

Nutrient loading in the winter snowfalls over the Clear Lake watershed

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Introduction

The Clear Lake watershed is centrally located on the Riding Mountain Uplands in southwestern Manitoba. The watershed drains an area of 142.18 km² of which over 65 percent is located in Riding Mountain National Park (Figure 1). Clear Lake represents approximately 20.7% of the watershed area.

Clear Lake is the focus of summer recreational activity in Riding Mountain National Park, Manitoba. Consequently water quality in Clear Lake is a fundamental concern identified in both the Park Management Plan and the Ecosystem Conservation Plan (Dubois et al., 1997). Parks Canada regulates human activities within Riding Mountain National Park in order to minimize pollution of the natural environment. Snowmelt accounts for an annual runoff inflow of approximately 27,000.00 dm³ or a 9.0 cm rise in lake levels (McGinn et al., 1997). This value represents twenty three percent of the estimated average annual runoff into Clear Lake. For the Park staff, monitoring the water quality of the snowmelt runoff from the Clear Lake watershed is seen as necessary in order to determine whether airborne pollutants are entering the Clear Lake system.

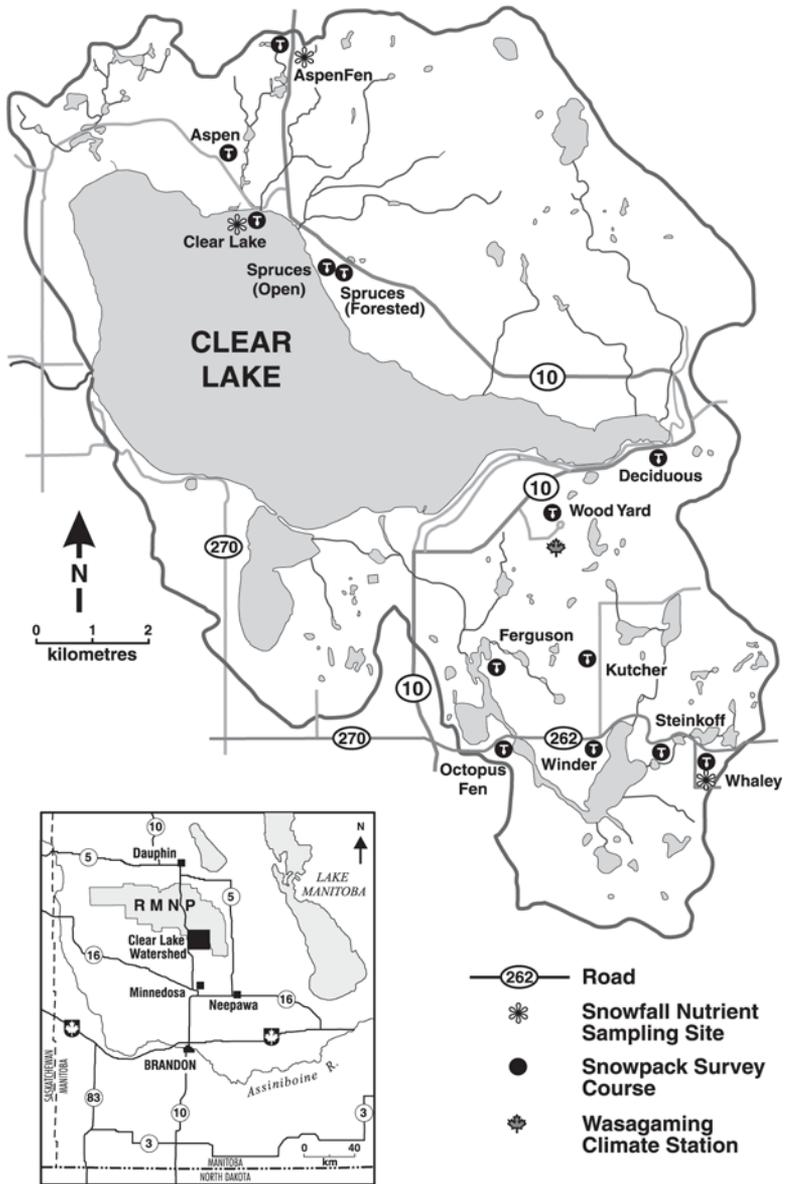


Figure 1: Location of study area.

Objective

Two objectives were identified at the onset of this pilot study:

- 1) To estimate the nitrogen and phosphorus loading in the annual winter snowfall over the Clear Lake watershed.
- 2) To evaluate the pilot study and make recommendations regarding the continuance of an atmospheric nutrient monitoring programme.

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, 1989). Allochthonous or outside sources of these nutrients include atmospheric concentrations of ammonia, ammonium, nitrates, nitrites, and phosphates, which can be directly deposited (dry deposition) on to water/ice surfaces. Furthermore, these nutrient aerosols can form nuclei of condensation and washout 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_3 (free ammonia or dissolved un-ionized ammonia gas), and as NH_4^+ (ammonium ions). In water the two forms (NH_3 and NH_4^+) 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 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 increases 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 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, the Water Encyclopedia, Table 6-51: Guidelines for Evaluating Quality for Aquatic Life, recommends that free ammonia (NH_3) should not exceed 0.5 mg L^{-1} (Van der leeden et al., 1990). Manitoba Environment has set the free (un-ionized) ammonia concentration in unpolluted water objective an order of magnitude lower, at the 0.020 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°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 0.0264 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 mg L^{-1} . This standard will be used as the benchmark for this study.

Nitrates and Nitrites:

Nitrate (NO_3^-) and nitrite (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.

Generally nitrate ion concentrations in water bodies in western Canada rarely exceed 5.0 mg L^{-1} of nitrogen in nitrate form and are usually below 1.0 mg L^{-1} of nitrate nitrogen (Williamson, 1988 and The Water Encyclopedia, Table 6-4: Principal Chemical Constituents in Water). Nitrate nitrogen ($\text{NO}_3^- \text{-N}$) 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 mg L^{-1} (Health Canada, 1996). This corresponds to maximum allowable nitrate nitrogen ($\text{NO}_3^- \text{-N}$) concentration of 10.0 mg L^{-1} (Williamson, 1988 and The Water Encyclopedia Table 6-22: Canadian Guidelines for Drinking Water Quality). The nitrate nitrogen concentration in unpolluted waters rarely exceeds 0.300 mg L^{-1} (Reid and Wood, 1976).

Nitrite nitrogen ($\text{NO}_2^- \text{-N}$) is found at lower concentrations than nitrate nitrogen, approximately 0.001 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 mg L^{-1} of NO_3^- or 1.0 mg L^{-1} for nitrite nitrogen (Williamson, 1988 and The Water Encyclopedia Table 6-22: Canadian Guidelines for Drinking Water Quality).

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 (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. In general hydrological/limnological studies the term “total phosphorus” and “phosphate content” are identical.

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

Airborne Phosphate (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 mg m² yr⁻¹. Bennett (1985) provides an estimate of aeolian phosphate concentrations in the Brandon, Manitoba area ranging from 0.01 - 0.04 mg m³ with a geometric mean value 0.2 mg m³, and suggests an atmospheric loading rate of 82.0 mg m² yr⁻¹. 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 m² yr⁻¹ in his study of twelve lakes in the south Riding Mountain Planning District.

Methodology

Sampling Sites:

In the Clear Lake watershed, three snowfall sampling sites were established. Two sites are located in Riding Mountain National Park and a third sampling site is situated outside the park over an

agricultural field (Figure 1). The *Clear Lake* site is 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 Procedures and Instruments:

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 fresh snow surface, collecting approximately 1200 cm³ of snow into a large plastic bag attached to the rear end of the instrument. Three or four sweeps were required to collect approximately 1 kg of snow (1.0 litres water equivalent) at each snowfall sampling site.

Water Quality Instruments:

The nutrient testing employed portable Ion Specific Meters (with LCD screen) made by Hanna Instruments. Samples were tested for total ammonium, nitrate and nitrite ion concentrations and soluble phosphate ion concentration. Electrical conductivity was estimated using a conductivity pen made by Hanna Instruments, model Commet 2 and a Fisher pH meter, model Acumet 600, measured pH in each sample.

Laboratory Procedures:

Each snowfall sample was melted at room temperature into a 1000 ml glass beaker. The melted sample was split into an A and B sub-sample. Both the A and B sub-samples were analyzed for ammonia (ammonium), nitrate, nitrite, and phosphate ion concentration, pH and electrical conductivity.

Ammonia, nitrate, nitrite and phosphate ion concentrations are estimated using the procedures specified in the Hanna Instruments:

Ion Specific Meters Instruction Manual. 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.

Phosphate occurred in the snowfall samples in both a soluble and insoluble form. The insoluble particulate was removed by filtration. A given volume (10.0 mL) of supernatant (sample solution plus precipitate) is placed into a 0.45 micron (mm) filter and drawn through the filter by a suction device. The phosphate ion concentration of the filtrate is measured using the Hanna Instruments. The amount of particulate phosphate retained in the filter is determined by subtracting the total available phosphate ion concentration measured in the free sample (supernatant) from the total available phosphate ion concentration recorded for the filtered sample (filtrate).

Approximately 25 percent of the phosphate ion concentration was removed following the 0.45 mm filtration. Consequently, additional filtration was employed. The 0.25 mm filter successfully removed most of the remaining phosphate reducing mean sample values to approximately 0.015 mg L^{-1} .

Significant Precipitation Events over the Clear lake Watershed, December 1999 - March 2000

Snowfall data were collected from the Environment Canada Wasagaming Climate Station located in Riding Mountain National Park at the Warden Stores Compound (Figure 1). Significant snowfall events are operationally defined as a precipitation event depositing at least 3.0 mm water equivalent depth during a 24 hour period. Using the 10:1 snowfall/water ratio, that would be a snowfall exceeding 3.0 cm in depth.

Two precipitation events occurred during the first 17 days of December resulting in a total of 1.1 mm water equivalent snowfall. The first significant winter snowfall (6.2 mm water equivalent depth) occurred on December 17-19, 1999 (Figure 2). The first nutrient sample survey was conducted during a light snowfall, two days later, on December 22. The results of the nutrient analyses are summarized in Table 1.

Four snowfall events took place during the last two days of December and in January 2000 (Figure 2). Total January snowfall is estimated to be 30.0 mm water equivalent depth. The late December - early January snowfall occurred over a 7-day period from December 30 to January 5 and could be sub-divided into two closely timed events. Total snowfall was estimated to be 14.0 mm water equivalent depth. Sampling was conducted six days into the event on January 4, 2000. The results of the nutrient analyses are summarized in Table 1.

On January 7 and 8, 3.3 mm water equivalent depth of snowfall was recorded at the Wasagaming Climate Station. This snowfall event was not sampled for nitrogen and phosphorus nutrients. The third significant January snowfall occurred from the 14-17,

Table 1: Nutrient concentrations in snowfall, Clear Lake watershed.

	N03- N	PO4--- P	N02- N	NH3 + NH4+	NH3	K+	Temperature	Conductivity	pH
	mg L-1	oC	mS cm-1						
Dec 22/99									
Aspen Fen	0.00	0.08	0.05	0.32	0.01	NA	20.1	0.010	8.30
Whaley	0.01	1.89	0.01	0.14	0.00	NA	20.1	0.015	6.20
Clear Lake	0.00	1.75	0.05	0.42	0.01	NA	20.1	0.010	8.14
Watershed	0.003	1.238	0.033	0.292	0.008	NA	20.1	0.120	7.55
Jan 04/00									
Aspen Fen	0.00	0.54	0.06	0.06	0.00	0.10	20.1	0.150	6.30
Whaley	0.00	0.87	0.24	0.69	0.02	0.12	20.1	0.010	6.20
Clear Lake	0.00	1.27	0.08	0.32	0.01	0.16	20.1	0.010	6.80
Watershed	0.000	0.893	0.123	0.353	0.009	0.123	20.1	0.012	6.43
Jan 18/00									
Aspen Fen	0.00	0.73	0.08	0.16	0.00	NA	19.9	0.010	5.70
Whaley	0.00	1.88	0.06	0.24	0.01	NA	19.9	0.010	5.80
Clear Lake	0.00	1.77	0.05	0.33	0.01	NA	19.9	0.010	5.30
Watershed	0.000	1.458	0.060	0.240	0.006	NA	19.9	0.010	5.80
*Feb 29/00									
Aspen Fen	0.00	0.07	0.02	0.20	0.01	0.05	20.1	0.010	6.30
Whaley	0.00	0.34	0.02	0.07	0.00	0.02	20.1	0.010	5.90
Clear Lake	0.00	0.25	0.06	0.04	0.00	0.02	20.1	0.010	5.40
Watershed	0.000	0.217	0.050	0.098	0.003	0.027	20.1	0.010	5.87
Mar 17/00									
Aspen Fen	0.00	0.91	0.02	0.12	0.00	0.04	20.1	0.010	6.70
Whaley	0.00	1.95	0.03	0.26	0.01	0.02	20.1	0.010	5.80
Clear Lake	0.00	1.82	0.01	0.30	0.01	0.02	20.1	0.010	5.60
Watershed	0.000	1.557	0.018	0.227	0.006	0.022	20.1	0.010	6.03

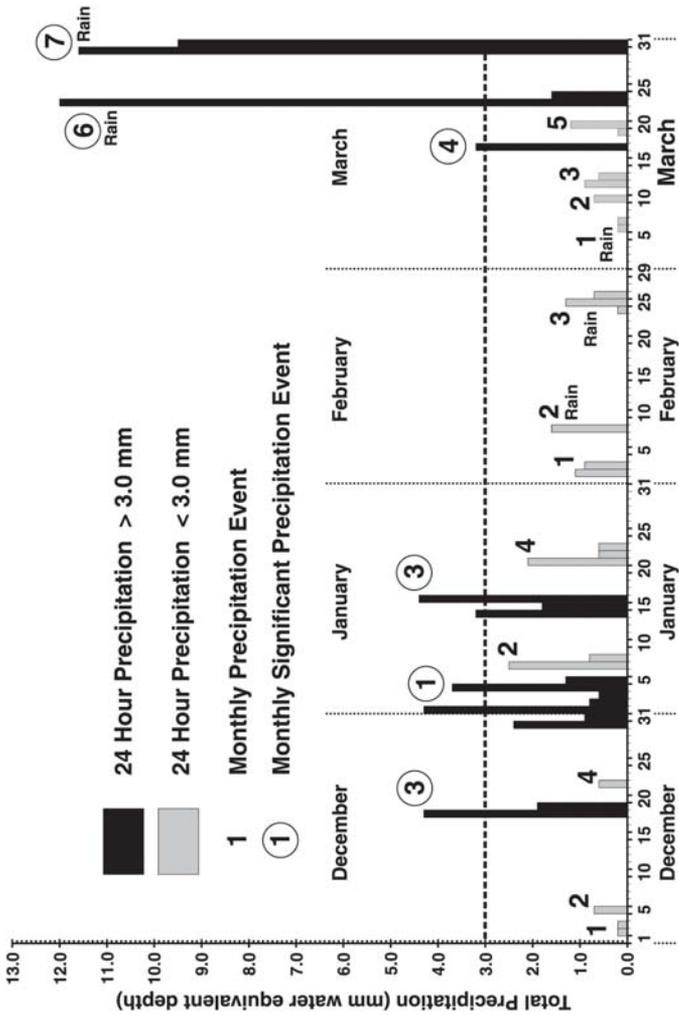


Figure 2: Wasagaming Climate Station, Riding Mountain National Park December 1999 - March 2000 precipitation.

depositing 9.4 mm water equivalent depth of snowfall (Figure 2). Sampling was conducted the following day (January 18). The results of the nutrient analyses are summarized in Table 1. A fourth significant snowfall event occurred on January 21-23 recording 3.3 mm water equivalent depth of precipitation (Figure 2). This snowfall event was not sampled for nitrogen and phosphorus nutrients.

Three precipitation events occurred in February 2000 (Figure 2). None were considered to be significant (greater than 3.0 mm water equivalent depth). During the last 10 days of February, maximum daily temperatures were above 0°C and the mean daily temperatures were 10.8°C above normal. This warming resulted in significant sublimation and melting of the snowpack. Consequently, the nutrient sampling survey conducted on February 29 collected samples from a ripe snowpack and not a fresh snowfall. A ripe snowpack is operationally defined as an isothermal body of settled snow at 0°C, which is saturated with respect to its liquid water content (LWC). In the Riding Mountain Uplands a ripe snowpack has a density greater than 300 kg m⁻³ and a LWC of approximately 35 percent. An Environment Canada ESC-30 Snow Sampler (61.804 mm diameter bore with an area of 30 cm²) was used to extract a vertical core of the snowpack, normal to the collecting surface, at each sampling site. The results of the nutrient analyses are summarized in Table 1.

One significant snowfall (3.2 mm water equivalent depth) and two other snowfall events occurred during the first 17 days of March (Figure 2). Four rainfall events occurred in March, two defined as significant, March 23-24 (13.6 mm) and March 30-31 (21.6), respectively (Figure 2). Following these rainfall events, the snowpack completely ablated. The final snowfall nutrient sampling was conducted on March 17, 2000 during the last significant snowfall event of the winter period. The results of the nutrient analyses are summarized in Table 1.

Nutrients in the Clear Lake Watershed

In the Clear Lake Watershed the 1999-2000 winter snowfall nutrient sampling survey was conducted at three established sampling sites: Aspen Fen, Clear Lake and Whaley (Figure 1). Sampling began on December 22, 1999 and continued following significant snowfall events throughout the winter accumulation period. The final snowfall nutrient survey was conducted on March 17, 2000. Snowfall nutrient concentrations for the three sampling sites located in the Clear Lake Watershed are recorded in Table 1.

Total Ammonia:

Total ammonia concentrations measured at the three sampling sites during the 1999-2000 winter are illustrated in Figure 3. The mean total ammonia concentration ($\text{NH}_3 + \text{NH}_4^+$) in the snowfall samples was 0.278 mg L^{-1} with a standard deviation of 0.168 mg L^{-1} . The coefficient of variation ($C = s / m$) was 0.60 or 60 percent. Total ammonia concentration in snowfall was less than Reid and Wood's observation for total ammonia concentration of 1.0 mg L^{-1} and less than the study objective of 0.667 mg L^{-1} .

The maximum mean total ammonia of 0.690 mg L^{-1} was recorded at the Whaley site on January 4, 2000. Employing the Emerson et al. formula for calculating percentage of free ammonia (NH_3), the maximum concentration of free ammonia was 0.018 mg L^{-1} , a value less than the Manitoba Environment standard of 0.020 mg L^{-1} (Williamson, 1988). The minimum concentration of total ammonia was recorded at Aspen Fen (0.06 mg L^{-1}) on January 4, 2000.

Nitrate Ion (NO_3^-):

Nitrate ion (NO_3^- ; N) concentrations were undetected except at the Whaley sampling site on December 22, 1999. The recorded value of 0.01 mg L^{-1} was less than the specifications of the instrument and considered undetected. During the winter, nitrate and nitrite concentrations are not expected to be significant since nitrification is dependent on temperature (Paton, personal communication).

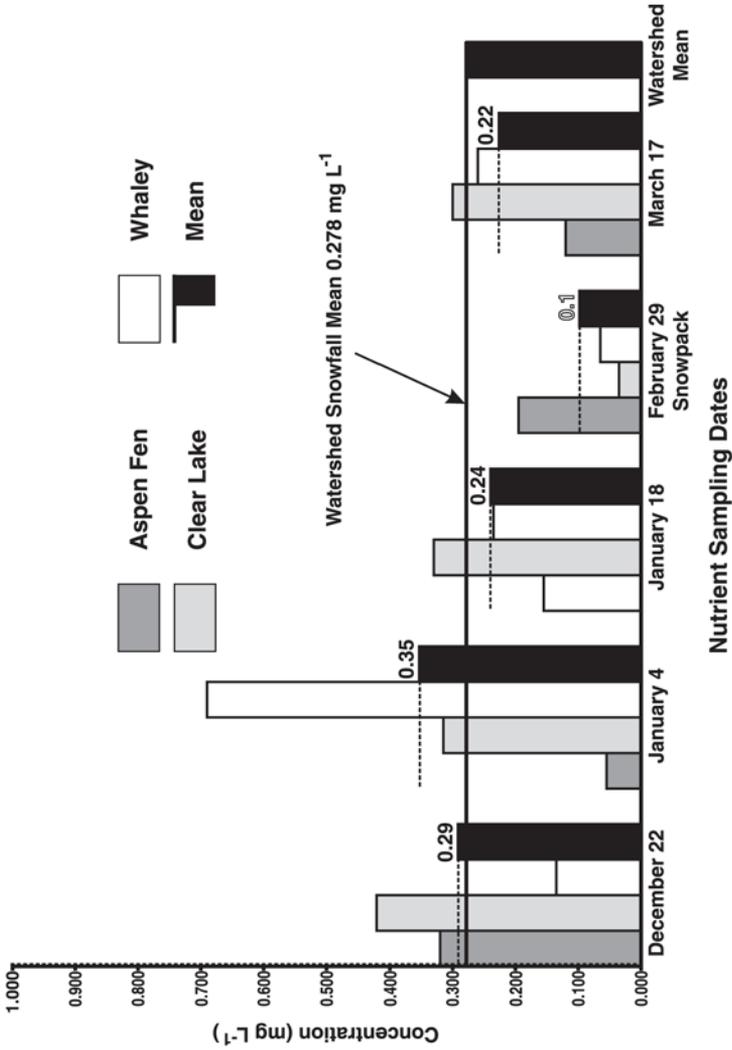


Figure 3: Total ammonia (NH_3 - N + NH_4^+ - N) concentration in snowfall, Clear Lake watershed.

Nitrite Ion (NO²⁻):

The mean nitrite ion concentration recorded for the sampled snowfalls (0.059 mg L⁻¹) was significantly less than the Manitoba Environment standard of 1.000 mg L⁻¹, but greater than Reid and Wood's observation of 0.001 mg L⁻¹ in unpolluted waters. Nitrite ion concentrations were variable with a standard deviation 0.060 mg L⁻¹ and a coefficient of variation equal to 1.02 or 102 percent. A maximum nitrite ion concentration of 0.235 mg L⁻¹ was recorded at the Whaley sampling site on January 4, 2000. The maximum concentration for the watershed was recorded on the same date. Interestingly, the maximum total ammonia concentration also was recorded during the January 4 sampling.

Phosphate (PO⁴⁻):

The mean phosphate ion concentration (PO₄⁻P) in the snowfall samples was 1.280 mg L⁻¹ with a standard deviation of 0.634 mg L⁻¹ (Figure 4). The coefficient of variation was 0.50. Comparatively, the mean phosphate concentration of 1.073 mg L⁻¹ recorded for all samples, snowfalls and the February 29 snowpack, was less than the snowfall mean concentration. The variance and standard deviation (0.722 mg L⁻¹) were greater, a statistic reflected in a 67 percent coefficient of variation.

The maximum mean phosphate ion concentration of 1.945 mg L⁻¹ was recorded at the Whaley site on March 17, 2000 (Figure 4). The minimum concentration of phosphate ion was recorded at Aspen Fen (0.080 mg L⁻¹) on December 22, 1999. Phosphate concentrations were consistently lower at the Aspen Fen highland sampling site. The mean phosphate ion concentration in the winter snowfalls on the Clear Lake watershed were significantly greater than expected and at least two orders of magnitude greater than Manitoba Environment objective of 0.025 mg L⁻¹.

It was hypothesized that the unusually high phosphate ion concentrations in the snowfalls could be attributed to particulate phosphate acting as a nuclei of condensation. Particulate phosphate occurs in both a soluble and insoluble form. The insoluble particulate can be removed by filtration. The 0.45 micron (mm) filter collects the particulate insoluble phosphate while a 0.25 mm

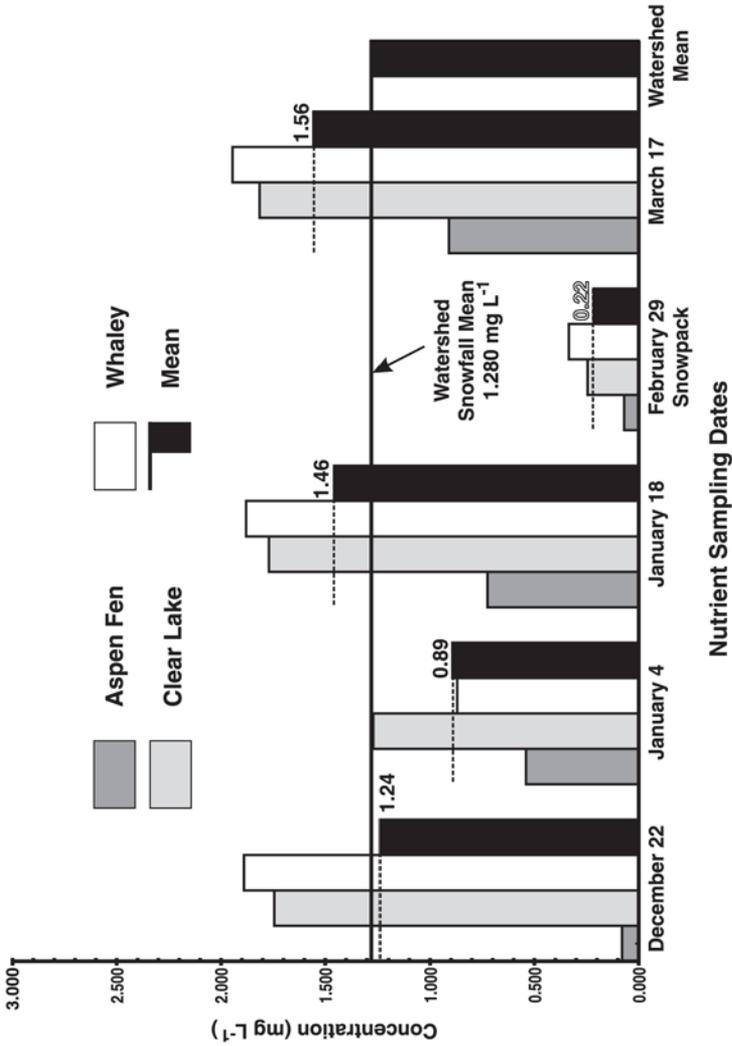


Figure 4: Phosphate ($PO_4^{---}P$) concentration in snowfall, Clear Lake watershed.

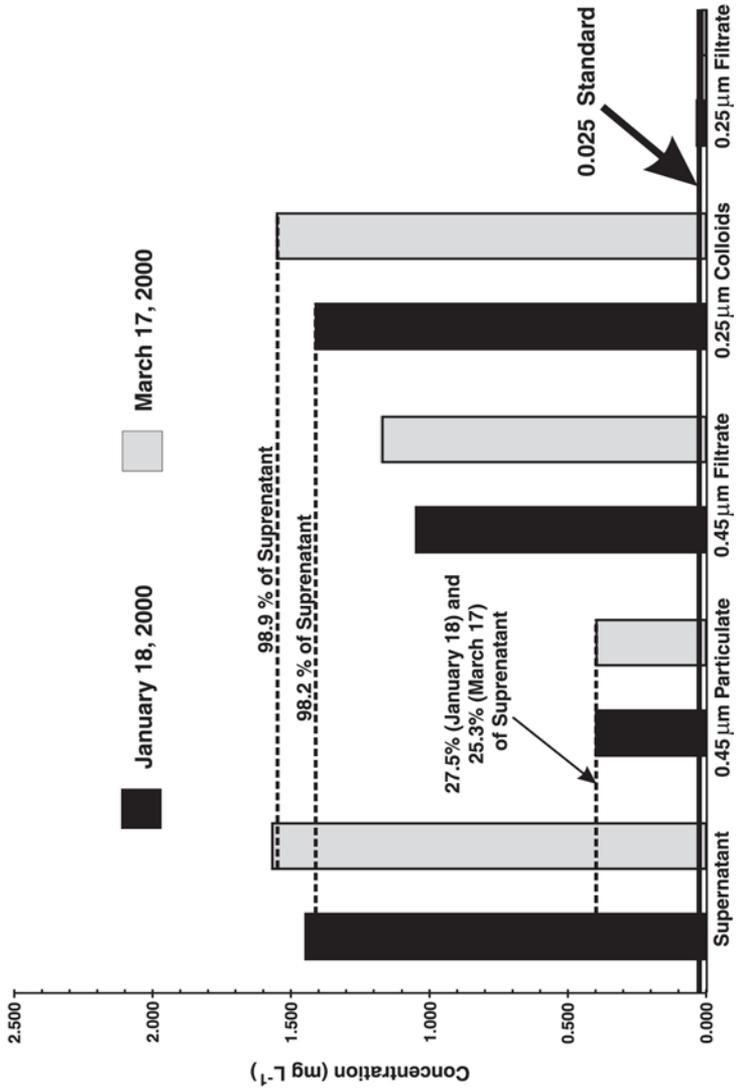


Figure 5: Particulate and colloidal filtration: total available phosphate, Clear Lake watershed.

filter can remove soluble phosphate bonded to colloidal particles. The two step filtration procedure for two snowfall events and the February snowpack sample is summarized in Figure 5.

The phosphate ion concentration was not significantly reduced following the 0.45 mm filtration (Figure 5). Mean concentrations in the snowfall samples remained greater than 1.0 mg L^{-1} .

The 0.25 mm filter successfully removed the particulate phosphate reducing mean sample values to expected values; approximately 0.015 mg L^{-1} (Figure 5). This suggests that the unusually high phosphate concentration found in the Riding Mountain Uplands snowfalls were being deposited in association with colloidal particles.

Conclusion

An unusually high concentration of airborne phosphate is being deposited in snowfall on the Clear Lake Watershed. Approximately 75 percent of this particulate phosphate is soluble and bonded to colloidal particles (Figure 5). The remaining 25 percent is insoluble particulate.

The concentrations of other macronutrients (nitrogen and potassium) do not exceed the recommended guidelines. However the number of snowfalls sampled and the number of sampling sites are too few for a proper scientific study. Further studies are required to evaluate the phosphate depositional loading during the winter on the lake surface.

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