

## Factors affecting nutrient content in the winter snowfall over the Clear Lake watershed

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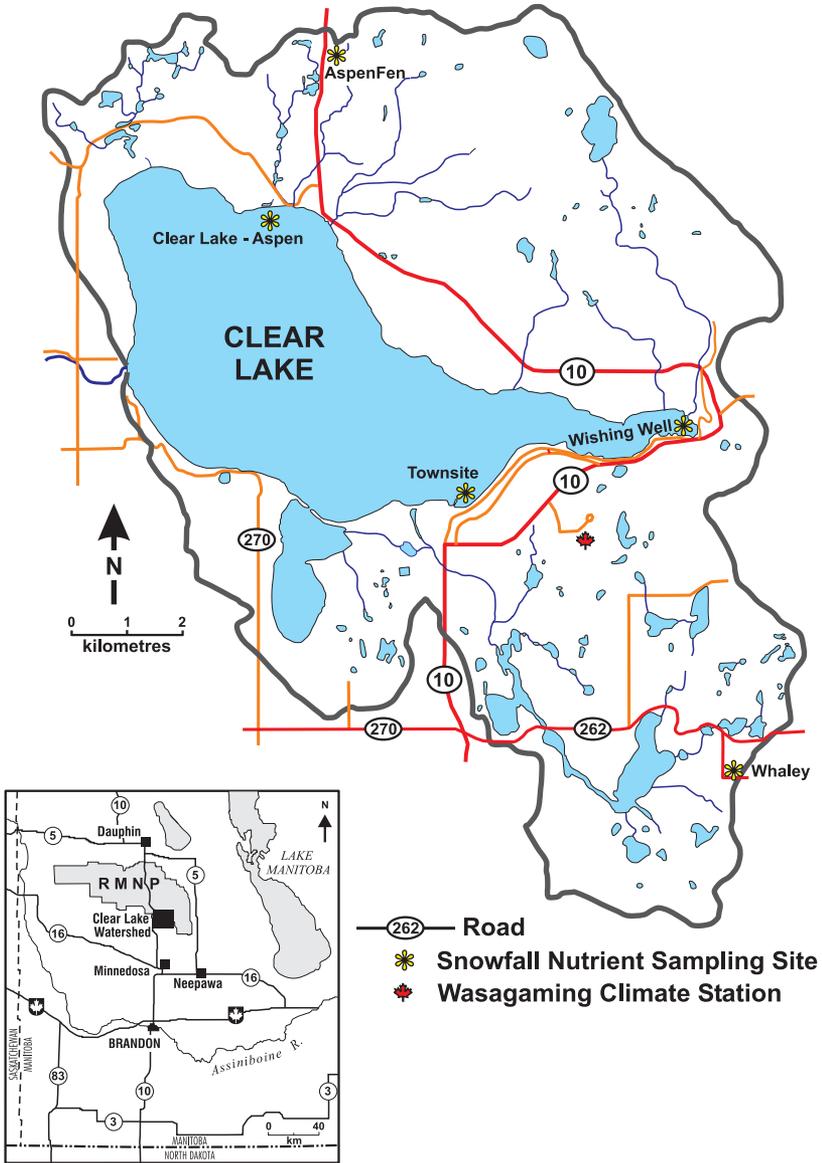
**Abstract:** A snowfall nutrient content sampling survey was conducted at five established sampling sites in the Clear Lake watershed throughout the winters of 1999-2000 and 2000-2001. Snowfall data were collected from the Environment Canada Wasagaming climate station located in Riding Mountain National Park. A high concentration of airborne phosphate is being deposited in early winter snowfalls on the Clear Lake watershed. Most of this particulate phosphate is soluble and bonded to colloidal particles. By mid-winter the accumulated snowpack has covered potential source regions for airborne nutrients and both total ammonia and phosphate ion concentrations in the snowfalls are significantly reduced. As temperatures warm, and the prairie snowpack melts, nitrogen and phosphorus concentrations increase substantially in the late winter snowfalls. The concentrations of other macronutrients (nitrate nitrogen and nitrite nitrogen) do not exceed the recommended standards.

*Key words: airborne nutrients, Clear Lake watershed, phosphorus, snowfall, snow cover, total ammonia*

### Introduction

The Clear Lake watershed is centrally located on the Riding Mountain Uplands in southwestern Manitoba. The watershed drains an area of 142.18 km<sup>2</sup> of which over 65% is located in Riding Mountain National Park. Clear Lake represents approximately 20.7% of the watershed area (Figure 1).

Clear Lake is the focus of summer recreational activity in Riding Mountain National Park. Consequently water quality in Clear Lake is a fundamental concern identified in both the Park Management Plan and the Ecosystem Conservation Plan (Dubois 1997). Parks Canada regulates human activities within Riding Mountain National Park in order to minimize pollution of the natural environment. Snowmelt accounts for an



*Figure 1: Clear Lake watershed: 1999-2001 Snowfall Nutrient Content Sampling Sites.*

average runoff inflow of approximately 4,400 - 6,800 dm<sup>3</sup> or a mean annual rise of 18.0 cm in the lake level (McGinn *et al.* 1998). This value is estimated to represent 23% of the estimated average annual runoff into Clear Lake. For the park staff, monitoring the water quality of the snowpack over the Clear Lake watershed is seen as necessary in order to determine whether airborne pollutants are entering the Clear Lake system.

## Objectives

Two objectives were identified at the onset of this study: 1) to estimate the nitrogen and phosphorus concentrations in the annual winter snowfall over the Clear Lake watershed; and, 2) to examine factors that appear to influence the concentrations of airborne phosphate in snowfalls over Riding Mountain National Park.

## Theoretical Considerations

Carbon, potassium, nitrogen, and phosphorus are the common macronutrients for aquatic plant life. In most lakes either nitrogen or phosphorus is the limiting factor in plant growth (Hammer and MacKichan 1981). Nitrogen and phosphorus nutrient loading of surface runoff accelerates natural eutrophication in streams, lakes and other aquatic systems (Reid and Wood 1976). Allochthonous or outside sources of these nutrients include atmospheric concentrations of ammonia, ammonium, nitrates, nitrites, and phosphates, which can be directly deposited (dry deposition) onto water surfaces. Furthermore, these nutrient aerosols can form nuclei of condensation and wash out as precipitation, some falling onto lakes and wetlands.

### Ammonia:

Ammonia is a colourless gaseous alkaline compound of nitrogen and hydrogen. It is an inorganic form of nitrogen that is very soluble in water and can be used directly by plants. Natural sources of ammonia in surface waters include the decomposition of plant material and animal waste, weathering of clays, nitrogen fixation by clays and gas exchange with the atmosphere (pure ammonia being a gas present in air). Ammonia is found in water as NH<sub>3</sub> (free ammonia or dissolved un-ionized ammonia gas), and as NH<sub>4</sub><sup>+</sup> (ammonium ions). In water the two forms (NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup>) exist in equilibrium and their combined concentration is referred to as total ammonia. Analytical methods are not readily available for the

measurement of free ammonia. Consequently, measures of ammonium ion concentration and equilibrium relationships are used to determine total ammonia ( $\text{NH}_3 + \text{NH}_4^+$ ) concentration. Ammonium is a major component in fertilizers and significant amounts can enter water bodies in runoff from cultivated fields. During application and post application, under the right conditions, volatilization significantly increases the ammonia concentration in the atmosphere.

The toxicity to aquatic organisms of ammonia in an aqueous solution is attributed to the un-ionized  $\text{NH}_3$  component of total ammonia (Williamson 1988). Since it is difficult to measure free (un-ionized) ammonia concentrations in a solution, equilibrium relationships are used to estimate the free ammonia concentration from total ammonia measurements. Water temperature and pH regulate this equilibrium. As temperature and/or pH increase the percentage of free ammonia in total ammonia increases.

In unpolluted waters free ammonia and ammonium occur in small quantities usually less than  $1.0 \text{ mg L}^{-1}$  (Reid and Wood 1976) and pose little or no risk to aquatic organisms. Health Canada has no guidelines for a maximum allowable concentration (MAC) of ammonia for drinking water. However, 'Guidelines for Evaluating Quality for Aquatic Life' in the *Water Encyclopedia* recommend that free ammonia ( $\text{NH}_3$ ) should not exceed  $0.5 \text{ mg L}^{-1}$  (Van der Leeden *et al.* 1990, 472). Manitoba Environment has set the free (un-ionized) ammonia concentration in unpolluted water objective an order of magnitude lower, at  $0.020 \text{ mg L}^{-1}$  (Williamson 1988).

Emerson *et al.* (1975), employ a formula to calculate the percentage of free (un-ionized) ammonia in a total ammonia solution. Using a melting temperature for snow of  $0^\circ\text{C}$  and the mean recorded pH of the snowfalls in the Riding Mountain area of 6.4 pH units, the maximum allowable concentration of free ammonia in snowfall should not exceed 0.03 percent of the total ammonia concentration. If the concentration of toxic free ammonia in snowfall should not be greater than 0.03 percent of the total ammonia concentration, the maximum total ammonia concentration in snowfall allowable by Manitoba Environment is calculated to be  $0.67 \text{ mg L}^{-1}$ . This standard will be used as the benchmark for this study.

### Nitrates and Nitrites:

Nitrate ( $\text{NO}_3^-$ ) and nitrite ( $\text{NO}_2^-$ ) are two inorganic forms of nitrogen found in water. Along with ammonia they are an important source of nitrogen for aquatic plants. Nitrates are used extensively as an ingredient

in nitrogen fertilizers; thus runoff from cultivated land is a common source of anthropogenic nitrate. Nitrates can also form from sewage, animal waste, plant and animal decay, as well as leachate from igneous rock.

Nitrate ion concentrations in water bodies in western Canada rarely exceed  $5.0 \text{ mg L}^{-1}$  of nitrogen in nitrate form and are usually below  $1.0 \text{ mg L}^{-1}$  of nitrate nitrogen (Williamson 1988 and Van der Leeden *et al.* 1990, 422-423). Nitrate nitrogen ( $\text{NO}_3^-$ -N) refers to the mass of nitrogen in the nitrate form. According to Health Canada the maximum allowable concentration (MAC) for nitrates should not exceed  $45.0 \text{ mg L}^{-1}$  (Health Canada 1996). This corresponds to maximum allowable nitrate nitrogen ( $\text{NO}_3^-$ -N) concentration of  $10.0 \text{ mg L}^{-1}$  (Williamson 1988 and Van der Leeden *et al.* 1990, 443). The nitrate nitrogen concentration in unpolluted waters rarely exceeds  $0.300 \text{ mg L}^{-1}$  (Reid and Wood 1976).

Nitrite nitrogen ( $\text{NO}_2^-$ -N) is found at lower concentrations than nitrate nitrogen, approximately  $0.001 \text{ mg L}^{-1}$  in unpolluted waters (Reid and Wood 1976). Sources for nitrite include industrial effluent, sewage and animal waste. The MAC for nitrite is  $3.2 \text{ mg L}^{-1}$  of  $\text{NO}_3^-$  or  $1.0 \text{ mg L}^{-1}$  for nitrite nitrogen (Williamson 1988 and Van der Leeden *et al.* 1990, 443).

### **Phosphorus:**

Phosphorus is an essential mineral nutrient for plant and animal life. In a freshwater aquatic setting it is considered to be the most important nutrient in determining the overall productivity in an ecosystem. Phosphorus in natural waters commonly occurs as phosphate, which is classified as orthophosphate ( $\text{PO}_4^-$ ), polyphosphates, and organically bound phosphates (Hammer and MacKichan 1981). These phosphate forms exist as filterable (dissolved) and non-filterable (particulate) forms. Filterable orthophosphate concentrations tend to be low in natural water bodies because living organisms assimilate phosphorus.

Total mean phosphorus content of most lakes ranges from  $0.010 - 0.030 \text{ mg L}^{-1}$  (Reid and Wood 1976). Total phosphorus (soluble phosphate phosphorus) content should not exceed  $0.025 \text{ mg L}^{-1}$  in any reservoir, lake or pond, or in any tributary at the point where it enters such bodies of water (Williamson 1988).

### **Airborne phosphate ( $\text{PO}_4^-$ ):**

Atmospheric contributions of phosphorus can be very significant in lakes with small drainage basins (Schindler *et al.* 1976). In the Experimental Lakes Area near Kenora, Ontario, Schindler *et al.* (1978) estimate an atmospheric phosphorus loading of  $24.0 - 53.0 \text{ mg m}^{-2} \text{ yr}^{-1}$ .

Bennett (1985) provides an estimate of aeolian phosphate concentrations in the Brandon, Manitoba area ranging from 0.01 - 0.04 mg m<sup>-3</sup> with a geometric mean value 0.2 mg m<sup>-3</sup>, and suggests an atmospheric loading rate of 82.0 mg m<sup>-2</sup> yr<sup>-1</sup>. The distribution of airborne phosphate is lognormal; therefore a geometric mean is appropriate. Beck (1985) rationalizes a slightly more conservative atmospheric contribution rate of 41.0 mg m<sup>-2</sup> yr<sup>-1</sup> in his study of twelve lakes in the south Riding Mountain Planning District.

## Methodology

### Sampling sites:

In the Clear Lake watershed, five snowfall sampling sites were established. Four sites are located in Riding Mountain National Park and a fifth sampling site is situated outside the park over an agricultural field (Figure 1). The Clear Lake sites (*Aspen*, *Wishing Well* and *Townsite*) are representative of the lake surface and lowest elevation (615 m) in the Clear Lake watershed. The *Aspen Fen* site is located in a wetland area, 39 m above lake level. The site is described as standing water, with rushes, sedges, dwarf birch, willows and alder. The *Whaley* site is a cultivated agricultural field of uncut alfalfa, 640 m in elevation. Both the *Aspen Fen* and *Whaley* sites represent highland areas located near the watershed divide, the former in the north and the latter in the south.

### Sampling procedure and implements:

A one metre square wooden platform was employed at each of the sites as a snow collection surface. The platform was constructed from ¾" plywood mounted on a two-by-four frame. A hole was drilled in one corner of each platform for the placement of a location indicator dowel, which extended one m above the surface.

The depth of fresh snow (fall and drift) on the platform surface constituted a sample. Nutrient content sampling occurred within 24 hours of snowfall. Samples were collected using a rectangular funneling instrument measuring 9.0 cm square at the mouth by 25.0 cm in length and tapering to 5.0 cm square at the rear. The funnel was swept across the snow collection platform, collecting snow into a large plastic bag attached to the rear end of the instrument. Depending on snow depth, multiple sweeps were required to collect the total sample. Following the collection of a sample, the platform was swept clear and placed on a level snow surface adjacent to the sampling site in preparation for the next snowfall event. Each snowfall sample was melted at room temperature into a 1,000

ml glass beaker. The melted sample was split into A, B, and C sub-samples. Each of the A, B, and C sub-samples were analyzed for ammonia (ammonium), nitrate, nitrite, and phosphate ion concentration, pH and electrical conductivity.

#### **Water quality instruments:**

The nutrient testing employed portable Ion Specific Meters (with LCD screen) made by Hanna Instruments (1999). These instruments employ a colorimetric analysis based on the principle that the specific components react with others and form a colour. The colour intensity is proportional to the concentration of the substance being measured. A light emitting diode emits radiation at a single wavelength intensity and a photoelectric cell collects the radiation, converting it to an electrical current. A microprocessor employing the Lambert-Beer Law equality converts the electrical potential to concentration. The specific instruments employed in this study have a resolution of  $0.01 \text{ mg L}^{-1}$ . Samples were tested for total ammonium, nitrate and nitrite ion concentrations and soluble phosphate ion concentration. Electrical conductivity was estimated using a Hach Sensi $\text{ion}$  5 portable conductivity meter. Recorded electrical conductivity values are in micro-Seimens per centimetre ( $\text{mS cm}^{-1}$ ). A Fisher pH meter, model Acumet 600, measured pH in each sample.

## **Airborne Nutrients in the Winter Snowfalls over the Clear Lake Watershed**

#### **Snowfalls:**

Snowfall data were collected from the Environment Canada Wasagaming climate station located in Riding Mountain National Park at the Warden Stores Compound (Figure 1). Thirteen snowfall events were recorded from December 1, 1999 to March 31, 2000 (Figure 2a). There were four rainfall events in late February and March. Six of the snowfalls were considered to be significant and four of these snowfalls were sampled (Figure 2a). Twenty-three snowfall events were recorded from November 1, 2000 to March 31, 2001 (Figure 2b). Seven of the snowfalls were considered to be significant and six of these snowfalls were sampled (Figure 2b). A significant snowfall is operationally defined as a precipitation event depositing at least 3.0 mm water equivalent depth during a 24-hour period, or a multiple day event in which the water equivalent depth of the snowfall exceeds 5.0 mm. Using the 10:1 snowfall/water ratio, that would be a

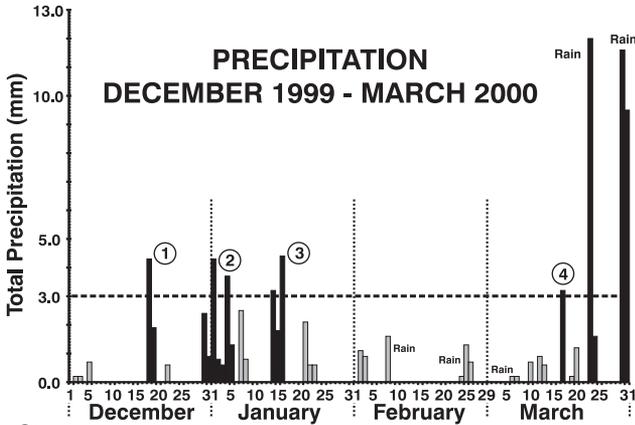


Figure 2a

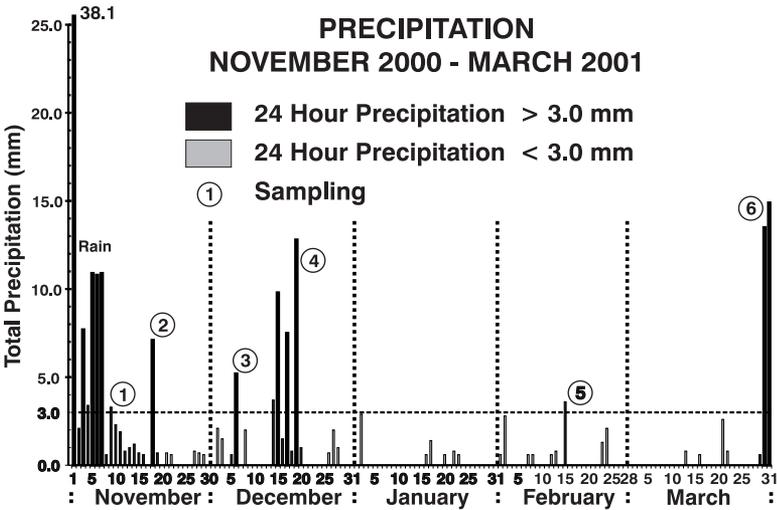


Figure 2b

Figure 2: Wasagaming climate station, Riding Mountain National Park.

snowfall exceeding 3.0 cm and 5.0 cm in depth, respectively. The final snowfall nutrient content survey was conducted on March 17, 2000 and April 5, 2001, respectively.

#### **Total ammonia ( $\text{NH}_3$ and $\text{NH}_4^+$ ):**

The watershed mean total ammonia concentration ( $\text{NH}_3 + \text{NH}_4^+$ ) detected in the 1999-2000 snowfalls was  $0.278 \text{ mg L}^{-1} \pm 0.057 \text{ mg L}^{-1}$  (McGinn and Thompson 2001). By comparison, the watershed mean total ammonia concentration in the snowfalls sampled in 2000-2001 was  $0.159 \text{ mg L}^{-1}$  with a standard deviation of  $0.089 \text{ mg L}^{-1}$ . The total ammonia nitrogen concentration recorded for all snowfall samples (1999-2001) was less than Reid and Wood's (1976) observation for total ammonia concentration of  $1.0 \text{ mg L}^{-1}$ , but often exceeded the Health Canada (1996) reference for ammonia and ammonia compounds of  $0.100 \text{ mg L}^{-1}$ . No site was consistently higher or lower than any other site (Figures 3a and 3b). Employing the Emerson *et al.* (1975) formula for calculating percentage of free ammonia ( $\text{NH}_3$ ), the maximum concentration of free ammonia in winter snowfalls was less than the Manitoba Environment standard of  $0.020 \text{ mg L}^{-1}$  (Williamson 1988).

It is difficult to establish a pattern to the total ammonia concentrations in snowfalls by comparing the 1999-2000 and 2000-2001 winter seasons. Winter drought appears to have occurred in both sampling seasons; late January to early March in 1999-2000 and January to mid-February and March, 2001 (Figures 2a and 2b). Consequently, the snowfall sampling results only can be compared on a general temporal continuum: early snowfalls (the first two or three), mid-season snowfalls and late season snowfalls (the last two). During both sampling periods, total ammonia concentrations appear to decline following the early season snowfalls (Figures 3a and 3b). In the 2000-2001 study, this decline was to virtually undetectable levels by late December (Figure 3b). In the late season snowfalls, total ammonia concentrations were found to increase to values approximating the seasonal overall mean concentration. It is speculated that this increase in total ammonia concentration could be attributed to volatilization from uncovered soil during late season thaws (Paton 2000: personal communication).

#### **Soluble phosphate phosphorus ( $\text{PO}_4^{3-}\text{P}$ ):**

In the 2000-2001 study, the mean soluble phosphate ion concentration in the snowfall samples was  $0.191 \text{ mg L}^{-1} \pm 0.130 \text{ mg L}^{-1}$ . This recorded value is significantly less than the mean soluble phosphate ion concentration

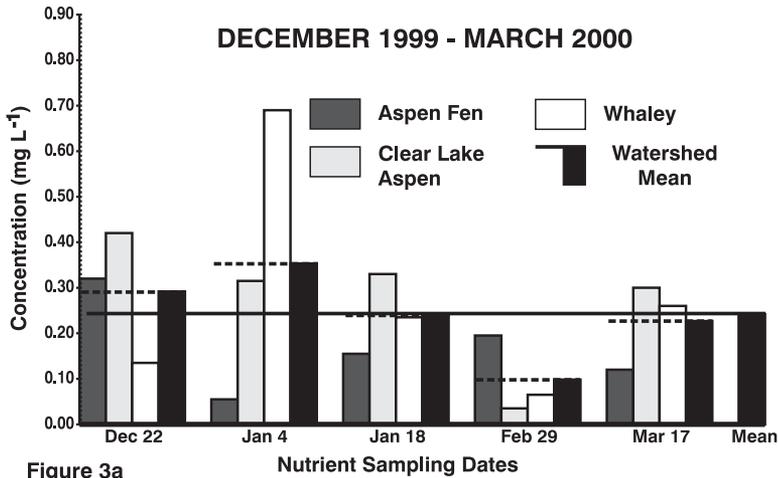


Figure 3a

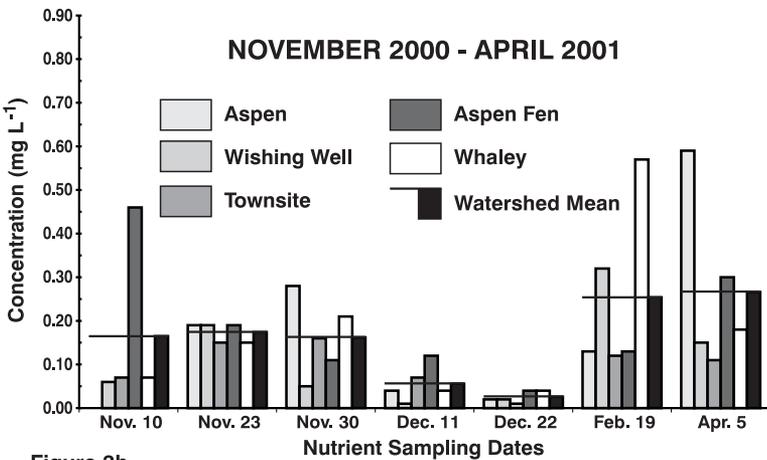


Figure 3b

Figure 3: Total ammonia ( $NH_3 N + NH_4^+ N$ ) concentration in snowfall: Clear Lake watershed.

in the 1999-2000 snowfalls of  $1.280 \text{ mg L}^{-1}$ ,  $\pm 0.634 \text{ mg L}^{-1}$  (McGinn and Thompson 2001). The mean soluble phosphate ion concentration in the 1999-2000 winter snowfalls on the Clear Lake watershed was significantly greater than expected and at least two orders of magnitude greater than the Manitoba Environment objective of  $0.025 \text{ mg L}^{-1}$ .

McGinn and Thompson (2001) hypothesized that the unusually high phosphate ion concentrations in the 1999-2000 snowfalls could be attributed to phosphate bonded to large (0.2 mm - 1.0 mm) diameter tropospheric aerosols. The researchers employed a two-step filtration procedure in their study to remove particulate phosphate and the soluble phosphate bonded to colloidal particles. In the 1999-2000 study, the phosphate ion concentrations were not significantly reduced following a 0.45 mm filtration to remove particulate insoluble phosphate. Mean concentrations in the snowfall samples remained greater than  $1.0 \text{ mg L}^{-1}$ . The 0.25 mm filter, however, successfully removed the particulate phosphate reducing mean sample values to expected values; approximately  $0.015 \text{ mg L}^{-1}$ . This suggested that the unusually high phosphate concentrations found in the 1999-2000 Riding Mountain Uplands snowfalls were being deposited in association with colloidal size particles.

During both the 1999-2000 and 2000-2001 sampling periods, soluble phosphate phosphorus concentrations appear to decline following early season snowfall (Figures 4a and 4b). In the late season snowfalls, however, soluble phosphate ion concentrations were found to rise above the seasonal watershed mean concentration.

#### **Nitrate ion ( $\text{NO}_3^-$ ):**

Nitrate ion ( $\text{NO}_3^- \text{ N}$ ) concentrations were less than the accuracy specifications of the instrument employed ( $0.01 \text{ mg L}^{-1}$ ) and considered undetectable. During the winter, nitrate and nitrite concentrations are not expected to be significant since nitrification is dependent on temperature (Paton 2000, personal communication).

#### **Nitrite ion ( $\text{NO}_2^-$ ):**

Nitrite ion ( $\text{NO}_2^- \text{ N}$ ) concentrations were generally less than the accuracy specifications of the Hanna Ion specific meter employed and are considered to be undetectable in the winter snowfalls 1999-2000 and 2000-2001.

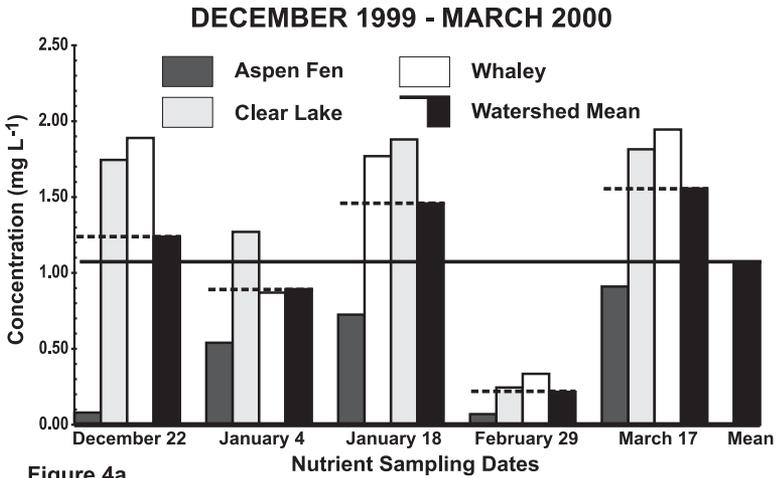


Figure 4a

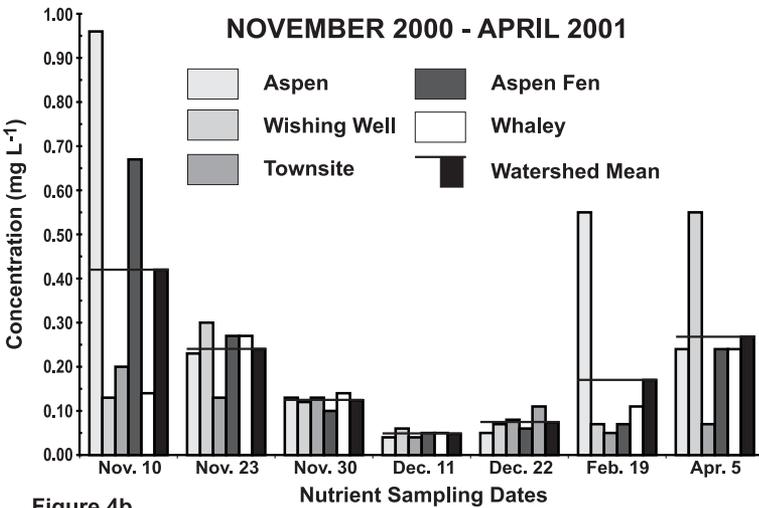


Figure 4b

Figure 4: Phosphate ( $PO_4-P$ ) concentration in snowfall: Clear Lake watershed.

## Factors Affecting Airborne Nutrient Loading

### The winter precipitation regimes: 1999-2000 and 2000-2001:

The winter precipitation regimes for the two sampling seasons (1999-2000 and 2000-2001) were different (Figures 2a and 2b). Total snowfall accumulation for the 2000-2001 winter season was three times the 1999-2000 accumulation (168.7 mm versus 54.1 mm water equivalent depth). The 1999-2000 winter precipitation regime began a month later than in the 2000-2001 season; December 2, 1999 versus November 1, 2000 and concluded almost a month earlier, March 17, 2000 versus April 5, 2001, respectively (Figures 2a and 2b). Four of the six significant snowfalls that occurred during the 1999-2000 winter period were sampled for nitrogen and phosphorus content (Figure 2a): the first sampling in mid-December, two samplings in January and the last sampling on March 17, 2000. By comparison, six of the seven significant snowfalls which occurred during the 2000-2001 winter were sampled for nitrogen and phosphorus content: twice in November, twice in December, in mid-February and on April 5, 2001 (Figure 2b).

### The antecedent precipitation index:

Rainfall totals prior to the winter accumulation season (May-October) for the two sampling periods also were different. The monthly Antecedent Precipitation Index (API) for 1999-2000 was calculated to be 1.23 or 23 percent above normal (Ryder *et al.* 2000). For the 2000-2001 winter season the API was estimated be 0.98 or approximately normal. However it was necessary to adjust the 2000-2001 API to include a 62.2 mm early November rainfall (November 1-6, Figure 2b). The 2000-2001 API, adjusted for the November rainfall, is calculated to be 1.68 or 68% above normal (Chubak *et al.* 2001).

The monthly antecedent precipitation index for Riding Mountain National Park is calculated using the form  $API = SA/SB$ , where:

SA = the sum of the monthly precipitation ( $P_n$ ) times an empirically derived constant "a"

SB = the sum of the normal monthly precipitation (1969-1999) times the same empirically derived constant "a"

"a" = 0.07, 0.08, 0.12, 0.18, 0.25 and 0.3 for May to October, respectively.

When there is a recorded November rainfall, the constant “a” is 0.5 and the API is referred to as the Adjusted API.

The heavy rainfall received in the first five days of November was followed by 21.7 millimetres water equivalent depth of wet snow on November 6 and 7 (Figure 2b). The wet snowfall continued intermittently for the next nine days, depositing an additional 12.4 millimetres water equivalent depth on the Clear Lake watershed. By the end of November approximately 45.3 millimetres (water equivalent depth) of snowfall had accumulated on the watershed as a mean 24.9 centimetres deep snowpack (Chubak *et al.* 2001). By contrast, meteorological records for the watershed (Wasagaming, Manitoba) indicate that November and December 1999 were drier than normal, recording no significant snowfalls or accumulated snow cover until late December (Figures 2a and 5).

#### **Snow cover:**

Figures 5a and 5b compare the regional extent of early seasonal snow cover for the two sampling periods. Figure 5a indicates that the southern prairies had little or no snow cover by mid-December 1999. Consequently, a large source region for airborne nutrients was exposed to the wind. By mid-December 2000, however, southeastern Saskatchewan and Manitoba were covered by at least 10 cm of snow and the nearest source region for airborne nutrients was limited to southwestern Saskatchewan, a region at least 300 km from the study area (Figure 5b).

## **Discussion**

The difference in total ammonia and soluble phosphate ion concentrations in the snowfalls of the two study periods can be attributed to differences in antecedent rainfall and snow cover. The heavy rainfall received in the first five days of November 2000 is believed to have washed nitrogen compounds and colloidal phosphate out of the troposphere. Consequently the 21.7 millimetres water equivalent depth of wet snow that fell on November 6 and 7 contained smaller concentrations of both ammonia nitrogen and phosphate phosphorus than those measured in the November 1999 snowfalls. Furthermore, this early November wet snowfall covered the local nutrient source regions with approximately 20 cm of snow. As a consequence, there was a relative paucity of airborne nutrients following this event and it was not surprising to measure undetectable concentrations of total ammonia and significantly lower concentrations

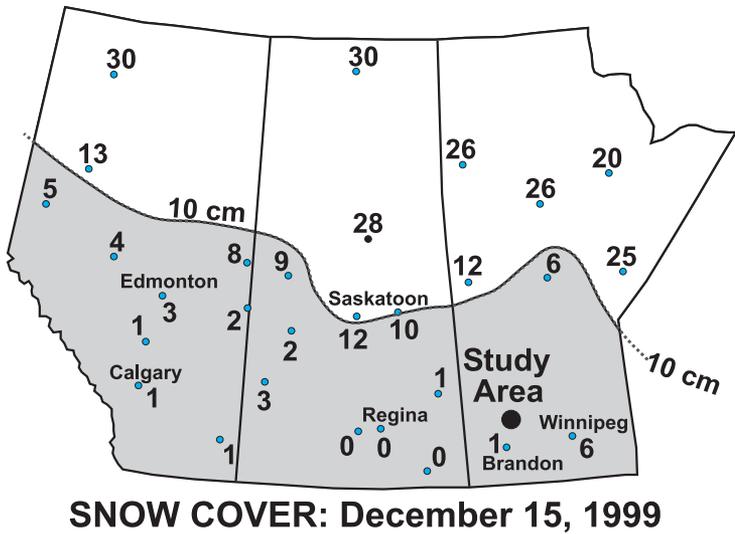


Figure 5a

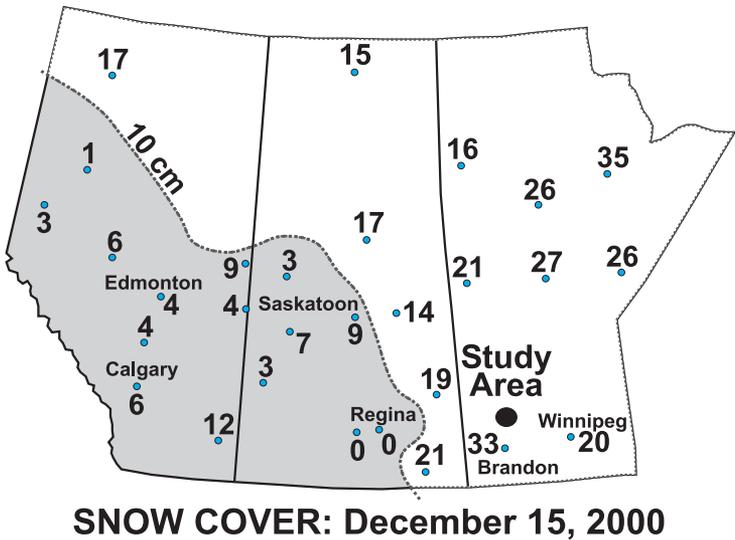


Figure 5b

Adapted from: [www.msc-sme.ec.ca/ccrp/SNOW?snow\\_swe.html](http://www.msc-sme.ec.ca/ccrp/SNOW?snow_swe.html)

Figure 5: Snow cover maps.

of soluble phosphate in the 2000-2001 mid-winter snowfalls over the Clear Lake watershed.

## Conclusions

High concentrations of airborne phosphate are being deposited in early winter snowfalls on the Clear Lake watershed. Approximately 75% of this particulate phosphate is soluble and bonded to colloidal particles. The remaining 25% is insoluble particulate phosphate. While the concentrations of soluble phosphate are recorded to be significantly higher than the recommended standard, they are variable over the winter season and from winter to winter. The autumn antecedent precipitation, the winter snowfall regime and snow cover appear to account for much of this variability.

By mid-winter the accumulated snowpack has covered potential source regions for airborne nutrients and total ammonia and phosphate ion concentrations in the snowfalls are significantly reduced. As temperatures warm and the prairie snowpack melts, potential source regions for airborne nutrients become exposed to the wind and nitrogen and phosphorus concentrations are found to increase in the late winter and early spring snowfalls. The concentrations of other macronutrients (nitrate nitrogen and nitrite nitrogen) do not exceed the recommended standards. Further studies are required to evaluate the phosphate depositional loading during the winter on the lake surface. Data are required regarding airborne distribution patterns and potential source regions.

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