded Florida cumuli: 1973–1975 results. *J. Appl. Meteor.*, **18**, 1044–1055.
- Young, K. C., 1974: The role of contact nucleation in ice-phase initiation in clouds. *J. Atmos. Sci.*, **31**, 768–776.