3.2 **AMMONIA AND NO_X IN SEEDED AND UNSEEDED SNOWFALL – AN AUSTRALIAN PERSPECTIVE**

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1.0 INTRODUCTION AND BACKGROUND

The Snowy Precipitation Enhancement Research Project (SPERP) is a six year cloud seeding trial currently in progress in the Snowy Mountains region of southeastern Australia. The trial commenced in the winter of 2004 and targets a study area of approximately 1000 square kilometers within the Kosciuszko National Park. For further information on the project, refer to Huggins *et al.* (2008).

Throughout the trial, cloud seeding is undertaken using a series of generator pairs which release minute particles of a seeding agent (silver iodide), and an inert tracer (indium sesquioxide). Potential ecological impacts of these releases are monitored through an extensive environmental monitoring program.

This paper addresses recent concerns raised by stakeholders of the SPERP over the possibility that cloud seeding may increase concentrations of ammonia and NO_X in snowfall, resulting in potential adverse increases in concentrations of ammonia and NO_X in alpine lakes in the park. To provide a measure of the relative concentrations of ammonia and NO_X in snow samples in the Snowy Mountains, concentrations are also compared against those in the Rocky Mountains snowpack available in the literature.

The concerns of the stakeholders are outlined, followed by details of the separate analysis undertaken to address these concerns, including a description of the sampling processes and an explanation of the statistical methods used. Finally, the results and discussion of the analysis are presented.

Monitoring undertaken by the New South Wales Department of Environment and Climate Change (NSW DECC) indicated that there was a peak in ammonia concentrations in alpine lakes during the winter period in 2007. This is depicted in the graph below in Fig. 1.

During August, 2007 all four lakes showed increased levels of ammonia, and whilst three continued to increase in September, the levels in Lake Albina showed an apparent decrease.

It was proposed by NSW DECC that these increases could possibly be attributed to effects of cloud seeding, proposing that by "*pumping excess particles to act as ice nucleators, cloud seeding could also provide additional particles to bring down more Nitrogen"* (Green, *pers. comm.*). This could therefore, result in increased deposition of nitrogenous compounds directly into the lakes, or transportation there via snow melt water.

For the conceptual model proposed by NSW DECC to be supported, the concentrations of ammonia and NO_X:

1. In modified snow (containing silver and indium, or indium alone) should be greater than the concentration of ammonia and NO_X in natural snow (containing no silver or indium); and

2. Should be sufficiently high to account for the observed increase in the lakes (i.e. considerably greater than the observed increase of up to 0.150 mg/L).

The conceptual model was tested by comparing concentrations of ammonia and NO_X in natural (unseeded) and modified (seeded and/or tracer added) snow samples.

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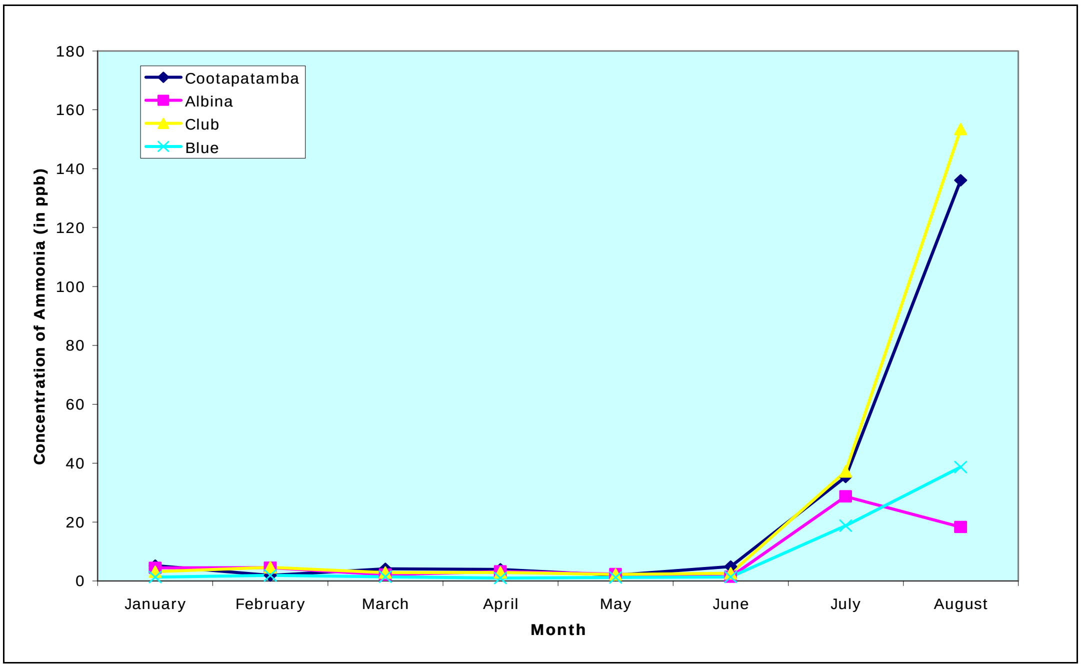

Figure 1: Concentrations of ammonia in alpine lake water (DECC, 2007)

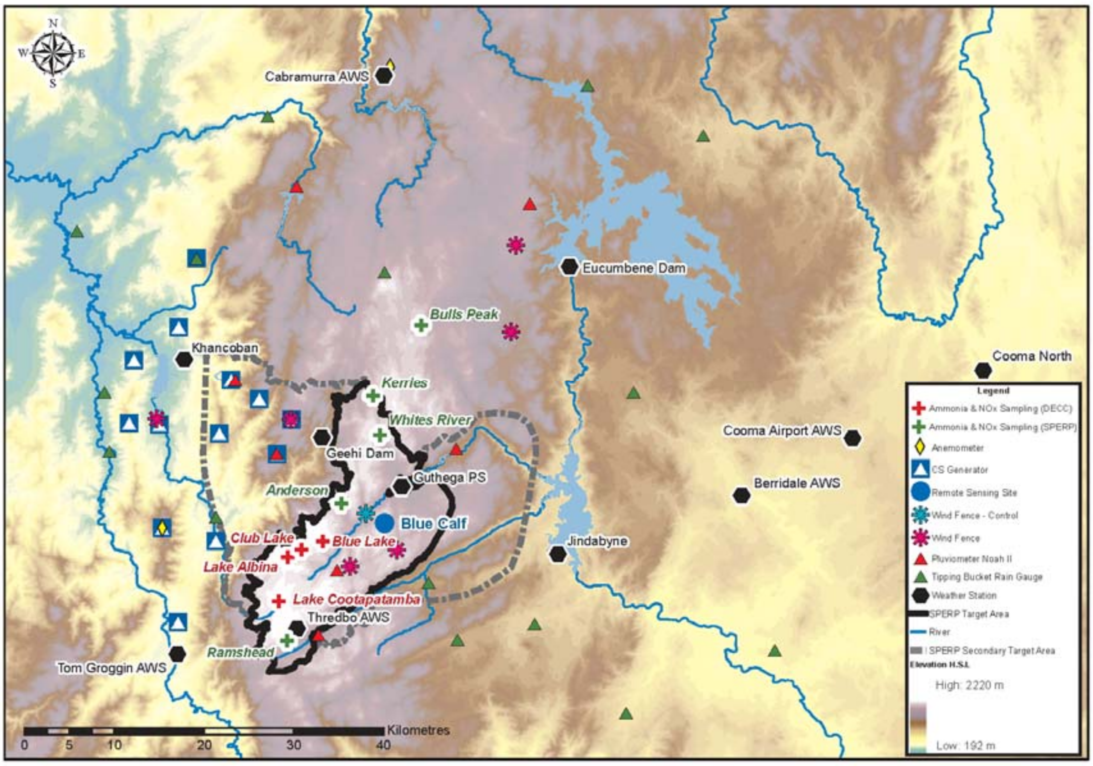

Figure 2: Map of the Snowy Mountain region with both the DECC and SPERP ammonia and NO_X sampling locations marked. The legend at the lower right identifies the various SPERP instrument sites. Note that there are additional wind fences at all the SPERP sampling sites which are not marked on this map.

2.0 STUDY METHODS

2.1 Collection of Snow Samples

Five locations were selected for investigation including Bulls Peak in the Northern Area and Whites River, Andersons, Kerries and Ramshead in the Target Area (Fig. 2). Snow samples were collected between 22 June 2007 and 7 August 2007.

During the first setup year (2004) of the trial, snow samples were collected using US designed profiler equipment, however, this equipment proved difficult to use under Australian conditions, and a more suitable system was designed and implemented for the subsequent seasons (Fig. 3).

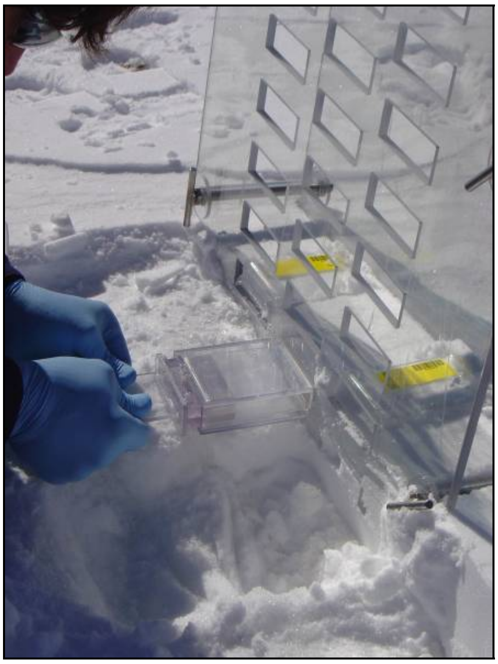

Figure 3: Sample collection using the snow sampling vials and template

The sampling procedure uses specially fabricated ultra-clean polycarbonate vials to enable detailed trace chemical analysis and water content analysis of the snowpack in the target area. Samples are collected as soon as possible after each cloud seeding operation.

A polyethylene base board is located at each snow profiling site to provide a reference datum so that only new snow is sampled. The board is repositioned on top of the snowpack following each sampling campaign. Snow profiling is undertaken by pushing the vials horizontally through a profiling template that is aligned vertically to the site base-boards. As a result of the low concentrations of silver and indium found in snowfall, ultra-hygienic collection techniques must be employed to ensure sample integrity.

The profiling template aligns the vials to sample 2-cm vertical increments of the snow profile. The vials are pushed past the face of the template to avoid contamination of the snow sample by the template. Once all vials are inserted, the template is removed, the end of each the vial is trimmed by a clean spatula and capped with a polyurethane water-tight end cap. Frozen samples are transported to the laboratory and analysed by a new generation Inductively Coupled Plasma Mass Spectrometer (ICPMS) to determine silver and indium concentration. This equipment is reliably capable of ultra-trace detection to below 1 part per trillion (ppt). A selection of samples were also analysed for NO_X-N and NH_3-N FIA using standard methods (Greenberg *et al*. 2005).

Collected snow samples were analysed for concentrations of silver and indium and classified as one of three treatments, either *Natural* (no silver or indium), *Modified 1* (containing silver and indium) or *Modified 2* (containing indium only). The number of samples collected for each treatment from each location is presented in Fig. 4.

2.2 Statistical Analyses

Means and 95% confidence limits were calculated for each treatment and site using all the data for the five main sites (Fig. 4).

The smallest number of samples collected for natural versus modified/site combination was n = 8, so 8 replicates were used for statistical analysis. The 8 replicates were selected at random (using a random number generator) from each treatment/site combination. The data sets for ammonia and NO_X obtained in this manner were analysed using a 2-way factorial Analysis of Variance (ANOVA) comparing Treatments (natural versus modified – Fixed factor) and Sites (5 main sites – Random factor). The two factors were orthogonal. Where the interaction between Treatment and Sites was non-significant ($p \geq 0.25$) the interaction term was pooled with the residual to increase the sensitivity of tests for main effects.

In addition to a comparison between natural versus modified at the five sites for which data were available, it was also feasible to compare the natural treatment to the two modified conditions: snowfall occurring at the time of seeding, which included silver and indium (denoted “Modified 1”); and snowfall occurring only when the tracer (indium) was released into the atmosphere (“Modified 2”). In order to balance the data for this analysis, it was necessary to remove the samples from Bulls Peak (which had no data available for the Modified 1 treatment); and to reduce the number of replicates to four per treatment and site (to balance all data against the availability of only four samples each for Ramshead (Modified 1) and Whites River (Modified 2). In this design, a 2-way ANOVA was used generally as described above, except here there were three Treatments, four Sites and four replicates used.

Prior to all analyses, data were checked for heteroscedasticity using Cochran's C test. Heterogeneous data was transformed (using ln(x+1) transformation) to stabilise or reduce variances. Where variances remained heterogeneous following transformation, any statistically significant results were interpreted conservatively (e.g. α reduced from 0.05 to 0.01).

3.0 RESULTS

No clear trend in the concentrations of NO_X and ammonia in seeded and unseeded snow was identified (Fig. 4) among the five sites.

No significant differences were identified between the concentrations of either NO_X or ammonia in seeded and unseeded snowfall (Table 1). There was no significant difference between the ammonia and NO_X concentrations between Natural, Modified 1 or Modified 2 treatments when assessed by ANOVA (Table 2).

The concentrations of NO_X in the snowpack were found to vary from a minimum of less than the limit of reporting (0.005 mg/L), to a maximum of 0.061 mg/L. Ammonia concentrations ranged from less than the limit of reporting (0.005 mg/L), to a maximum of 0.36 mg/L The concentrations of NO_X and ammonia for the snowpack in the Rocky Mountains, reported by Ingersoll *et al.*, (2005), are presented in Table 3. Although not assessed statistically, the concentrations of NO_X determined in this current study were found to be less than those reported by Ingersoll *op. cit*.

The maximum concentrations of ammonia reported in alpine lake waters varied from approximately 0.030 mg/L and 0.040 mg/L (in Lake Albina and Blue Lake respectively) to 0.140 mg/L and 0.150 mg/L (in Lake Cootapatamba and Club Lake respectively). These concentrations in Lake Cootapatamba and Club Lake are threefold greater than the mean concentrations of 0.057 mg/L and 0.061 mg/L reported for natural and modified snowfall respectively.

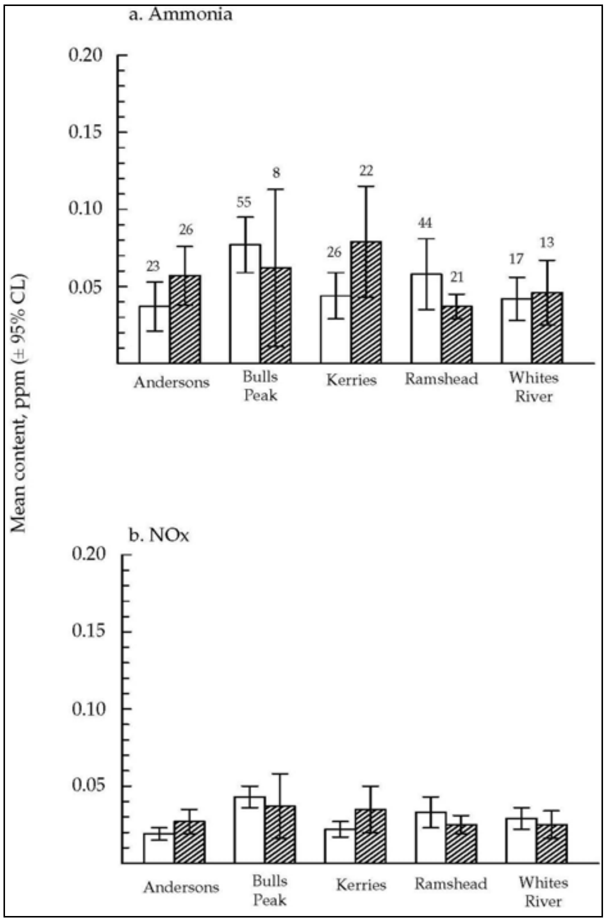

Figure 4: Mean and 95% confidence limits for content of ammonia and NO_X (mg/L) in snowfall, 2007. Open bars = natural; hatched bars = modified. Numbers of samples identical for ammonia and NO_X and shown above bars in ammonia graph

Table 1: ANOVA comparing 2 treatments

a. Ammonia (Variances homogeneous, C = 0.2173, raw data used)

Source	SS	DF	MS	F	P
Tr	0.0019	1	0.0019	1.00	0.3206
Si	0.0111	4	0.0028	1.47	0.2188
*TrXSi	0.0056	4	0.0014	0.74	0.5698
*RES	0.1383	70	0.0020		
TOT	0.1569	79			
1-POOLED DATA	0.1439	74	0.0019		

b. NO_X (Variances homogeneous, C = 0.2600, data transformed to ln(x+1)

Source	SS	DF	MS	F	P
Tr	0.0000	1	0.0000	0.00	1.000
Si	0.0018	4	0.0004	1.00	0.4131
*TrXSi	0.0011	4	0.0003	0.75	0.5612
*RES	0.0293	70	0.0004		
TOT	0.0322	79			
1-POOLED DATA	0.0304	74	0.0004		

(Tr = Natural and Modified) and 5 Sites (Si).

Table 2: ANOVA comparing 3 treatments (Natural and Modified 1 & 2) and 4 Sites.

a. Ammonia (Variances heterogeneous, C = 0.3802, $p < 0.05$; data transformed to ln(x+1))

Source	SS	DF	MS	F	P
Tr	0.0049	2	0.0025	1.32	0.2791
Si	0.0028	3	0.0009	0.47	0.7023
*TrXSi	0.0112	6	0.0019	1.00	0.4380
*RES	0.0669	36	0.0019		
TOT	0.0858	47			
1-POOLED DATA	0.0781	42	0.0019		

b. NO_X (Variances homogeneous, C = 0.3264, raw data used)

Source	SS	DF	MS	F	P
Tr	0.0010	2	0.0005	2.50	0.0942
Si	0.0002	3	0.0001	0.50	0.6843
*TrXSi	0.0009	6	0.0001	0.50	0.8047
*RES	0.0095	36	0.0003		
TOT	0.0115	47			
1-POOLED DATA	0.0104	42	0.0002		

(Tr = Natural and Modified) and 4 Sites (Si).

Table 3: Concentrations of ammonia and NO_X in seeded and unseeded snowfall and the Rocky Mountains (in mg/L).

Analyte		Natural	Modified	Rocky Mtns[1]
Ammonia	Min	0.008	<0.005	0.025
	Max	0.320	0.360	0.240
	Mean	0.057	0.061	0.074
NO_X	Min	<0.005	<0.005	0.143
	Max	0.160	0.120	0.936
	Mean	0.029	0.033	0.490

[1] Data from Ingersoll *et al.*, 2005, reported as NH_4^+ and NO_3, rather than total ammonia and NO_X.

4.0 DISCUSSION

No significant difference was identified between the concentrations of ammonia or NO_X in seeded and unseeded snowfall. This was the case whether seeded and unseeded snow or whether Natural, Modified 1 or Modified 2 treatments were compared. Therefore, there was no detectable effect of cloud seeding on the concentrations of nitrogenous compounds in snowfall.

In addition, the mean concentrations of ammonia in the snowpack (of 0.057 mg/L and 0.061 mg/L) were too low to account for the increases observed in alpine lakes in the Kosciuszko National Park (up to 0.155 mg/L). Therefore, the conceptual model that cloud seeding could have led to the observed increases in ammonia concentrations in alpine lakes is not supported and is rejected.

A review of the available literature on ammonia and NO_X compounds in snowfall and alpine lakes indicated that fluctuations in the concentrations of ammonia and NO_X in the winter season are influenced by a number of anthropogenic activities (e.g. motor vehicle pollution, agriculture or power station outputs) and by wet and dry deposition (Burns, 2003; Ingersoll *et al.*, 2005; Tarnay *et al.*, 2001). Variations in ammonia and NO_X concentrations in alpine lakes may also be a product of naturally occurring physico-chemical changes in the lacustrine ecosystem (Satoh *et al.*, 2000; Ellis and Stefan, 1989). These are, however, unrelated to the cloud seeding operations.

The concentrations of ammonia in the Snowy Mountains snowpack, (mean of 0.059 mg/L) appear similar to those published values for the Rocky Mountains snowpack (0.074 mg/L) (Ingersoll *et al.*, 2005), however, these studies did not compare the same measurements for ammonia and this was not assessed statistically.

The mean concentration of NO_X in the Snowy Mountains snowpack (0.031 mg/L) was approximately one order of magnitude less than the published mean values for NO_3 in the Rocky Mountains snowpack (0.49 mg/L) (Ingersoll *et al.*, 2005), however, this also has not been assessed statistically.

5.0 CONCLUSIONS

The concentrations of NO_X in snowfall in the Snowy Mountains were considerably less than those of the Rocky Mountains

There was no statistically significant difference between the concentrations of ammonia and NO_X in seeded and unseeded snowfall. The concentrations in snowfall were too low to account for the observed increases in the alpine lakes. The conceptual model proposing that increases in ammonia in alpine lakes could be attributed to cloud seeding is, therefore, not supported and is rejected. A review of literature sources indicated that the observed increases may be a product of natural processes occurring in alpine lakes.

6.0 ACKNOWLEDGEMENTS

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