

## EVALUATION OF GLACIOGENIC CLOUD SEEDING USING TRACE CHEMISTRY

James M. Fisher<sup>1</sup>, Marion L. Lytle<sup>1</sup>, Melvin L. Kunkel<sup>2</sup>, Derek Blestrud<sup>2</sup>,  
Vincent P. Holbrook<sup>2</sup>, Shaun K. Parkinson<sup>2</sup>, P. Ross Edwards<sup>3</sup>, Shawn G. Benner<sup>1</sup>

<sup>1</sup>Department of Geosciences, Boise State University, Boise, ID

<sup>2</sup>Idaho Power Company, Boise, ID

<sup>3</sup>Curtin University, Bentley, Perth, Western Australia

Corresponding Author: Shawn Benner, Email: [sgbenner@gmail.com](mailto:sgbenner@gmail.com)

**ABSTRACT:** Glaciogenic cloud seeding with silver iodide (AgI) has been used to enhance precipitation for over 60 years. Assessments of AgI impact and dispersion are often quantified using atmospheric processes models with impact assessed by comparing models with and without the inclusion of cloud seeding modules. However, there is inherent uncertainty in these models. Quantifying AgI distribution in the snowpack following cloud seeding can both validate and improve model performance. The purpose of this study is to demonstrate the capacity to document the dispersion of AgI by measuring silver (Ag) enrichments in snow.

This study develops clean field and laboratory procedures to detect trace seeding signatures in alpine snowpack. Unique laboratory layout and protocols are employed to reduce contamination potential within a traditional ICP-MS laboratory setting (not housed in a Class 100 Clean Room). Using these methods, we sample a series of snow profiles within the target area of active cloud seeding in the central mountains of Idaho. The results demonstrate the ability of the new methods to reproduce distinct elevated Ag concentrations over a small scale (0.25 km<sup>2</sup>) and at the basin (2,400 km<sup>2</sup>) scale. The trace chemical analysis of snow samples from eight snow pits over an area of 0.25 km<sup>2</sup> and six sites separated up to 65 km (basin scale) identify potential seeding signatures from two seeded storms. A localized enrichment factor is used to identify and replicate this seeding signature at all six sites within the basin. This enrichment factor can delineate a seeding signature at sites far downwind from AgI sources, where Ag concentrations are only 1-3 parts per trillion above background levels. The localized enrichment factors at all six sites contain chemical snow profiles generally corresponding to peak Ag concentrations and known cloud seeding events.

## INTRODUCTION

### A. A Brief Description of Cloud Seeding

Glaciogenic cloud seeding is a method of enhancing the fraction of super cooled liquid water precipitating from a given storm. Precipitation tends to be inefficient at higher cloud temperatures due to the lack of active natural ice nuclei (DeMott, 1995). The addition of artificial ice nuclei active at temperatures, greater than -12 °C, may result

in an increase in snow precipitation, especially in orographic clouds (Breed et al. 2014). Silver iodide (AgI) is the artificial nucleating agent most often used in winter orographic cloud seeding. An acetone-silver iodide solution, usually containing 1-2% AgI and solubilizing agents, can produce more than 10<sup>15</sup> artificial ice nuclei depending on atmospheric conditions (Garvey, 1975). Recent estimates suggest the addition of artificial ice nuclei from AgI enhances precipitation by 3 - 15% (Manton and Warren, 2011; WWMPP, 2014).

## B. Current validation techniques

The impact of cloud seeding is often quantified using physical, statistical and modeling techniques. Models, such as the Weather Research and Forecasting (WRF) model, can be used to predict the spatial and temporal presence of AgI in the atmosphere and its associated impact on precipitation (Xue et al. 2013). However, AgI plumes can be difficult to model amid complex terrain. Some physical studies found AgI plumes can be trapped in valleys, lacking the uplift to effectively nucleate orographic clouds (Super and Heimbach, 1983; Super, 1990). A model may incorrectly identify enhancements downwind of valley-trapped AgI plume. Therefore, there is a need for physical validation of these techniques (NRC, 2003; Breed et al. 2014). One such validation tool is trace chemical analysis, validating the success in AgI targeting only. Assessing the magnitude of precipitation enhancement (using modeling and statistical techniques) with targeting effectiveness (trace chemical analysis) allows for a more comprehensive evaluation of cloud seeding effectiveness.

## C. Prior efforts to quantify Ag seeding signals in snow

Trace chemical methods have been utilized to evaluate cloud seeding for years. This method was first used in 1968 using a neutron activation technique (Warburton and Young, 1968). However the importance of clean techniques was not universally understood until the early 1990's (Boutron, 1990) and results prior to this period should be evaluated accordingly (Wen et al. 2002). There have been several recent studies utilizing clean techniques that have provided reliable results. For instance, new approaches were developed to evaluate cloud seeding in a project at Lake Almanor, in California, including a source-receptor method and a dual-tracer method. The source-receptor method sought to correlate the timing of AgI releases to Ag concentrations in snow (Warburton et al. 1995a; Warburton et al. 1995b). Ag enrichments above typical background concentrations did not necessarily imply successful cloud seeding because concentrations

could have been contributed by anthropogenic contamination or dry deposits from dust. Background Ag concentrations, on the other hand, were evidence of poor targeting. The dual-tracer method provided better physical understanding of high Ag concentrations in target zones due to AgI seeding (Chai et al. 1993; Warburton et al., 1996; Huggins et al. 2005). This method released AgI in conjunction with  $\text{In}_2\text{O}_3$ , a non-active nuclei of similar size as AgI. Because  $\text{In}_2\text{O}_3$  does not participate in nucleation processes, the enhancement of indium concentrations in snow is likely only due to scavenging processes. Therefore, snow samples with Ag to In ratios greater than expected from scavenging (approximately one) implied that enhanced Ag concentrations were primarily due to nucleation.

These dual-tracer techniques were replicated in the Payette Basin, Idaho (Edwards et al. 2004) and in the Snowy Mountains, Australia (Huggins et al. 2008). These dual-tracer studies showed that Ag concentrations above background (1 ppt and 3 ppt in the Payette Basin and Snowy Mountains, respectively) were almost always correlated to high Ag to In ratios, demonstrating the differential nucleating capacity of AgI. The most recent trace chemical analysis, Wyoming Weather Modification Pilot Project (WWMPP), found the source-receptor method useful in identifying seeded snow layers (WWMPP, 2014). In the study presented here, like the WWMPP, the source-receptor method was used to identify seeded snow layers.

## D. What is the gap in knowledge?

Although measuring Ag enrichments in snow has been done for years, there are limited field-based studies regarding the spatial distribution of AgI at various scales (Huggins et al. 2008). Understanding spatial variability is critical to both establishing the appropriate amount of samples to collect in the field, as well as the reliability of trace chemical methods in defining a seeded layer. Additionally, several recent studies utilized a high resolution inductively coupled plasma mass spectrometer (HR-ICP-MS) housed in a Class 100 Clean Room. This study utilized a quadru-

pole ICP-MS with higher limits of detection and was not housed in a clean room. Because high resolution ICP-MS instruments housed in clean laboratories can be cost prohibitive as a validation tool, the feasibility of using a traditional laboratory for analyzing trace Ag and other trace metal concentrations was evaluated in this study.

### E. Purpose and objectives of the research

The purpose of this study was to quantify trace Ag enhancements in snow from AgI cloud seeding using the source-receptor approach. This was accomplished by developing appropriate field and laboratory techniques to produce limits of detection for Ag below one part per trillion (ppt). The analysis techniques were tested to determine if seeding signatures could be detected over a small scale (0.25 km<sup>2</sup>) and also over a basin scale (2,400 km<sup>2</sup>). The approach described in this paper can be used to assess WRF model accuracy and cloud seeding impacts.

Specifically, the four questions posed by this study are:

1. *Is a traditional quadrupole ICP-MS laboratory suitable for trace chemical analysis of snow samples?*
2. *Are low signal to noise Ag enhancements in field samples replicable and reliable?*
3. *Are the identification of Ag cloud seeding signals replicable over a small scale?*
4. *Can the distribution of seeding signals be reliably determined over a basin scale?*

## METHODOLOGY

### 2.1 Field Methods

The target area for the cloud seeding activities in this study is the Payette Basin, located in southwestern Idaho, USA (Figure 1). The Payette Basin is approximately 2,400 km<sup>2</sup> and is bounded by latitudes 43° 57'N to 44° 33'N and longitudes

115° 57'W to 116° 04'W. Elevations range between 970 and 2,830 m. A centrally located weather station at median elevation reveals an average annual temperature and precipitation of 3.8 °C and 81.9 cm respectively (Deadwood Dam Meteorological Station, 1,640 m elevation). The sites sampled in this study primarily resided in the southern Payette Basin (Table 1).

The field and lab methods necessary to quantify trace amounts of Ag in snow have been outlined in several studies, primarily in arctic regions (Barbante et al. 1999; Planchon et al. 2001; Barbante et al. 2004; Hong et al. 2004; Krachler et al. 2008). Slight modifications of these methods were applied for this study. Note that all acids described in this paper were quartz double distilled in a Class 100 Clean Room. All acid percent concentrations were computed on a volume per volume basis.

Field equipment was cleaned and packaged to minimize the potential for contamination. Field equipment in direct contact with snow underwent three nitric acid baths while subsidiary equipment soaked in a 2% nitric acid bath until use (see Laboratory Methods). All field equipment used for sampling, including attire, was packed in a Class 100 Clean Room. Equipment was sealed within two polyethylene bags. Only the inner bags were acid washed (Boutron, 1990). Inner polyethylene bags were leached in 4% nitric acid (HNO<sub>3</sub>) for 48 hours (Snyder-Conn et al. 1997). Bags were rinsed in ultra-pure water, and then dried in a vertical laminar flow station (AirClean PCR Workstation AC600) for 12 hours. Clean field equipment was packed and sealed under these workstations as well.

To prevent contamination, technicians wore clean room attire and constructed snow pits far from potential contamination sources. Clean gear attire consisted of a High-Density Polyethylene (HDPE) Tyvek suit, 2 pairs of nitrile gloves, face masks, and Low-Density Polyethylene (LDPE) bags tied around the technician's feet. Technicians approached the sampling location from downwind to prevent particulates migrating from

the technician to the snow about to be sampled. Sampling locations were always in remote areas

and at least 400 m from potential contamination sources, such as snow mobile tracks or roads.

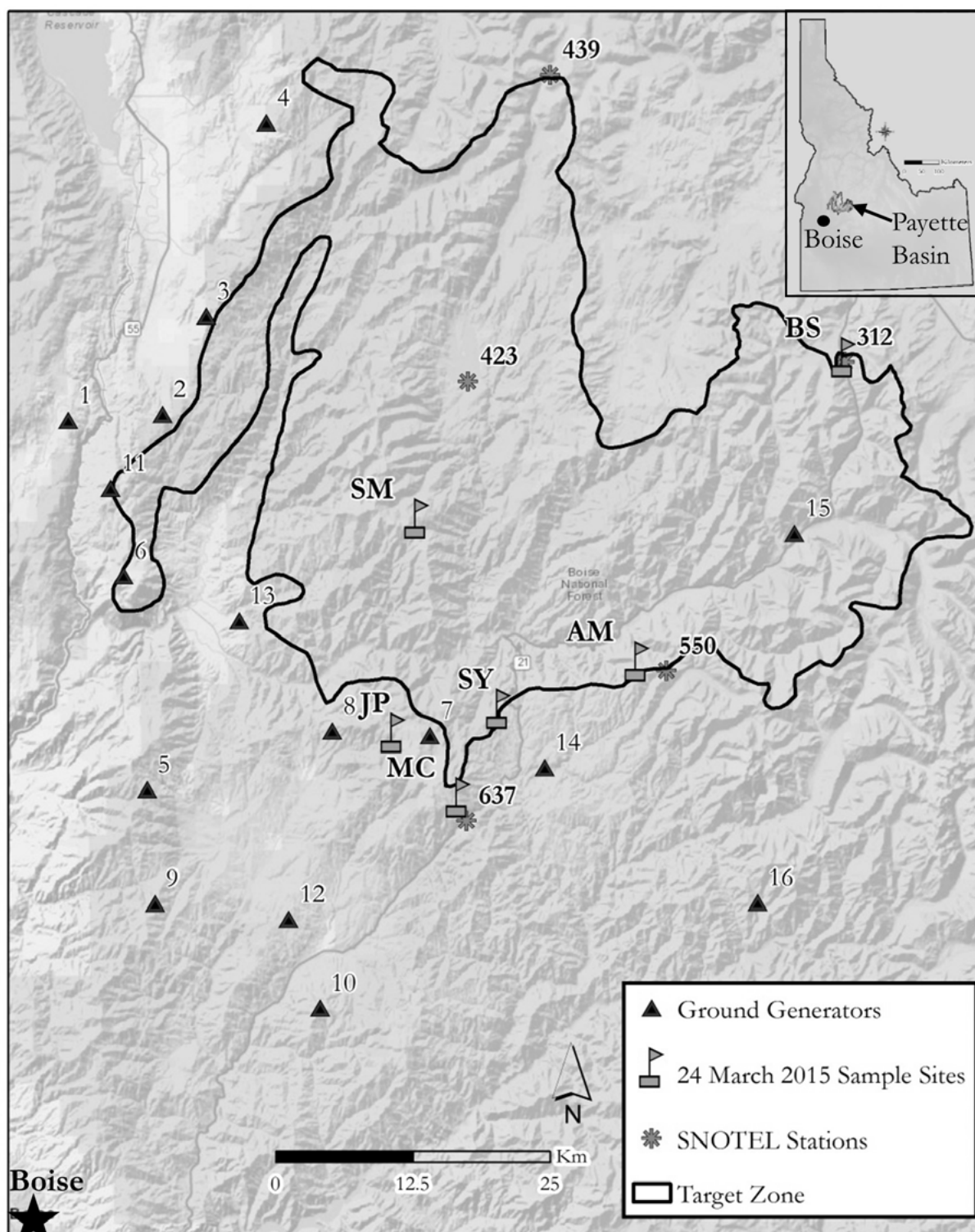


Figure 1: The black outline delineates the Payette Basin. Above there are five SNOTEL sites, six sampling sites, and 16 ground generators near the Payette Basin. Three-digit identification numbers are listed above SNOTEL sites.

Table 1. Sampling Locations in the 2015 Field Campaign

| Date Collected [2015]   | Site Name | Location                            | Elevation [m] | Samples Analyzed | Ag Enhancement? |
|-------------------------|-----------|-------------------------------------|---------------|------------------|-----------------|
| 09 January <sup>a</sup> | SY-1      | 44° 1' 28.45"N<br>115° 37' 53.22"W  | 1,890         | 110              | No              |
| 24 March                | SY-2      | 44° 1' 16.03"N<br>115° 37' 53.22"W  | 1,946         | 30               | Yes             |
| 24 March <sup>b</sup>   | BS        | 44° 18' 13.68"N<br>115° 13' 51.42"W | 2,137         | 124              | Yes             |
| 25 March                | MC        | 43° 56' 56.74"N<br>115° 40' 44.43"W | 2,303         | 24               | Yes             |
| 25 March                | AM        | 44° 3' 29.43"N<br>115° 28' 22.39"W  | 2,092         | 18               | Yes             |
| 07 April <sup>b</sup>   | SM        | 44° 10' 41.03"N<br>115° 43' 15.95"W | 2,256         | 248              | Yes             |
| 11 April                | JP        | 44° 0' 10.45"N<br>115° 45' 6.22"W   | 2,185         | 70               | Yes             |

<sup>a</sup> Inter-laboratory comparison was performed on these samples

<sup>b</sup> Multiple snow pits were constructed at one site to understand hillslope-scale Ag variability

Snow samples were collected from the wall of an excavated snow pit. The snow pit was first excavated using an aluminum shovel. Snow pit faces were then decontaminated prior to sampling by removing 2 cm of snow perpendicular to the pit face using a clean polypropylene scraper. The pit face was decontaminated again with a triple cleaned LDPE scraper, removing an additional 2 cm (Boutron, 1979) of snow. Snow was then sampled using 50 mL, 3 cm diameter polypropylene centrifuge vials (FisherBrand, Pittsburgh, PA, USA). Columns of vials were staggered 1.5 cm (Figure 2) to obtain a higher depth resolution (Edwards and Simeral, 2006).

A “clean hands/dirty hands” technique was employed while sampling in which one member of the team was designated as “clean hands”, this person collected samples while a second member of the team was designated as “dirty hands” and conducted activities other than snow collection (Snyder-Conn et al. 1997). “Clean hands” would only handle the LDPE scraper for decontamination and areas of sample vials untouched by “dirty hands”. “Dirty hands” would attend to tasks more susceptible to contamination, such as

labeling vials with permanent markers and opening acid cleaned bags of vials.

After sample collection, vials were immediately double bagged (clean inner bag), shipped back to Boise State University in a dry ice cooler and then stored at -20 °C until analysis. Samples were kept frozen to mitigate trace element adsorption in the sampling vials.

## 2.2 Laboratory Methods

Our laboratory Milli-Q 18.2 mΩ (MQ) water and HNO<sub>3</sub> prepared in the laboratory were compared to known pure standards. Blanks were validated using SeaStar Chemicals (Sidney, BC, Canada) BASELINE<sup>®</sup> HNO<sub>3</sub> (Lot No. 1214070) and BASELINE<sup>®</sup> water (Lot No. 9214020). SeaStar HNO<sub>3</sub> and water were both certified to less than 0.05 ppt Ag. Differences between our lab MQ water and SeaStar Chemicals were always less than 0.4 ppt for Ag, within our method detection limit. Upon dilution to 2% HNO<sub>3</sub>, negligible differences resulted from SeaStar Chemicals HNO<sub>3</sub> and the reagent-grade HNO<sub>3</sub> double distilled in our Class 100 Clean Room. The importance of

blanks cannot be understated. The quality of blanks, not the sensitivity of modern ICP-MS instruments, are often the most impactful factor in lowering an instrument-limit of detection (Rodushkin et al. 2010).

Equipment in direct contact with samples or acid underwent a triple acid bath with increasing purity (Boutron, 1990; Hong et al. 2000; Edwards and Simeral, 2006) and decreasing concentrations of  $\text{HNO}_3$  (10%, 5%, and 0.1% respectively). MQ water rinses followed each bath. All non-critical equipment (permanent markers and polypropylene scrapers) remained in a 2%  $\text{HNO}_3$  until needed for sampling. Non-critical equipment was rinsed in MQ water after the acid bath. All equipment was then dried in a laminar flow clean bench and double sealed in polyethylene bags.

Polyfluoroalkoxy (PFA) Teflon bottles were used to hold the trace element standard solutions used to calibrate the ICP-MS. Teflon was used to hold

samples and standards at room temperature because it adsorbs Ag at the lowest rate relative to other laboratory materials (Wen et al. 2002). Fifteen mL Teflon vials (Savillex, Eden Prairie, MN, USA) were used to hold prepared samples for ICP-MS analysis. Both varieties of Teflon labware were washed twice in 48-hour baths of 1% hydrofluoric acid (HF) and 2%  $\text{HNO}_3$ <sup>1</sup>. MQ water rinses followed each bath.

Analyses were performed with a multi-use Thermo Scientific X-Series 2 Inductively Coupled Plasma Mass Spectrometer (ICP-MS) coupled with an Elemental Scientific Inc. SC-FAST Automated Sample Introduction System (hereafter, autosampler). The ICP-MS laboratory was not a Class 100 Clean Room. Therefore, special steps were undertaken to limit contamination sources from airborne particulates in the ICP-MS laboratory and from memory effects within the ICP-MS resulting from other experiments.

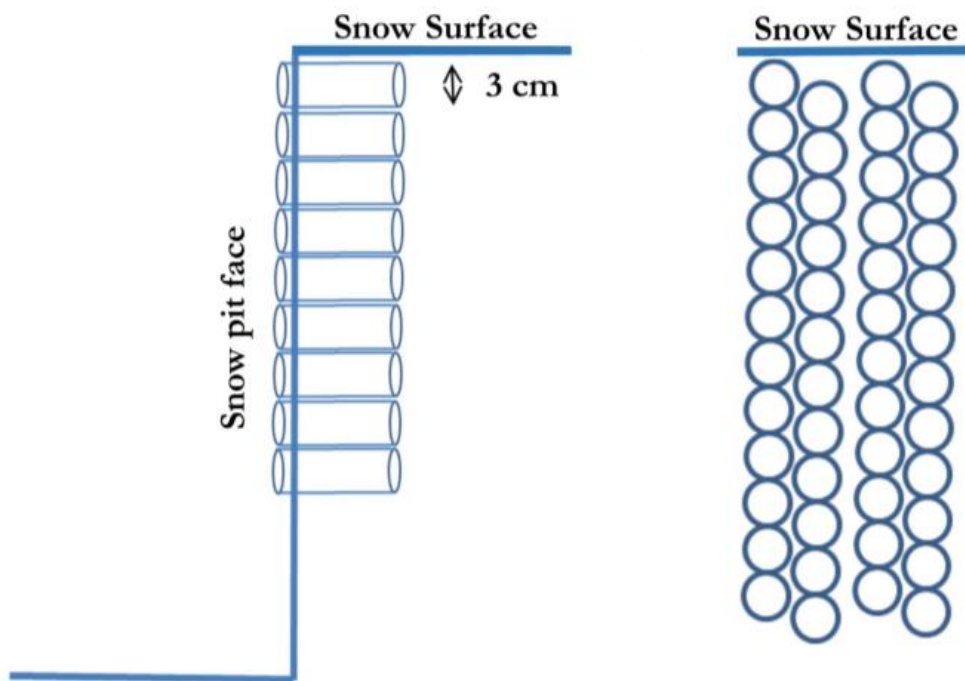


Figure 2: Diagram illustrating the snow sample collection method. A) 3 cm diameter vials were inserted perpendicular to the snow pit face. B) Four columns of vials were used to collect samples from each snow pit. Vials in each two-column set were are staggered by 1.5 cm.

<sup>1</sup><http://www.savillex.com/Content.aspx?PageName=Guide%20to%20Cleaning%20PFA%20Labware>. Accessed 1-10-16.

Contamination from airborne particulates in the ICP-MS laboratory was mitigated by eliminating direct exposure of samples to the ICP-MS laboratory environment. Contamination potential was reduced by placing the autosampler within a laminar flow clean bench (AirClean AC4000 Workstation, Raleigh, NC, USA). The autosampler encased samples in plastic to further prevent particulate infiltration (Figure 3). Likewise, all samples were prepared and thawed in a Class 100 Clean Room.

High background Ag counts in the ICP-MS from unrelated experiments had to be minimized prior to analysis. This instrument was frequently used for laser ablation of geologic materials, resulting in disruptive memory effects from Ag. Ag counts were reduced in two ways. First, a 4%  $\text{HNO}_3$  ultra-pure solution was delivered through the ICP-MS until Ag counts stabilized. Counts stabilized to  $30 \pm 10$  counts per second in 1 - 12 hours, depending antecedent conditions. Second, a dedicated set of internal parts for the ICP-MS was used for this analysis. A nickel micro-skimmer cone (Meinhard, Golden, CO, USA), nickel sampler cone (Meinhard), perfluoroalkoxy (PFA) tubing, quartz cyclonic spray chamber (ESI, Omaha, NE, USA), and a quartz nebulizer (ESI) and injector (ESI) were used exclusively for this study.

Samples were acidified as per the EPA Direct Analysis Method 200.8 (Telliard, 2008). This acidification method was chosen primarily because it has been the conventional method for analyzing precipitation and natural waters for decades. Snow was acidified to 2%  $\text{HNO}_3$  and stored at room temperature to thaw. Once prepared, samples were stored in the dark for 24 hours within the clean room prior to analysis. Adopting this method allowed for direct comparison with other studies, because element concentrations at these low values can be altered by both acidification duration and strength (Koffman et al. 2014). However, it should be noted that samples were acidified within their field vials and prior to thawing. When samples were thawed and decanted from the polypropylene field vials to the Teflon test vials prior to acidification, 45% lower Ag concentrations resulted ( $n = 9$ , Figure 4).

This was likely due to adsorption and/or the bonding of solid Ag particulates to the field vial walls. Therefore, previous studies that acidified samples after decanting into analysis vials may have underestimated Ag concentrations in snow.

Samples were prepared in the clean lab prior to being transported to the ICP-MS laboratory. After the 24 hour acidification period, samples were decanted from the 50 mL polypropylene field vials to the 15 mL Teflon test vials in the clean lab. Test vials were sealed with Parafilm, placed in a clean LDPE rack, and sealed again in a clean HDPE tub before being transported to the ICP-MS laboratory. The LDPE sample rack was loaded directly into the autosampler, housed within a laminar flow clean bench.

The ICP-MS was calibrated using three serial dilutions of 1,000 mg/L (1,000 ppm) standards to analyze the following crustal tracers: Na, Al, Cr, Co, Sr, Ba, La, Ce, and Pb. Ag was calibrated using serial dilutions of 1,000 ppm to concentrations to 1,000 parts per trillion (ppt), 100 ppt, 10 ppt, and 1 ppt. The Ag calibration linear regression lines were re-calibrated a minimum of three times per analysis to address drift. Drift was further mitigated by analyzing a 10 ppb indium internal standard throughout the analysis. Blank (2%  $\text{HNO}_3$ ) rinses followed each calibration to reduce memory affects from 100 ppt and 1,000 ppt standards. Blanks were also analyzed every 10 samples to ensure instrument precision. Standard operating conditions for the ICP-MS are listed in Table 2.

Samples were prepared in the clean lab prior to being transported to the ICP-MS laboratory. After the 24 hour acidification period, samples were decanted from the 50 mL polypropylene field vials to the 15 mL Teflon test vials in the clean lab. Test vials were sealed with Parafilm, placed in a clean LDPE rack, and sealed again in a clean HDPE tub before being transported to the ICP-MS laboratory. The LDPE sample rack was loaded directly into the autosampler, housed within a laminar flow clean bench.



Figure 3: A) 4%  $\text{HNO}_3$  rinse solution B) Autosampler C) Plastic cover surrounding the autosampler D) Tubing delivering sample from the autosampler to the ICP-MS.

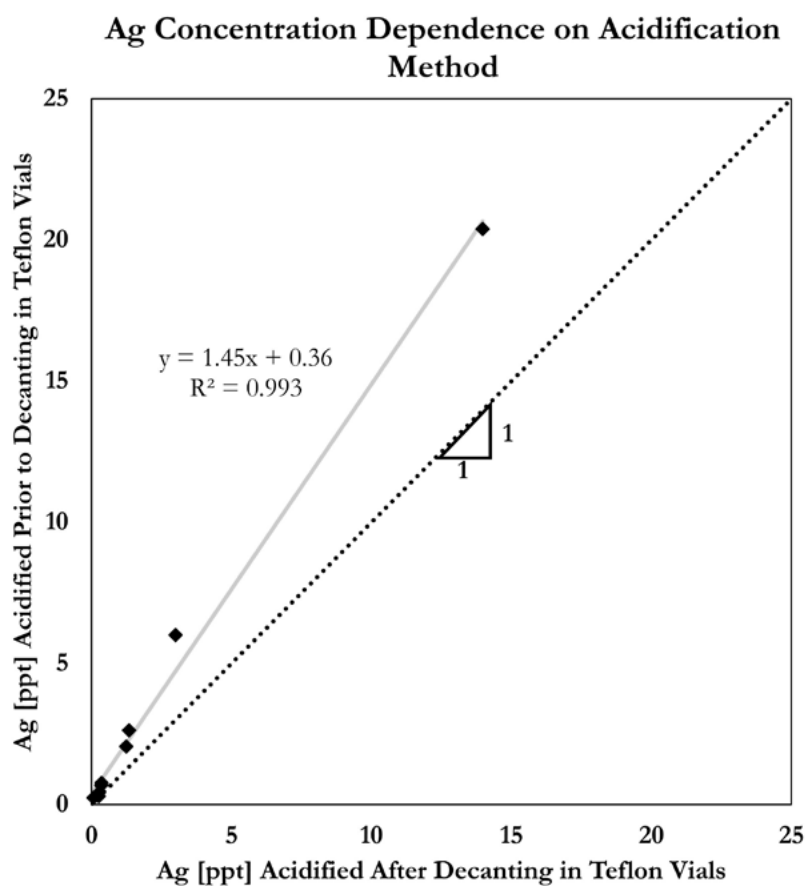


Figure 4: Ag concentrations depend on the acidification method. Each point represents a lab replicate analyzed two ways: acidifying prior to decanting to Teflon vials (y-axis) and after decanting to Teflon vials (x-axis).



The ICP-MS was calibrated using three serial dilutions of 1,000 mg/L (1,000 ppm) standards to analyze the following crustal tracers: Na, Al, Cr, Co, Sr, Ba, La, Ce, and Pb. Ag was calibrated using serial dilutions of 1,000 ppm to concentrations to 1,000 parts per trillion (ppt), 100 ppt, 10 ppt, and 1 ppt. The Ag calibration linear regression lines were re-calibrated a minimum of three times per analysis to address drift. Drift was further mitigated by analyzing a 10 ppb indium internal standard throughout the analysis. Blank (2% HNO<sub>3</sub>) rinses followed each calibration to reduce memory affects from 100 ppt and 1,000 ppt standards. Blanks were also analyzed every 10 samples to ensure instrument precision. Standard operating conditions for the ICP-MS are listed in Table 2.

## RESULTS

### 1. Is a traditional quadrupole ICP-MS laboratory suitable for trace chemical analysis of snow samples?

Our methods produced limits of detection for Ag low enough to identify distinct snow layers that contain elevated Ag concentrations. A detection limit, calculated as three times the standard deviation of Ag in blanks, of 0.4 ppt were obtained. This detection limit was necessary to identify trace Ag seeding signatures as low as 2 ppt (Figure 5). However, most Ag-enriched layers identified exhibited greater Ag enhancements, generally ranging from 8 to 25 ppt.

Table 2: Operating conditions of the ICP-MS and data acquisition parameters for the determination of selected trace elements in snow.

|                            |                                                       |
|----------------------------|-------------------------------------------------------|
| Forward power              | 1400 W                                                |
| Cooling                    | 13 L/min                                              |
| Expansion Pressure         | 2.0 * 10 <sup>0</sup> mbar                            |
| Analyzer Pressure          | 4.0-4.2 * 10 <sup>-7</sup> mbar                       |
| Turbo Pump Speed           | 1000 Hz                                               |
| Vacuum Pump Load           | 0.8 - 1.2 A                                           |
| Pole Bias                  | 1.0                                                   |
| Hex Bias                   | 4.0                                                   |
| Sample Cone                | Ni, 1.1 mm aperture inner diameter                    |
| Micro-Skimmer Cone         | Ni, 0.8 mm aperture inner diameter                    |
| Sample Depth               | Adjusted daily <sup>1</sup>                           |
| Lens settings              | Adjusted when appropriate                             |
| Nebulizer back pressure    | ~ 2.0 bar, optimized daily <sup>1</sup>               |
| Nebulizer Flow Rate        | 400 µL/min                                            |
| Sample Uptake Time         | 20 s                                                  |
| Rinse Time between Samples | 20 s                                                  |
| Elements Measured          | Na, Al, Cr, Co, Sr, Ag, Ba, La, Ce, Pb                |
| Dwell Time per Element     | Ag: 200 ms; Na, Al, Cr, Co, Sr, Ba, La, Ce, Pb: 10 ms |

<sup>1</sup> Optimized to obtain a stable and high <sup>115</sup>In signal (>500,000 cps for 10 ppb) and lowest possible oxide formation rate.

An inter-laboratory comparison was done to test the accuracy of our methods. Eight columns of snow samples were collected in one snow pit. Four columns were analyzed by Boise State University and four by Curtin University's Trace Research Advanced Clean Environment (TRACE) laboratory. Curtin University housed a High Resolution ICP-MS (Thermo Scientific ELEMENT 2), with an Ag detection limit of 0.05 ppt. Profiles analyzed in both laboratories were comparable even though the low Ag concentrations from this site oscillated about Boise State's detection limit (Figure 5).

While the ICP-MS used in this study was not in a clean laboratory, the team had access to, and used, a clean lab for cleaning of sampling and analysis materials as well as preparation of samples and standards. This capacity was considered essential to the success of the project. Therefore, an ICP-MS housed outside a trace metal clean room can be used to measure Ag concentrations to sub-ppt precision if clean environments are accessible and all relevant equipment is nitric acid washed.

## 2. Are low signal to noise Ag enhancements in field samples replicable and reliable?

Because the anticipated Ag concentrations associated with cloud seeding are almost always less than 50 ppt, natural Ag in the snow or dust within the snow can often exceed Ag contributed to the snow by cloud seeding. Ag enhancements from AgI can be as small as 1 ppt (Warburton et al. 1995a). Minor enhancements due to cloud seeding can be difficult to quantify relative to background Ag concentrations. In the Western United States, background Ag concentrations have been documented to range from 1 ppt in Idaho (Edwards et al. 2004) to 5 ppt in Wyoming (Edwards and Simeral, 2006). From the current study the background Ag concentration was found to be one ppt in the Payette Basin; in agreement with the most recent trace analysis performed here (Edwards et al. 2004). The background Ag concentration was established by collecting snow samples ( $n = 105$ ) at a control site 63 km upwind and north of the nearest ground generator.

Another challenge is to discern the fraction of Ag due to AgI compared with other anthropogenic or naturally occurring contaminants like dust. Ag concentrations greater than 15 ppt due to dust have been observed in remote, non-seeded regions. The primary source of Ag this region was attributed to dust (Edwards and Simeral, 2006). Anthropogenic contamination in non-seeded regions can cause Ag concentrations to be as high as 107 ppt, as seen in the Alps (Barrante et al. 1999). Because the Payette Basin is far from anthropogenic contamination sources, we assumed high background Ag concentrations were primarily derived from dust. The average Ag enriched snow storm layer (corresponding to a known seeding event) contained Ag concentrations of 14 ppt ( $n = 14$  seeded layers), similar to Ag concentrations observed in non-seeded snow in Wyoming. Therefore, Ag concentrations alone are not necessarily useful in identifying seeded snow layers.

To resolve the cloud seeding signature from Ag in the snow associated with dust, we used a normalizing approach in which we calculate an enrichment factor for Ag relative to the other elements found in the snow sample. This local enrichment factor (LEF), computed as in Equation 1, identified where significant Ag enrichments existed relative to elements commonly abundant in dust within a snow pit. An LEF of 1 or less suggests Ag concentrations in the sample are primarily due to dust. The crustal isotopes of the elements used in Equation 1 were  $^{27}\text{Al}$ ,  $^{140}\text{Ce}$ ,  $^{88}\text{Sr}$ , and  $^{137}\text{Ba}$ .

$$\text{Equation 1: LEF} = \left( \frac{\text{Ag}_i}{\text{Al}_i / q_{50}(\text{Al}_t)} * \frac{\text{Ag}_i}{\text{Ce}_i / q_{50}(\text{Ce}_t)} * \frac{\text{Ag}_i}{\text{Sr}_i / q_{50}(\text{Sr}_t)} * \frac{\text{Ag}_i}{\text{Ba}_i / q_{50}(\text{Ba}_t)} \right)^{0.25}$$

$\text{Ag}_i$  = Concentration of Ag in sample  $i$  [ppt]

$X_i$  = Concentration of element  $X$  in sample  $i$  [ppt]

$q_{50}(X_t)$  = Median concentration of element  $X$  at snowpit  $t$  [ppt]

Hereafter, "seeding signatures" will refer to snow samples that meet the following three criteria. First, the Ag concentration must exceed the established background in the Payette Basin of one

ppt. Second, the LEF factor must exceed two, indicating the Ag was not primarily sourced from dust. Third, Ag enhancements must correspond to some known AgI seeding event.

Seeding signatures from samples with Ag concentrations near background were resolved using the unitless LEF Factor. Ag enhancements due to AgI as low as 1 ppt were reliably identified using the LEF. Figure 6 shows three Ag concentration profiles (dotted lines) where the highest Ag con-

centrations were located at the base of the storm snow layer. However, Ag enriched samples analyzed at the base of the storm layer contained a visible dust layer (Figure 6) and was not likely enriched in Ag by cloud seeding. The corresponding LEF (black lines) indicated the base of the snowpack was not enriched ( $LEF \approx 1$ ) while the upper half of the storm layer showed LEFs in excess of 4. This trend was seen elsewhere in the Payette Basin in the March 24<sup>th</sup> storm snow layer. The upper half of the snowpack from this storm

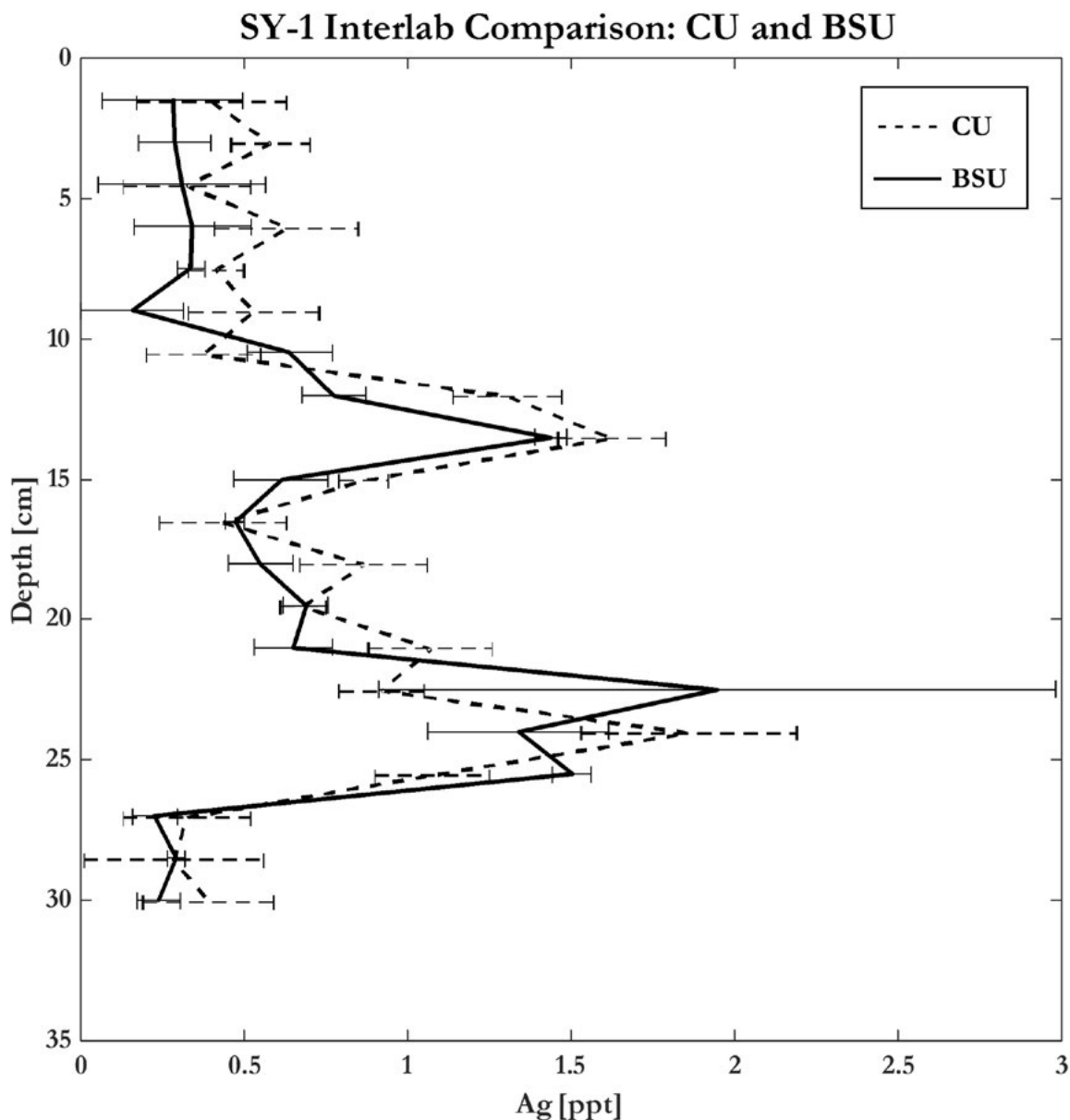


Figure 5: Boise State University's (solid) Ag profile was comparable to the profile analyzed at Curtin University's TRACE laboratory (dotted). Error bars denote the range of values obtained from the replicate profiles analyzed.

resulted in high Ag enrichment factors at all 6 sites (Figure 9). Four sites contained high Ag concentrations ranging from 5 to 28 ppt with LEFs greater than 4. However, two sites only had Ag concentrations ranging from 2 to 4 ppt yet the location of the enriched layer in the snowpack corresponded to ground generator seeding times. Also, the minor Ag enrichment at these two sites still resulted in LEFs greater than 4. Because the LEF profile in Figure 6 correspond to seeding times and produced similar LEF profiles as adjacent sampling sites in the Payette Basin (with Ag concentrations up to 28 ppt), the upper 4 cm in Figure 6 appears to be affected by AgI. Therefore, the LEF equation may be an effective tool to delineate Ag concentration enhancements as low as 1 ppt.

### 3. Are the identification of Ag cloud seeding signals replicable over a small scale?

A small scale variability test was conducted for two reasons: (1) to validate our field and laboratory methods and (2) to determine how many snow pits were necessary to describe local seeding signature trends. This test was conducted by sampling 1-3 profiles from 8 snow pits within a 0.25 km<sup>2</sup> area (noted as site SM in Figure 1). Samples from two seeded storm events (March 24<sup>th</sup> and April 5<sup>th</sup>) were collected on April 7, 2015 (at the locations shown in Figure 7). These two storms were delineated by noting snow stratigraphy and using a nearby high-resolution precipitation gage operated by Idaho Power Company. The snow accumulation rates at these locations differed significantly, so Ag signatures were present at different absolute depths within the profiles (Table 3). However, assuming a constant accumulation rate during each storm layer, normalizing each seeded storm snow layer to one depth revealed a consistent Ag signature in the profiles across the area.

The normalized Ag concentration profiles from the snow pits show similar trends. Depth-normalized snow pit showed nearly identical chemical profiles in the April 5<sup>th</sup> storm (sampled 36 hours following the storm). The March 24<sup>th</sup> storm layer (sampled 14 days following the storm) showed more variability (Figure 8). This may be due to differential melting rates between the 8 pits. The March 24<sup>th</sup>

storm contained a thick ice crust at the top of the storm snow layer and had an average density of 0.34 g cm<sup>-3</sup> at the SM site, indicating significant metamorphism since deposition. Differences in accumulation due to wind effects could have also contributed to these differences in depth. These two processes resulted in a shallower snow depth for the outlier profile (denoted P5), which only had a total snow depth of 130 cm (Table 3). This pit contained 55 cm less snow than the next lowest pit and had 32% less than the average total snow depth of the 8 pits constructed at SM. The Ag seeding signatures at P5 in the upper snowpack of the April 5<sup>th</sup> and March 24<sup>th</sup> storm showed identical Ag concentrations and relative locations within the storm snow layer prior to being normalized, but were located at greater depths relative to the other seven snow pits after normalization. Normalizing depths at P5 was therefore unsuccessful due to excessive alteration of snowpack after deposition.

Based on these results, one snow pit was sufficient to identify a representative seeding signature on a small scale in these two storm situations. Figure 9A and Figure 9D show the average deviation ( $\epsilon_d$ ) associated with each depth after normalizing snow depths (omitting the outlier profile P5 for Figure 9A). The average Ag concentration deviation at a given depth is 1.9 ppt. However,  $\epsilon_d$  was lower than 1.9 ppt in 71% of the depth intervals ( $n = 31$ ). All samples with  $\epsilon_d$  lower than the average were also not suspected of AgI enrichment.

$$\text{Equation 2: } \epsilon_d = \frac{1}{N} \sum_{i=1}^N \mu - x_i$$

$\epsilon_d$  = average deviation at depth d [cm]

N = number of snow pits at site SM

i = snow sample number collected at site SM

$\mu$  = mean Ag concentration of 8 pits at normalized depth d [ppt]

$x_i$  = Ag concentration at depth d [ppt]

Seeding signals were found to be replicable over a small area. This was even observed in snow deposited two weeks prior to sampling having

undergone extensive metamorphism as well as freshly deposited snow. Therefore, one snow pit can identify a seeding signature amid this terrain and storm conditions and despite considerable snow metamorphism. However, more than one pit may be necessary if a representative peak Ag concentration of a hillslope is desired.

Table 3: SM - Total Snow Depth at Each Pit

| Snow Pit ID | Total Snow Depth [cm] |
|-------------|-----------------------|
| P1          | 191                   |
| P2          | 219                   |
| P3          | 210                   |
| P4          | 195                   |
| P5          | 130                   |
| P6          | 185                   |
| P7          | 202                   |
| P8          | 220                   |

### Delineation of AgI Influence using the LEF

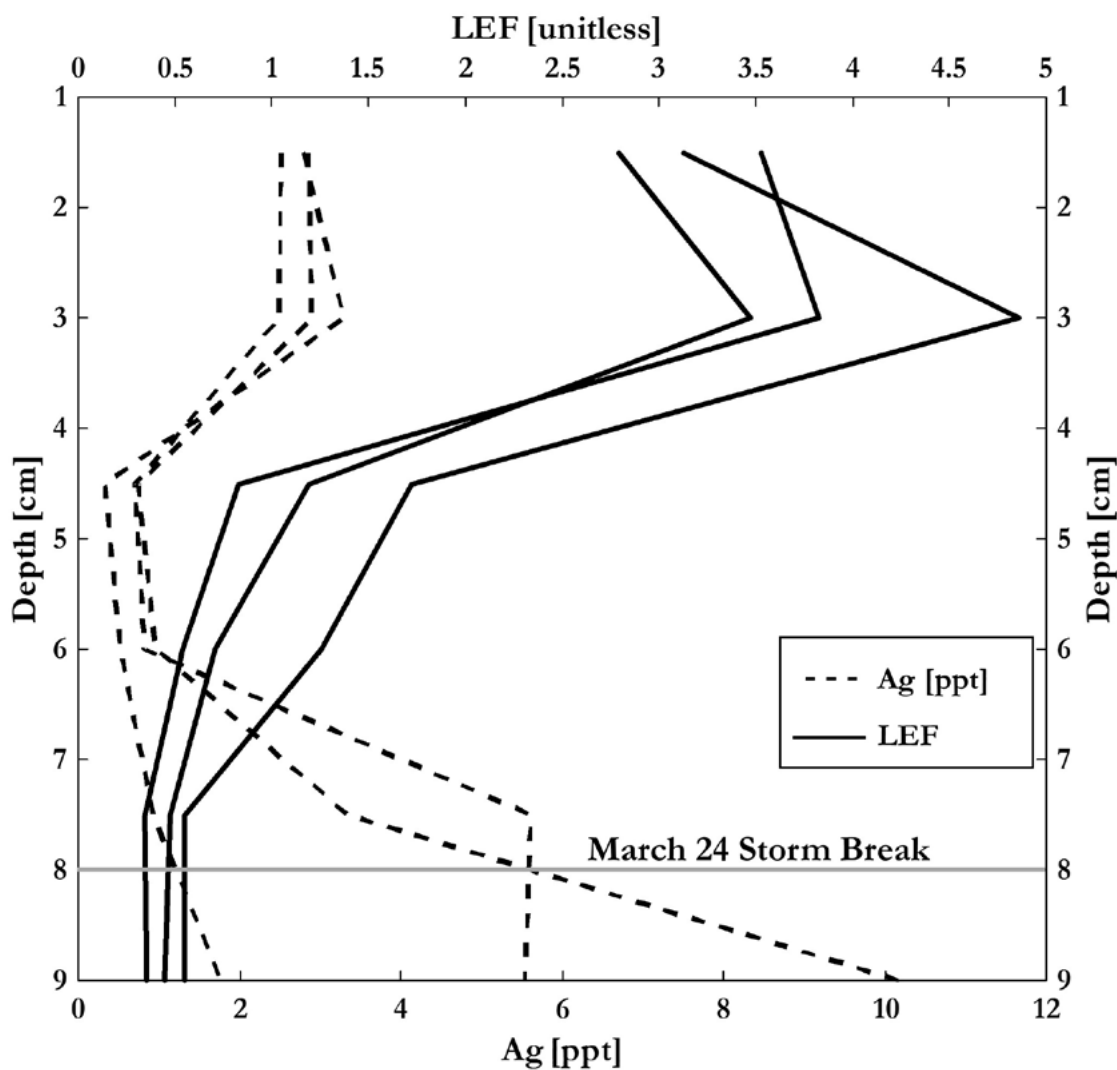


Figure 6. Three replicate profiles of Ag concentrations (dotted) were analyzed at site AM. The corresponding LEF values (solid) normalize silver concentrations to 4 other trace elements commonly associated with dust.

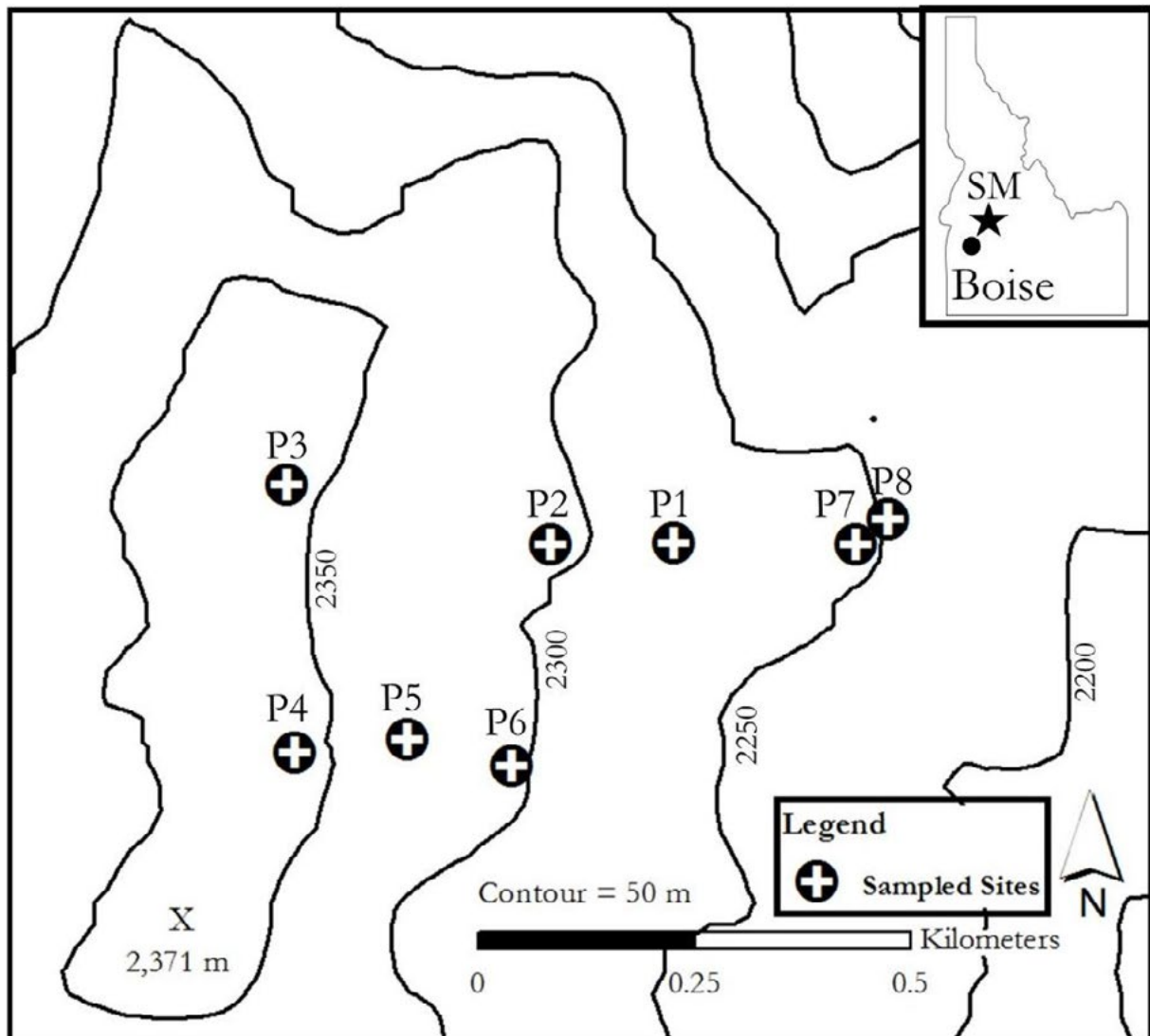


Figure 7: A small-scale variability test was conducted within this 0.25 km<sup>2</sup> area where sampling sites were as indicated.

4. Can the distribution of seeding signals be reliably determined over a basin scale?

A ground generator and aircraft seeded event took place on March 24, 2015 during a two-day storm event (March 23<sup>rd</sup> - March 24<sup>th</sup>). At 700 mb, wind speeds and temperatures in the Payette Basin averaged 271 at 16 m s<sup>-1</sup> and -10 °C, respectively. Ground generators around the Payette Basin started at variable times on March 24<sup>th</sup> between 03:47 and 07:44 MST (Table 4). Based on SNOTEL sites within the basin, 50-66% of the snow-water equivalent from this two-day storm was deposited when the first ground genera-

tor was activated. Figure 10 shows one of those SNOTEL stations in the southern target zone. The highlighted regions denote AgI release times and the corresponding snowpack potentially enriched with AgI. This data suggests Ag seeding signatures could only be present in the upper half of this storm layer.

Samples from the March 24 storm were collected at six widely separated sites (see Figure 9) in the Payette Basin (2,400 km<sup>2</sup>) to determine if a seeded layer could be identified at every site. Profiles collected and analyzed from all six sites contained samples with LEFs exceeding 4, de-

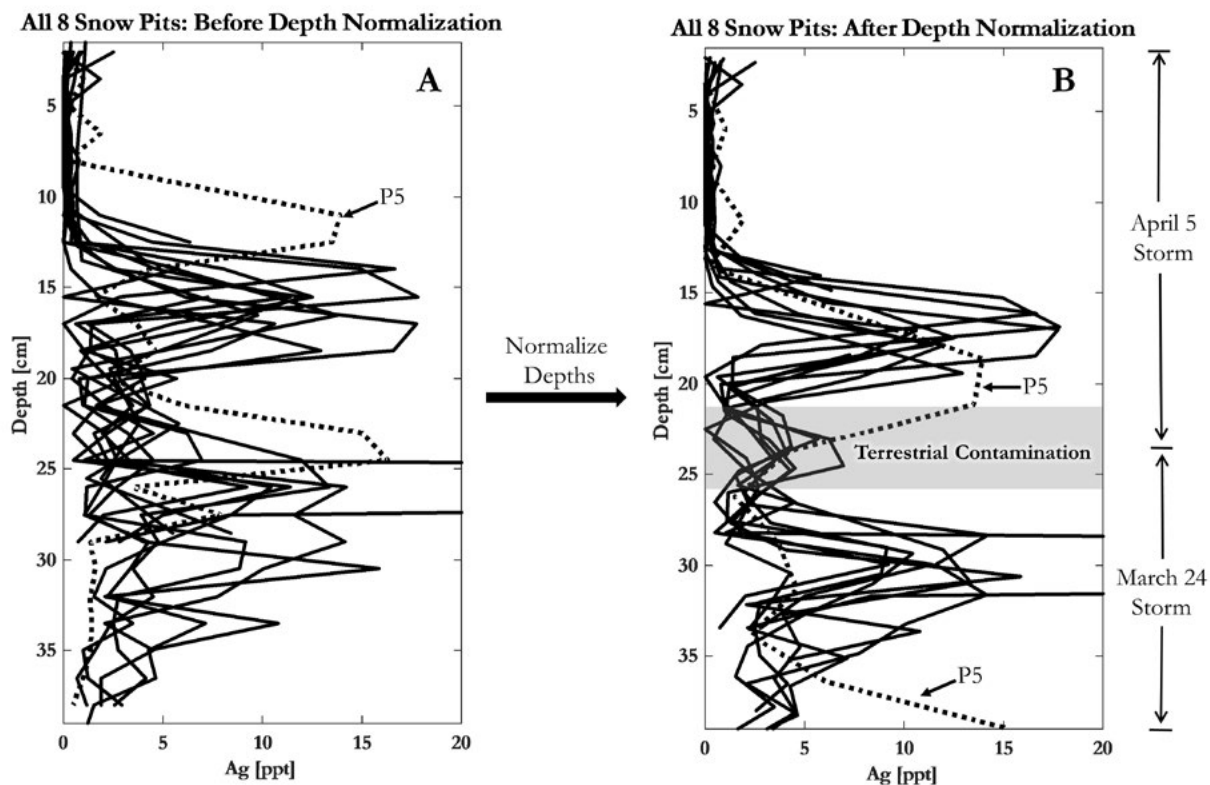


Figure 8: Plots of Ag concentration from all eight snow profiles used in the small-scale study. A: Ag concentration profiles using the actual snow depths at each site. B: Ag concentrations using profile depths normalized to the snow pit with the greatest depth. Storm delineations are shown to the right of Plot B. The shaded region in Plot B shows the storm break with a visible dust layer. The outlier Ag profile, P5, was plotted as a dotted line.

noted by the square points on Figure 9. These enrichments were present in the upper half of every snow storm layer, in agreement with AgI seeding times.

Samples from the March 24<sup>th</sup> storm were collected at six widely separated sites (see Figure 9) in the Payette Basin (2,400 km<sup>2</sup>) to determine if a seeded layer could be identified at every site. Profiles collected and analyzed from all six sites contained samples with LEFs exceeding 4, denoted by the square points on Figure 9. These enrichments were present in the upper half of every snow storm layer, in agreement with AgI seeding times.

Sites in the eastern Payette Basin had relatively lower Ag concentrations. Ag enrichments be-

tween 1-3 ppt was analyzed at the two easternmost sites. LEFs were necessary to delineate AgI signatures at these downwind sites (Figure 9D and 9E). High LEFs (>2) were found in the upper half of each storm regardless of the Ag concentration or terrestrial Ag contamination. These observations appear to demonstrate the documentation of a cloud seeding Ag signature within the snowpack across the basin. This suggests that the sampling and analysis method has the potential to constrain Ag enrichment, in both time and space, within the snowpack at the basin scale. However, it needs to be stressed that the results show that Ag from seeding reached the various sites in the basin, but does not quantify the microphysical impacts of seeding.

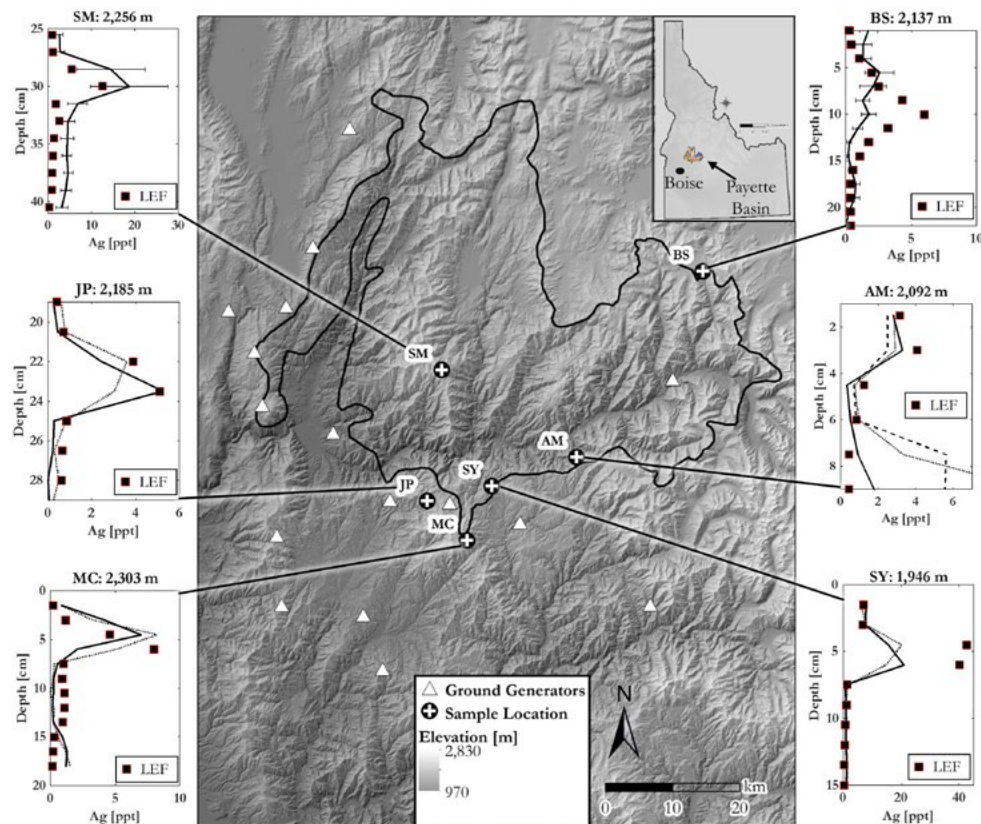


Figure 9: Six sites were sampled for the March 24<sup>th</sup> seeded storm event. Multiple pits sampled were constructed at plots A ( $n = 8$  pits) and D ( $n = 4$  pits). Plots A and D display the mean Ag concentration and average error for each snow pit layer (Equation 2) computed using 1.5 cm moving window. Ag profile depths in plots A and D were normalized relative to the total snow depth of the deepest snow profile.

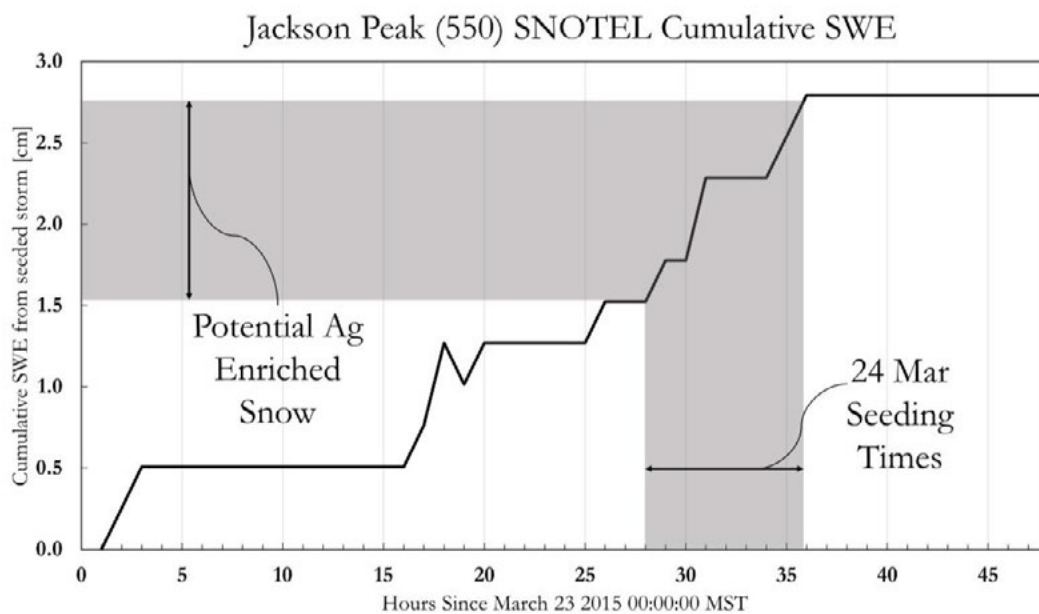


Figure 10. Cumulative SWE of a SNOTEL site within the Payette Basin. Shaded region covers the duration of AgI seeding and corresponding snow potentially enriched with AgI. Note that 0–24 on the x-axis is the snow deposited from March 23 (unseeded).



Table 4: AgI Seeding Times for the March 24<sup>th</sup> Storm

| Ground Generator ID | Duration of AgI Seeding Time [MST] | Time Active [hr] |
|---------------------|------------------------------------|------------------|
| Aircraft            | 04:56 - 06:32                      | 1.4              |
| 1                   | 04:08 - 07:26                      | 3.3              |
| 2                   | 03:48 - 07:26                      | 3.6              |
| 3                   | 03:50 - 07:26                      | 3.6              |
| 4                   | 03:47 - 07:27                      | 3.7              |
| 5                   | 03:50 - 08:31                      | 4.7              |
| 6                   | 03:48 - 08:31                      | 4.7              |
| 7                   | 04:46 - 08:52                      | 4.1              |
| 8                   | 04:25 - 08:52                      | 4.4              |
| 9                   | 04:25 - 08:52                      | 4.5              |
| 10                  | 03:49 - 08:52                      | 5.0              |
| 11                  | 03:50 - 08:50                      | 5.0              |
| 12                  | 03:49 - 08:55                      | 5.1              |
| 13                  | 03:48 - 08:54                      | 5.1              |
| 14                  | 04:52 - 09:12                      | 4.3              |
| 15                  | 04:50 - 09:13                      | 4.4              |
| 16                  | 06:25 - 10:58                      | 4.6              |

Like other studies, Ag enrichments were identified and replicated in ripe snow. Figure 9A and 9B were collected 14 and 16 days following the storm event, respectively. Snow densities were greater than  $0.34 \text{ g cm}^{-3}$  at all depths at both sites, suggesting considerable compaction and metamorphism. Ag signatures were reliably identified at both sites despite these conditions. However, these sites had the most variability between field replicates relative to samples collected within 48 hours, suggesting some degradation of the signal.

## CONCLUSIONS

The purpose of this study was to demonstrate sampling and analysis methods to quantify trace Ag enhancements from cloud seeding using AgI as the nucleation agent. The effectiveness of the developed methods was evaluated in several ways. First, we verified that trace Ag enhancements can be detected using an ICP-MS housed outside of a trace metal clean room. Access to a Class 100 Clean Room for cleaning and sample preparation was essential to detect the 1-28 ppt Ag enhance-

ments above background. Next, we evaluated the reproducibility of snowpack Ag profiles at various spatial scales. Reproducible profiles were evident over a  $0.25 \text{ km}^2$  area and across the entire basin targeted for precipitation enhancement. The evidence of Ag from seeding was less obvious at the furthest downwind sites but use of an LEF ratio suggested Ag enhancements as small as 1-3 ppt could have been present. These results suggest this approach may be suitable to evaluate cloud seeding efforts. These data can be used to validate model predictions of the spatial and temporal presence of AgI over cloud seeding target areas, provide field data to improve the model targeting, and may provide a basis for direct quantification of cloud seeding impacts.

## ACKNOWLEDGEMENTS

The authors wish to thank L. Thomas Oltheim, Rob Florence, Clay Roehner, and Kerrie Weppner for their assistance in sample collection. We are also indebted to Mark Schmitz of Boise State University's Isotope Geology Laboratory. His expertise on clean methods and use of his clean room facilities were instrumental to our success.

## REFERENCES

- Barbante, C., Cozzi, G., Capodaglio, G., Van De Velde, K., Ferrari, C., Boutron, C., and Cescon, P. 1999. "Trace Element Determination in Alpine Snow and Ice by Double Focusing Inductively Coupled Plasma Mass Spectrometry with Micro-concentric Nebulization." *Journal of Analytical Atomic Spectrometry* **14**: 1433-38.
- Barbante, C., Schwikowski, M., Doring, T., Gaggler, H. W., Schotterer, U., and Tobler, L. 2004. "Historical Record of European Emissions of Heavy Metals to the Atmosphere since the 1650s from Alpine Snow/Ice Cores Drilled near Monte Rosa." *Environmental Science Technology* **34**: 4085-90.
- Boutron, C. 1979. "Reduction of Contamination Problems in Sampling of Antarctic Snows for Trace Element Analysis." *Analytica Chimica Acta* **106**: 127-30.

- Boutron, C. 1990. "A Clean Laboratory for Ultralow Concentration Heavy Metal Analysis." *Fresenius Journal of Analytical Chemistry* **337** (5): 482–91.
- Breed, D., Rasmussen, R., Weeks, C., Boe, B., and Deshler, T. 2014. "Evaluating Winter Orographic Cloud Seeding: Design of the Wyoming Weather Modification Pilot Project (WWMP)." *Journal of Applied Meteorology* **53**: 282–89.
- Chai, S., Finnegan, W., and Pitter, R. 1993. "An Interpretation of the Mechanism of Ice-Crystal Formation Operative in the Lake Almanor Cloud-Seeding Program." *Journal of Applied Meteorology* **32**: 1726–32.
- DeMott P. 1995. "Quantitative Descriptions of Ice Formation Mechanisms of Silver Iodide-Type Aerosols." *Atmospheric Research*, **38**: 63–99.
- Edwards, R., Huggins, A., and McConnell, J. 2004. "Trace Chemistry Evaluation of the IPCo 2003-2004 Cloud Seeding Program". Desert Research Institute.
- Edwards, R., and Simeral, D. 2006. "Baseline Silver Concentrations in Freshwater and Snow in the Wyoming Weather Modification Project Target Area". Desert Research Institute.
- Garvey, D. 1975. "Testing of Cloud Seeding Materials at the Cloud Simulation and Aerosol Laboratory, 1971–1973," *Journal of Applied Meteorology*, **14**, no. 5, pp. 883–890.
- Hong, S., Lluberas, A., and Rodriguez, F. 2000. "A Clean Protocol for Determining Ultralow Heavy Metal Concentrations: In Application to the Analysis of Pb, Cd, Cu, Zn, and Mn in Antarctic Snow". Polar Research Center.
- Hong, S., Barbante, C., Bourtron, C., Gabrielli, P., Gaspari, V., and Cescon, P. 2004. "Atmospheric Heavy Metals in Tropical South America during the Past 22,000 Years Recorded in a High Altitude Ice Core from Sajama, Bolivia." *Journal of Environmental Monitoring* **6**: 322–26.
- Huggins, A., Edwards, R., and McConnell, J. 2005. "Summary of Trace Chemical and Physical Measurements of Snowfall in Two Nevada Cloud Seeding Target Areas." Desert Research Institute (Reno, NV), 1–5.
- Huggins, A., Kenyon, S., Warren, L., Peace, A., Billish, S., and Manton, M. 2008. "The Snowy Precipitation Enhancement Research Project: A Description and Preliminary Results." *Journal of Weather Modification* **40**: 28–53.
- Koffman, B., Handley, M., Osterberg, E., Wells, M., and Kreutz, K. 2014. "Dependence of Ice-Core Relative Trace Element Concentration on Acidification." *Journal of Glaciology* **60** (219): 103–12.
- Krachler, M., Zheng, J., Fisher, D., and Shotyk, W. 2008. "Atmospheric Inputs of Ag and Tl to the Arctic: Comparison of High Resolution Snow Pit (AD 1994-2004) with a Firn (AD 1860-1996) and an Ice Core (previous 16,000 Yr)." *Science of the Total Environment* **399**: 78–89.
- Manton, M., and Warren, L. 2011. A Confirmatory Snowfall Enhancement Project in the Snowy Mountains of Australia. Part II: Primary and Associated Analyses. *Journal of Applied Meteorology and Climatology* **50**: 1448–1458.
- NRC. 2003. Critical Issues in Weather Modification Research. National Research Council of the National Academies. Washington, D.C.: The National Academies Press.
- Planchon, F., Boutron, C., Barbante, C., Cozzi, G., and Gaspari, V. 2001. "Ultrasensitive Determination of Heavy Metals at Teh Sub-Picogram per Gram Level in Ultraclean Antarctic Snow Samples by Inductively Coupled Plasma Sector Field Mass Spectrometry." *Analytica Chimica Acta* **450**: 193–205.
- Rodushkin, I., Engstrom, E., and Baxter, D. 2010. "Sources of Contamination and Remedial Strategies in the Multi-Elemental Trace Analysis Laboratory." *Analytical and Bioanalytical Chemistry* **396**: 365–77.

- Snyder-Conn, E., Garbarino, J., Hoffman, G., and Oelkers, A. 1997. "Soluble Trace Elements and Total Mercury in Arctic Alaskan Snow." *Arctic* 50 (3): 201–15.
- Super, A., and Heimbach, J. 1983. "Evaluation of the Bridger Range Winter Cloud Seeding Experiment Using Control Gauges." *Journal of Climate and Applied Meteorology* 22 (12): 1989–2011.
- Super, A. 1990. "Winter Orographic Cloud Seeding Status in the Intermountain West." *Journal of Weather Modification* 22 (1): 106–16.
- Telliard, W. 2008. "Method 200.8: Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma - Mass Spectrometry". Environmental Protection Agency.
- Warburton, J., and Young, L. 1968. "Neutron Activation Procedures for Silver Analysis in Precipitation." *Journal of Applied Meteorology* 7: 433–43.
- Warburton, J., Stone, R., and Marler, B. 1995a. "How the Transport and Dispersion of AgI Aerosols May Affect Detectability of Seeding Effects by Statistical-Methods." *Journal of Applied Meteorology* 34 (9): 1929–41.
- Warburton, J., Young, L., and Stone, R. 1995b. "Assessment of Seeding Effects in the Snowpack Augmentation Programs: Ice Nucleation and Scavenging of Seeding Aerosols." *Journal of Applied Meteorology* 34: 121–30.
- Wen, L., Santschi, P., Gill, G., and Tang, D. 2002. "Silver Concentrations in Colorado, USA, Watersheds Using Improved Methodology." *Environmental Toxicology and Chemistry* 21 (10): 2040–51.
- WWMPP. 2014. "The Wyoming Weather Modification Pilot Project: Level II Study. Executive Draft Summary."
- Xue, L., Tessendorf, S., Nelson E., Rasmussen R., Breed D., Parkinson S., Holbrook P., and Blestrud, D. 2013. "Implementation of a Silver Iodide Cloud-Seeding Parameterization in WRF. Part II: 3D Simulations of Actual Seeding Events and Sensitivity Tests." *Journal of Applied Meteorology & Climatology* 52 (6): 1458–76. doi:10.1175/JAMC-D-12-0149.1.