# ENVIRONMENTAL MONITORING AND ASSESSMENT: A STATISTICAL ANALYSIS OF CONCENTRATIONS OF SILVER AND INDIUM AT GENERATOR LOCATIONS

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Abstract: The Snowy Precipitation Enhancement Research Project commenced during 2004, following proclamation of the Snowy Mountains Cloud Seeding Trial Act 2004 (NSW). This legislation mandates the use of silver iodide as the seeding agent, permits the use of indium (III) oxide as an inert tracer, and requires that cloud seeding operations be ground based only. It also requires an Environmental Management Plan to be developed and implemented for the project. That Plan includes an explicit obligation to monitor silver and indium concentrations across the study area.

Samples taken prior to the commencement of the trial showed measurable concentrations of silver and indium within all matrices (soil, moss, peat, water, sediment) and at all locations monitored. Routine sampling takes place each year during the winter months and following the cessation of cloud seeding experiments for the season.

This paper examines trends in the concentrations of silver and indium in soil samples collected from 13 generator locations (the locations from which the seeder and tracer agents are dispensed) between 2004 and 2009. Comparison of the concentrations with the relevant environmental Guideline Trigger Values showed mean concentrations and 95% confidence limits were always well below the trigger value, and statistical analysis of the data indicated that temporal trends in concentrations were variable across locations. The analysis of statistical power, used to determine the likelihood of detecting adverse effects before they reach a scale of environmental significance, indicated that a statistically significant increase (i.e. above the pre-seeding levels) would be detectable well before any level of concern is reached.

## 1. BACKGROUND

The Snowy Precipitation Enhancement Research Project (SPERP) is a cloud seeding research program being undertaken by Snowy Hydro Limited in the Snowy Mountains region of New South Wales (NSW), Australia. The objective of the trial is to determine if cloud seeding can be used to augment natural snowfalls in a cost effective way without significant adverse environmental impacts or downwind effects (see for example Heggli et al., 2005; Huggins et al., 2008; Manton et al., 2009; and Manton et al., 2011).

Much of the SPERP target area lies within Kosciuszko National Park, a place of legislated National Heritage Significance and a UNESCO declared World Biosphere Reserve (NPWS, 2004). Consequently, the trial is authorized by special enabling legislation, the *Snowy Mountains Cloud Seeding Trial Act 2004 (NSW)* (the Act). The Act mandates that all cloud seeding operations must be ground based, and that silver iodide must be used as the seeding agent. It also permits the use of indium (III) oxide as a tracer agent, and requires an Environmental Management Plan (EMP) to be implemented for the project.

The EMP was approved by the NSW state government, and includes explicit provisions for the environmental monitoring of silver and indium concentrations at various locations across the study area. It also describes the associated Guideline Trigger Values (GTV) for each element and the management intervention actions required if any sample exceeds the prescribed concentration limits.

The SPERP commenced in 2004 and was initially conducted over a target area of approximately 1000 km². In 2008, the target area was expanded to 2150 $km^2$ and the trial extended until April 2015. Cloud seeding experiments over the expanded target area commenced in June 2009.

Prior to the commencement of the trial, various environmental matrices were sampled and analyzed to establish background concentrations of silver and indium throughout the study area (Williams and

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Denholm, 2009). Routine sampling has continued each year following cessation of winter cloud seeding experiments.

Ten generator sites were established in 2004, with three additional sites established in 2005. Each cloud seeding generator site has two separate generators to dispense the silver iodide and indium (III) oxide (see Figure 1).

During cloud seeding experiments, seeder and tracer aerosols are rapidly diluted in large volumes of air; however, previous studies have shown, for various reasons, that these sites are places in the landscape where silver and indium may accumulate (Teller et al., 1976; in Harasymiw and McGee, 1993). For this reason they have been selected as the focus of this study, and in this paper we present the outcomes of the statistical analysis of the data from the 13 generator locations operational between 2004 and 2009.

## 2. SAMPLING COLLECTION AND ANALYSIS

### 2.1 Sample Collection

Soil samples were collected each year at predetermined points at each generator location: four points at each corner of the generator site footprint (a rectangle of approximately 60 x 70 meters containing the seeder and tracer generators), and four points along a downwind transect of approximately 200 meters. One sample was taken at each point for the pre-trial sets and post-season 2004. In all other years, five samples were collected at each point.

Each sample of soil was collected from within the top 2 cm of the ground surface using a stainless steel trowel which was washed thoroughly between samples with ultra-pure water. Samples were collected in hygienic, single-use 250 mL screw top polycarbonate or acrylic containers and analyzed for total silver and total indium.

Monitoring results and an analysis of trends at various sampling locations are reported to the NSW government each year. The government refers the results to an independent agency for review and recommendations. The outcomes of those reviews have resulted in refinements to the sampling program, e.g. increased numbers of sites and samples.

Table 1 presents the total number of generator soil samples analyzed. All pre-trial and 2004 samples were analyzed. In 2005, three of the five samples collected at each point were selected at random for analysis. From 2008, two samples selected at random from each corner of the generator pairs were analyzed. If any samples returned an elevated concentration of silver or indium, the program required that all remaining samples from the sampling point(s) would be analyzed and the bioavailability of silver assessed.

*Figure 1: Typical ground generator site (location Stoney Rises).*

| Table 1: Number of samples analyzed for silver and indium at each of the 13 generator locations between 2004 and 2009. | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **LOCATION** | **PERIOD** | | | | | | | |
| | **Pre-trial 2004** | **Post-season 2004** | **Pre-trial 2005** | **2005** | **2006** | **2007** | **2008** | **2009** |
| Granite Knob | 8 | 8 | - | 24 | 40 | 40 | 40 | 8 |
| Grassy Flat | 8 | 8 | - | 24 | 40 | 40 | 8 | 8 |
| Grey Hill | 8 | 8 | - | 24 | 40 | 40 | 8 | 8 |
| Indi | 8 | 8 | - | 24 | 40 | 40 | 8 | 8 |
| Major Clews | 8 | 8 | - | 24 | 40 | 40 | 8 | 8 |
| Murray 1 Valve House | 8 | 8 | - | 24 | 40 | 40 | 8 | 8 |
| Pinnacle | 8 | 8 | - | 24 | 40 | 40 | 8 | 8 |
| Stoney Rises | 8 | 8 | - | 24 | 40 | 40 | 8 | 8 |
| Tiger Trail | 8 | 8 | - | 24 | 40 | 40 | 8 | 8 |
| Youngal | 8 | 8 | - | 24 | 40 | 40 | 8 | 8 |
| Spring Creek | - | - | 8 | 24 | 40 | 40 | 8 | 8 |
| Scammels | - | - | 8 | 24 | 40 | 40 | 8 | 8 |
| Khancoban 330 kV | - | - | 8 | 24 | 40 | 40 | 8 | 8 |
| **Total Samples** | **80** | **80** | **24** | **312** | **520** | **520** | **136** | **104** |

2.2 Analysis Methods

Collected soil samples were dried at 30°C for 24 hours. Approximately 5 g of the < 0.5 mm fraction of dried soil was then separated by screening and crushed in an agate mixer mill. An aliquot of approximately 0.2 g of this material was then weighed into a Teflon vial with 2 ml of hydrofluoric and 3 ml nitric acid then added[1]. The vials were capped and heated at 135°C for 12 hours.

Following this treatment, vials were then uncapped and the solution evaporated to dryness. The sample was refluxed with nitric acid and dried, and the residue dissolved with 2 ml of nitric acid and 6 ml of ultra-pure water[2]. Vials were then re-capped and left for 12 hours at 100°C. The solution was transferred to a centrifuge tube and diluted with ultra-pure water and weighed. An aliquot of this solution was transferred to a new centrifuge tube and a Rhodium internal standard added. Sample dilution factors were approximately 1:1200.

The solutions were analysed on a Varian 810 ICPMS operating in a Class 100 clean room. A four point calibration through the blank was performed and a procedural blank prepared and analyzed with each batch of samples. The maximum top standard concentration used for soil is 650 pg/g. A re-slope calibration including a blank was performed every 12 samples. A calibration blank was also analyzed after the re-slope calibration standard as a check blank. A dwell time of 20 milliseconds was used and 7 replicates of 70 scans measured. Interferences were measured and corrected for.

Soil standards were run as unknowns and solutions of 11.5 pg/g Ag and In, spiked with levels of interferences similar to those present in the samples, were analyzed during the runs to check minimum detection limits. These were less than 8 ng/g for soil samples.

Digestions of the Geological Survey of Japan soil standard JSo-1 have been prepared with each batch of soil samples since the commencement of the project and were analyzed both at the start of a run and at the end to check for drift. Duplicate samples and triplicate samples, spiked with the equivalent of 2 μg/g of silver and indium, were also analyzed with every run (A. Grieg 2011, pers. comm., 9 March).

1 All acids described were quadruple distilled. Acid concentrations used for the digests were 28N HF (hydrofluoric acid) and 16N $HNO_3$ (nitric acid). All plastic ware was acid washed, and separate dedicated sample probes, tubing, nebulisers, spray chambers and torches were used.

2 The ultra-pure water referred to is 18+ megaohm deionised water.

## 3. STATISTICAL ANALYSES

The mean total silver and indium concentrations and their 95% confidence limits were calculated for each location and period, and compared with the GTV for total silver in soil of 1 mg/kg (ANZECC and

ARMCANZ Guidelines 2000). The ANZECC Guidelines (op. cit.) do not include a GTV for indium; however, the SPERP EMP prescribes a value of 1 mg/kg be used for this purpose.

The data were also analyzed using PERMANOVA+, a permutation program for uni- and multivariate data that analyzes the responses of variables to experimental factors within an Analysis of Variance framework (Anderson et al., 2008). This program was used to test the following hypotheses:

1) There were no statistically significant differences in the mean concentrations of silver or indium over time;
2) There were no statistically significant differences in the mean concentrations of silver or indium among locations; and
3) Temporal patterns in the mean concentrations of silver and indium did not differ in a statistically significant way among locations.

### 3.1 Comparison between Sampling Periods and Locations

The emphasis in the interpretation of these analyses is on interactions between Period and Location, as this provides information on whether differences among locations are related to cloud seeding events. A statistically significant interaction may indicate an effect of cloud seeding resulting, for example, in the concentrations of silver or indium increasing at some Locations after the cloud seeding trial had commenced, but decreasing or showing no change through time at other Locations. The main factors of Period and Location become redundant if a statistically significant interaction exists, because neither can be interpreted without reference to the other.

### 3.2 Statistical Sensitivity and Power

Power analysis was used to determine the likelihood of being able to statistically detect a change in the concentration of silver or indium coincident with cloud seeding.

The power analysis was based on a 1-tailed t-test, with the null hypothesis that the mean concentration at one sampling period in the future was greater than the pre-trial mean. Power was calculated for effect sizes that increased in 25% increments until a power of 0.8 or better was achieved. This effect size was then expressed as a percentage of the GTV.

The mean concentration of silver and indium during the pre-trial period was used as an indicator of the baseline condition for each generator location. Effect sizes were calculated as 25% increases above the pre-trial means and the measure of variability used was the pooled standard deviation between pre-2004 and 2007, based on eight samples. The eight samples used for 2007 were selected at random from the 40 samples for each location.

For the data collected in 2008 and 2009, the standard deviations for each location were compared with those from 2007 to determine whether the variance within the most recent set of data had increased. This provides a rapid means of assessing the likelihood that the power may have changed, without undertaking formal power analysis.

## 4. RESULTS

### 4.1 Comparison to the Guideline Trigger Value

The mean concentrations and 95% confidence limits of total silver and indium for each generator location during each period of the trial are shown in Figure 2. Generally, mean concentrations of silver and indium were 10% or less than the GTV at all generator locations.

One location, however, Granite Knob, had consistently elevated levels of silver compared to other locations for all periods, including pre-trial. This indicates that Granite Knob had elevated silver independent of the SPERP. In 2006, one sample at Granite Knob exceeded the GTV for indium, but subsequent bioavailability analysis yielded concentrations < 0.01% of the GTV, hence further management response was not warranted. In 2008, two of the 40 samples analyzed exceeded the GTV for silver, although the mean concentration was below the GTV. The subsequent bioavailability analysis undertaken showed very low values (less than 0.05% of the GTV). None of the samples analyzed in 2009 exceeded the GTV.

### 4.2 Comparison among Sampling Periods and Locations

Mean concentrations of both silver and indium within locations were not consistent through time.

Granite Knob had a statistically greater concentration of indium in 2006 than at other times, all of which had similar concentrations. Grey Hill had statistically greater concentrations of indium from 2006 to 2009 than beforehand. None of the other locations showed statistically significant variation among periods for silver and indium.

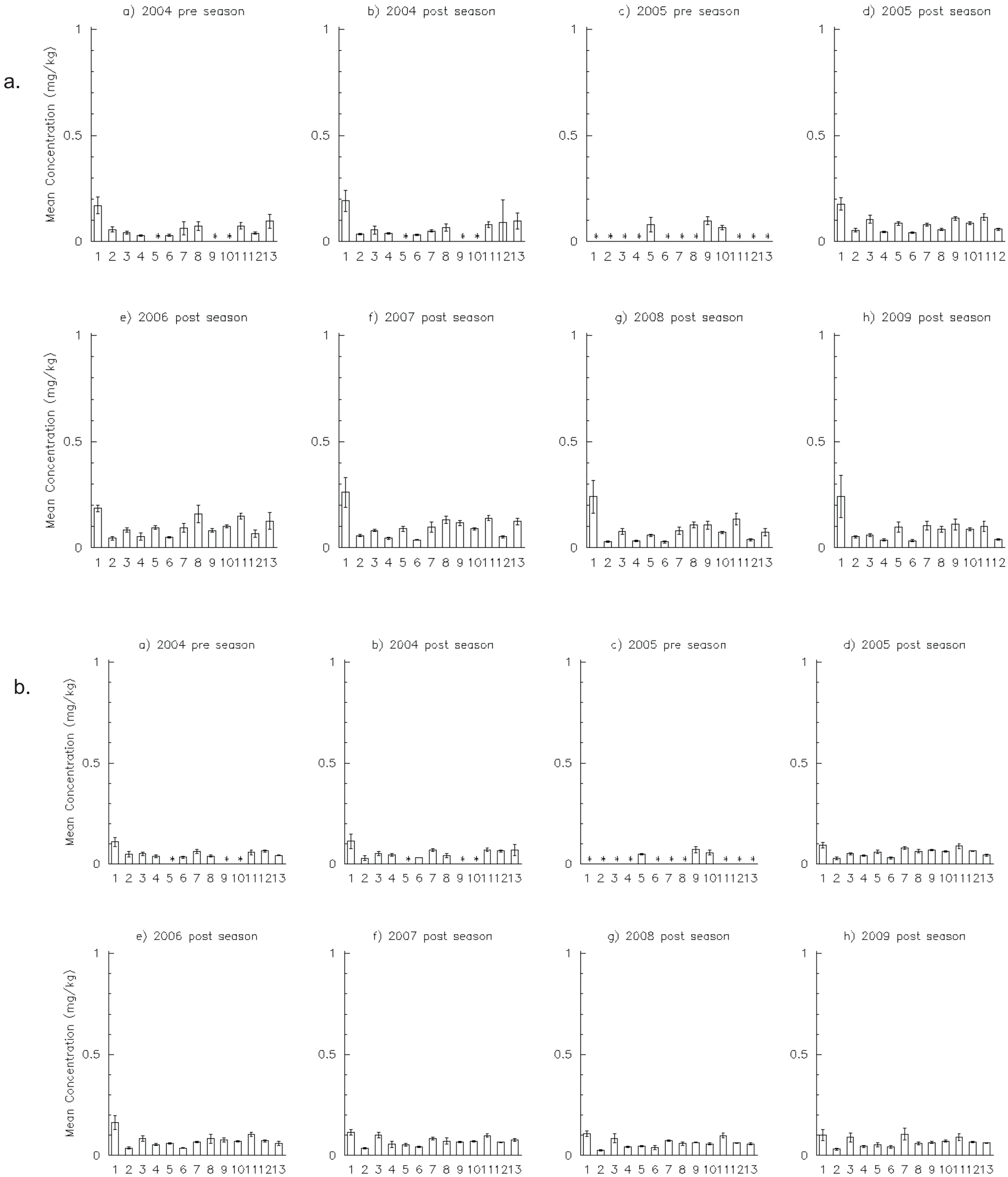


*Figure 2: Mean concentration and 95% confidence limits (scaled to the GTV) of a) silver and b) indium (mg/kg) at generator locations (1=Granite Knob; 2=Grassy Flat; 3=Grey Hill; 4=Indi; 5=Khancoban; 6=Major Clews; 7=Murray 1 Valve House; 8=Pinnacle; 9= Scammels; 10=Spring Creek; 11=Stoney Rises; 12=Tiger Trail; 13=Youngal). * = Periods when locations were not sampled.*

**Table 2: Results of PERMANOVA+ tests comparing the effects of Periods of time (Pe) and Locations (Lo) on silver and indium concentrations within the soil samples. Significant terms are highlighted in bold-face type; SS = Statistical Significance; DF = Degrees of Freedom; RED = term is redundant due to significant interaction.**

| Source | Silver | | | | | Indium | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | SS | DF | MS | Pseudo F | P | SS | DF | MS | Pseudo F | P |
| Pe | 2.36E+11 | 7 | 3.37E+10 | 5.4 | RED | 2.36E+11 | 7 | 3.37E+10 | 1.6041 | RED |
| Lo | 6.19E+11 | 12 | 5.16E+10 | 8.28 | RED | 8.11E+11 | 12 | 6.76E+10 | 9.142 | RED |
| PeXLo | 1.65E+12 | 68 | 2.42E+10 | 3.89 | 0.0002 | 1.55E+12 | 68 | 2.27E+10 | 3.0743 | 0.0022 |
| Residual | 1.07E+13 | 1720 | 6.23E+09 | | | 1.27E+13 | 1720 | 7.40E+09 | | |
| **Total** | **1.50E+13** | **1807** | | | | **1.67E+13** | **1807** | | | |

The temporal variation in mean concentrations of both silver and indium was not consistent across locations (i.e. significant statistical interaction between Period and Location - see Table 2). Hypothesis 3, that temporal patterns in concentrations of silver and indium did not vary statistically between generator locations was therefore rejected. Hypotheses 1 and 2, relating to consistent variation over time and space, became redundant due to the significant interaction term.

4.3 Statistical Sensitivity and Power

Based on 2007 data, the effect size detectable with a power $\geq 0.80$ for silver ranged from 50% to 100%, with a mean effect size of 73%, of the pre-trial mean at the Generator locations. Expressed as a percentage of the GTV, these effect sizes ranged from about 4.3% (Indi) to 30% (Granite Knob). Calculation of power for indium yielded similar results. Overall, the mean effect size detectable with 80% power was about 60% (range: 25% to 125%).

**Table 3: Estimates of the variation (Standard Deviations) in silver and indium concentrations recorded at Generator Locations after cloud seeding in 2007, 2008 and 2009 compared between 2007 and 2009 and ratios of deviation in 2008 and 2009 versus preceding year. Uses only the 10 Locations that were sampled continuously.**

| Location | Silver | | | | | | Indium | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Standard Deviations | | | Ratios | | | Standard Deviations | | | Ratios | | |
| | 2007 | 2008 | 2009 | 08/07 | 09/07 | 09/08 | 2007 | 2008 | 2009 | 08/07 | 09/07 | 09/08 |
| Granite Knob | 279,419 | 400,595 | 144,758 | 1.43 | 0.52 | 0.36 | 36,783 | 61,033 | 37,912 | 1.66 | 1.03 | 0.62 |
| Grassy Flat | 19,300 | 6,100 | 7,840 | 0.32 | 0.41 | 1.29 | 12,261 | 4,449 | 8,154 | 0.36 | 0.66 | 1.83 |
| Grey Hill | 14,491 | 20,885 | 8,163 | 1.44 | 0.56 | 0.39 | 65,669 | 33,582 | 30,760 | 0.51 | 0.47 | 0.92 |
| Indi | 22,873 | 6,859 | 7,029 | 0.30 | 0.31 | 1.02 | 4,492 | 3,013 | 6,431 | 0.67 | 1.43 | 2.13 |
| Major Clews | 7,036 | 7,420 | 6,442 | 1.05 | 0.92 | 0.87 | 4,606 | 14,864 | 9,331 | 3.23 | 2.03 | 0.63 |
| Murray 1 Valve House | 27,306 | 25,372 | 30,558 | 0.93 | 1.12 | 1.2 | 20,850 | 6,042 | 41,469 | 0.29 | 1.99 | 6.86 |
| Pinnacle | 57,924 | 21,181 | 19,386 | 0.37 | 0.33 | 0.92 | 9,933 | 12,834 | 11,200 | 1.29 | 1.13 | 0.87 |
| Stoney Rises | 43,232 | 38,065 | 33,043 | 0.88 | 0.76 | 0.87 | 18,523 | 16,883 | 25,803 | 0.91 | 1.39 | 1.53 |
| Tiger Trail | 24,143 | 7,261 | 4,186 | 0.30 | 0.17 | 0.58 | 6,053 | 2,203 | 6,200 | 0.36 | 1.02 | 2.81 |
| Youngal | 85,731 | 23,999 | 21,668 | 0.28 | 0.25 | 0.90 | 6,044 | 6,385 | 4,701 | 1.06 | 0.78 | 0.74 |
| **Mean of SDs** | **58,145** | **55,774** | **28,307** | **0.73** | **0.54** | **0.84** | **18,521** | **16,129** | **18,196** | **1.03** | **1.19** | **1.89** |

f the 17 statistical analyses carried out, all but five showed statistically significant interactions of Period and Location, leading to rejection of the null hypothesis of no interaction (Hypothesis 3). This means that there are no concerns regarding Type II errors for these tests as the null hypotheses were rejected. For the remainder, given the very low concentrations of silver and indium relative to the GTV, an increase in concentration would be statistically detectable well before the GTV was reached.

Generally, standard deviations of the mean concentrations of silver and indium remained similar from 2007 to 2009; and in some cases declined in 2009 (i.e. ratio < 1). The mean standard deviation for these years is similar for silver and indium (Table 3), although there has been an increase in variability at Granite Knob (silver and indium), Grey Hill (silver) and Major Clews (indium). These concentrations are still small relative to the GTV. Thus, the monitoring program remains sensitive to increases that would approach the GTV and hence trigger further management response.

## 5. CONCLUSIONS

Managing environmental risk is a major component of the SPERP and an obligation under the enabling legislation. That obligation includes a requirement to monitor total silver and total indium concentrations at various locations and environmental matrices across the study area.

Previous investigations (Harasymiw and McGee, 1993) have reported that generator sites are places in the landscape likely to show evidence of accumulation of silver and indium. For that reason, these sites were the focus of this investigation.

While all SPERP generators are equipped with an array of in-built safety features and alarms to minimize risk of environmental harm, a number of factors could contribute to localized accumulation of silver and indium. Risk factors include the total mass of silver and indium dispensed from the site, local air turbulence during storm events and the frequency with which the aerosol plumes impact the adjacent ground surface (*op. cit*).

Samples collected before the commencement of the trial showed both silver and indium to be present in the soil at all locations monitored. Mean concentrations of silver and indium in samples taken after each season remain very low compared to the specified GTV. Statistical analysis also showed that the mean concentrations of silver and indium within locations were not consistent through time and the majority of locations did not show statistically significant variation among periods.

Importantly, the analysis of statistical power for silver and indium in soil from the generator locations indicated a high likelihood that a statistically significant increase (i.e. above the pre-seeding levels) would be detected well before the GTV was reached.

The program of investigation described here provides a powerful tool for environmental management of cloud seeding projects. It quantifies spatial and temporal patterns of variation in key response variables (i.e. concentrations of silver and indium in selected environmental matrices) and enables rapid response by management well before concentrations can accumulate in the environment to levels of potential concern

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