COMPARATIVE DIFFERENCES IN THE CHEMISTRY OF SNOWPACK AND

BULK PRECIPITATION SAMPLES COLLECTED AS SNOW AND RAIN

D.C. Pierson and C.H. Taylor

Department of Geography, Trent University Peterborough, Ontario K9J 7B8

ABSTRACT

Bulk precipitation samples were collected from a small (47.5 ha) watershed near Peterborough, Ontario, throughout the winter and spring of 1980. Snow samples were collected weekly from three shielded gauges placed under differing vegetation, and by snow course sampling just prior to melt. Rain samples were collected at varying intervals, depending on storm frequency and magnitude, from one collector in an open field. The importance of cation sources to the basin and depositional processes within it were deduced from spatial concentration differences in the snowcourse samples, and concentration differences between snowcourse, snow gauge, and rain samples.

Significantly higher concentrations of several cations were found in snowcourse samples collected from forested, rather than open areas. Surprisingly, these cations are most strongly associated with inorganic sources, which seems to indicate that enhanced particle impaction by the forest canopy, rather than organic leaching, resulted in elevated cation concentrations in the snowpack under forest cover. Comparison of all bulk precipitation and snowcourse data found greater concentrations of cations associated with both organic and inorganic sources in the snowpack, which suggests it to be a more efficient collector of particulate matter than the snow or rain gauges. When considering the snowpack concentrations it is impossible to estimate the amount of cations gained from sources internal to the watershed, rather than external from it. The data collected here suggests that the influx of cations, especially those associated with inorganic sources, may be underestimated by gauges which are elevated above the grounds surface. On the other hand, snowpack samples probably overestimate ion inputs as a result of autocthonous contamination.

INTRODUCTION

Rates of ion deposition from atmospheric sources are commonly derived from bulk precipitation measurements, and then used to monitor anthropogenically induced changes in ion loading (e.g. Doveland et al. 1976, Scheider et al. 1979), or to quantify the influx of ions to experimental watersheds (e.g. Likens et al. 1967). Bulk precipitation can be defined as precipitation obtained from collectors which are left uncovered between storms. It therefore, measures both wet and dry depositional processes, since particulate matter which settles onto the collector's surface is washed into the collector by subsequent precipitation. Wet and dry depositional processes are well described by Junge (1963), White and Turner (1970), and Schlesinger and Reiners (1974). Ions deposited by wet processes are removed from the atmosphere either through the incorporation of aerosols into rain and snow as it forms (rainout), or by precipitation scavenging the atmosphere of aerosols as it travels downward (washout). Dry deposition occurs through the gravitational settling of particulate matter (sedimentation) or by the deposition of aerosols onto obstacles which they strike in their normal course of movement through the atmosphere (impaction).

The accuracy of bulk precipitation measurements as a true representation of both Proceedings, Eastern Snow Conference, V. 28, 40th Annual Meeting, Toronto, Ontario, June 2-3, 1983

wet and dry depositional processes is questionable since impaction inputs are underestimated by most precipitation collectors (Miller and Miller 1980). Furthermore, it has been well demonstrated that rain, and especially snow gauges underestimate precipitation amounts as a result of air turbulence near their orifice (Larson and Peck 1974, Goodison 1978). Such gauge inefficiencies will also influence ion catch, especially that resulting from dry deposition, since particles entering the collector would have a much slower settling velocity than wet precipitation and would, therefore, be more strongly affected by gauge aerodynamics.

Collector underestimation of ion deposition has been demonstrated experimentally by Nihlgard (1970) and Miller and Miller (1980) who showed that precipitation gauges covered with plastic netting collected greater amounts of ions than uncovered control gauges. Schlesinger and Reiners (1974) obtained similar results when open buckets containing artificial foliar were used. Schlesinger and Reiners (1974) and Miller and Miller (1980) found the enhanced catch of the experimental gauges to be caused primarily by the coalescence of mist and frost, while Nihlgard (1970) found impaction processes to be of greatest importance. As a result of the type of errors illustrated by these experiments, bulk precipitation measurements may at times lead to serious underestimations of ion influx. For example, by comparing estimated rates of chloride deposition and export (via river discharge) Eriksson (1960) estimated a net loss of this inert element, and found the magnitude of the imbalance to be greatest in forested areas. He attributed these results to enhanced chloride interception by the forest canopy. More recently Gosz (1980) concluded that the major cation input to a mixed conifer watershed was underestimated by up to one order of magnitude for similar reasons.

Bulk precipitation measurements may also overestimate ion deposition to a given area, if ions within that area are incorporated into the precipitation sample. Such errors can be caused by canopy leaching, or from sample 'contamination' by autochthonous organic and inorganic particulate matter.

This paper examines the chemistry of bulk precipitation samples collected from a small watershed near Peterborough in south-central Ontario. Emphasis is placed on examining bulk precipitation collected as snow, since it plays an important role in controlling the flux of ions through the study basin (Pierson and Taylor 1980, Pierson in prep.), and because its chemistry can be examined in more detail than would be the case for rain. The great advantage of studying snow in this respect is that is accumulates within the basin; thus, allowing a large spatially representative sample to be obtained which is devoid of errors associated with collector inefficiency, but which at the same time may show enhanced autochthonous contamination. Direct measurement of wet and dry depositional processes, or of snowpack enrichment are beyond the scope of this study; however, comparison of spatially representatige snow survey data with standard bulk precipitation data should allow the relative importance of these processes to be deduced, and sources of error and contamination to be assessed. The purpose of this paper is to provide such an analysis.

THE STUDY AREA

This study was carried out in the Telford basin: a small (47.5 ha) watershed, located 5.6 km northwest of Peterborough. The bedrock of the area is Ordovician limestone overlain by Pleistocene glacial till, which varies in depth from 2 meters in the lower parts of the catchment to 30 meters in the drumlin which forms the southern drainage divide (Fig. 1). The central part of the catchment is occupied by a swamp which fluctuates in size on a seasonal basis. Soils within the swamp are largely organic mucks and peats. Outside the swamp soils are Otonabee loams (loams and sandy loams) which have a more calcareous composition.

The basin is in rural land use with 50% in forest, 35% in pasture, and 15% in cultivated fields (Fig. 1). It received little use or visitation throughout the duration of this study. The forest is secondary growth and of mixed deciduous-coniferous composition. White cedar is the dominant species having a relative density 1f approximately 50%, as determined by point-quarter vegetation analysis (Cox 1976). The remainder of the forest is composed mainly of deciduous species such as sugar maple, hornbeam, poplar, and birch, although balsam fir and white pine are also present.

The climate of the Peterborough area has been thoroughly described by Adams (1978). Mean annual precipitation is 780 mm and is fairly evenly distributed throughout the year. Normally most precipitation falling from December to March is snow which accumulates in the basin. However, during the winter of this study (1979-1980) above average amounts of rain and below average snowfall prevented a persistent snow cover from developing until 21 January (Fig. 2). The water equivalent of the peak snowpack was well below normal, being only 42% of the average value measured at Trent University during the previous ten years (Adams 1978). The majority of snowmelt occurred during a rain or snow event (76.7 mm rain) that took place between 20 and 22 March. Snow disappeared completely from the open areas by 2 April, and from the wooded areas by 9 April.

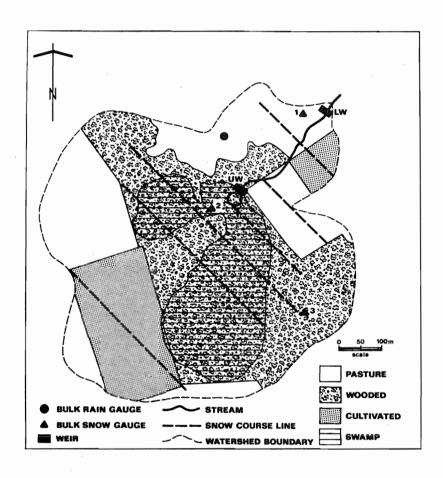
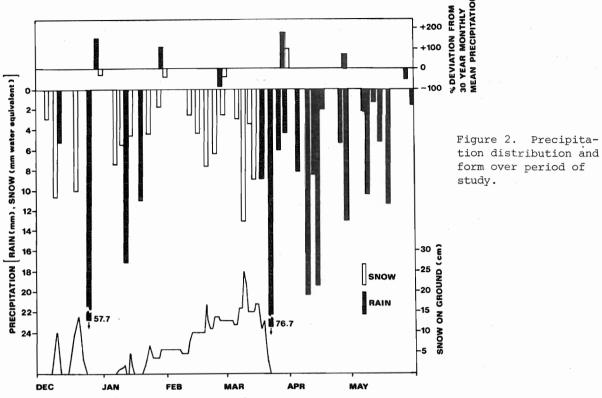


Figure 1. Basin Land Use and Instrumentation

METHODS

Bulk precipitation in the form of snow was collected using three alter-shielded Sacramento storage gauges which were placed under differing vegetation cover as shown in Figure 1. Clean plastic bags were fitted over the gauge orifice so that samples for chemical analysis could be obtained on a weekly basis. Bulk precipitation was collected as rain from one location in an open field (Fig. 1), using the collection system described by Likens et al. (1967). This collector was usually emptied within 24 hours of the end of a storm or series of storms. Only bulk precipitation samples collected between 21 January (the initiation of continuous snow cover) and 19 May (the end of spring streamflow) are considered here. In total, snow samples were collected on five occasions, and rain



samples were collected on ten occasions.

A peak snow survey was carried out on $10\,\mathrm{March}$, ten days prior to the first significant snowmelt event, along the snow course shown in Figure 1. The snow course was designed to run perpendicular to the prevailing winds, and to sample open and wooded areas equally. Sixty nine sample sites were randomly chosen along lines 50 meters long which ran perpendicular to the snow course lines every 35 meters. A Canadian Atmospheric Environment Service (MSC) snow tube was used to obtain snow cores and measure snowpack depth. The cores were placed in clean plastic bags, weighed in the lab, and then stored at $-30\,\mathrm{^{\circ}C}$ until they could be chemically analysed.

All samples were analysed to determine their calcium, magnesium, sodium, potassium, and chloride concentrations; and pH. Snow samples were allowed to thaw overnight and then filtered, as necessary, to remove particulate matter. The pH of all gauge samples was determined within 24 hours of collection, and before filtration. The pH of the snow course samples was similarly determined after thawing. In order to avoid residual junction potential errors (Galloway et al. 1979), standard 1 x 10^{-3} N, 1 x 10^{-4} N, and 1 x 10^{-5} N HCl solutions were used to calibrate the pH meter. All pH measurements were made after a 10 minute equilibrium period in quiesient solutions. Calcium and magnesium concentrations were determined by atomic absorption spectro-photometry, after the addition of lanthanum chloride to the samples. Sodium and potassium were determined by flame emission spectropotometery (APHA 1975, Varian 1978). Chloride was measured by colorometric analysis after the addition of ferric ammonium sulfate and mercuric thiocyanate to the sample (ASTM 1976).

RESULTS OF THE PEAK SNOW SURVEY

The data obtained from the snow survey are presented in Table 1, and show that snow samples from the wooded areas had significantly lower densities and higher calcium, magnesium, and sodium concentrations.

It is somewhat surprising that the depth and water equivalent of the snowpack was similar in both wooded and open areas, as one would expect spatial variations in wind, interception, and solar radiation to lead to significant differences in the snowpacks

physical properties (e.g. Adams 1976). Perhaps the unusually short period of snow accumulation prevented spatial variations in snowpack depth and water equivalent by limiting the cumulative affects of the above environmental parameters. Since no significant difference between snow depth or water equivalent was found, the apparent differences in density is probably meaningless, resulting from a fortuitous reduction in variance when snow core depths and weights were transformed into densities.

TABLE 1. RESULTS OF T TEST COMPARING SNOW COURSE SAMPLES FROM FIELD AND WOODED AREAS

Number of Standard Level of Significant											
Parameter		Samples	Mean	Standard Deviation	Level of Significant Difference						
rarameter		Samples	Mean	Deviation	Difference						
H ⁺	Open	20	11.61	1.8	No difference						
(micro eq/liter)	Wooded	36	12.06	9.1	NO difference						
(micro eq/irter)	Total watershed	56	11.84	9.1							
	Total watershed	50	11.04								
Ca ⁺⁺	Open	28	128.24	34.9	5%						
(micro eq/liter)	Wooded	36	150.70	48.4	36						
(MICIO eq/IICEI)	Total watershed	64	138.22	40.4							
	Total watershed	64	130.22								
Mg ⁺⁺	Open	32	13.16	3.8	1%						
(micro eq/liter)	_	32 37	18.10	10.7	1.9						
(micro eq/iiter)	Total watershed	69	15.63	10.7							
	iotal watershed	69	13.63								
Na ⁺	Onon	32	12 05	6.1	1.0						
	Open Wooded	32 37	13.05		1%						
(micro eq/liter)			19.57	10.4							
	Total watershed	69	16.53								
K ⁺	0	2.0	15.00	2.1	31.55						
	Open	32	15.09	3.1	No difference						
(micro eq/liter)	Wooded	37	14.58	3.3							
	Total watershed	69	14.83								
Cl -											
	Open	15	33.28	7.1	No difference						
(micro eq/liter)	Wooded	20	31.87	12.1							
	Total watershed	35	32.72								
,											
Depth	Open	32	24.0	3.4	No difference						
(cm)	Wooded	37	25.0	5.1							
	Total watershed	69	24.5								
Water equivalent	Open	32	45.0	7.5	No difference						
(mm)	Wooded	37	42.6	12.5							
	Total watershed	69	43.8								
	.*										
Density	Open	32	0.19	0.018	1%						
(g/cm^3)	Wooded	37	0.17	0.027							
	Total watershed	69	0.18								
	*										

There are numerous observations, for both coniferous and deciduous forests, which show the cation concentration of rain to increase as a result of passing through the canopy (Madwick and Ovington 1959, Abrahamsen et al. 1976, Feller 1977, Brinson et al. 1980). The same phenomenon has also been observed to enrich the ionic concentrations of snow by Wolfe (1980) and Fahey (1979). Wolfe (1980) found higher potassium concentrations in wooded areas of the Kawartha heights basin in Peterborough, while Fahey (1979) found snow from wooded areas in southeastern Wyoming to be enriched in sodium, potassium, calcium and magnesium. Presumably enrichment of precipitation results from the combined effects of canopy leaching, and the washing and desolution of particulate matter from the canopy's surface.

The research of Eaton et al. (1973) with deciduous vegetation, and Feller (1977) with coniferous vegetation have both shown that potassium is leached from the forest

canopy in greater quantities than calcium, magnesium or sodium. It therefore, seems unlikely that canopy leaching is the major cause of spatial differences in snow cation concentrations between open and wooded areas since potassium, a readily leachable element, does not show a significant difference between areas, while less mobile elements do. Also, canopy leaching would probably be diminished in the winter as a result of lower temperatures and the form of the precipitation.

Calcium and magnesium are the major constituents of the calcareous dust associated with the geology of this area. The impaction of dust onto the forest canopy, therefore, seems a plausible mechanism to explain differences in the concentrations of these elements in the snow. The concentration differences of sodium, an element present in limestone in only trace quantities (Pettijohn 1957), may similarly result from enhanced aerosol interception by the forest canopy. These aerosols would largely be of oceanic origin.

A COMPARISON OF THE IONIC CONCENTRATIONS OF PRECIPITATION COLLECTED AS SNOW AND RAIN

The data in Table 2 and Fig. 3 allow the ionic concentrations of precipitation collected as snow, by the snow gauge and snow course samples, and as rain to be compared. The snow course values are based on the data in Table 1, while the snow and rain gauge values are average concentrations which were weighed by precipitation depth. In the case of the snow gauge data, samples collected on one occasion had pH values greater than 5.0 (5.94 - 6.61), which shows bicarbonate to be present (assuming equilibrium with atmospheric carbon dioxide). The snow gauge hydrogen concentrations were accordingly adjusted to take into account the neutralizing effect of bicarbonate (Reuss 1975). The snow gauge values shown in Table 1 were calculated by averaging the weighted mean concentrations of the individual gauges, in the hope that a reasonable representation of the quantity and chemistry of snow entering the basin could be obtained. Since the mean snow gauge catch is similar to the snowpacks water equivalent, as measured by the snow course, this seems to have been a fair assumption.

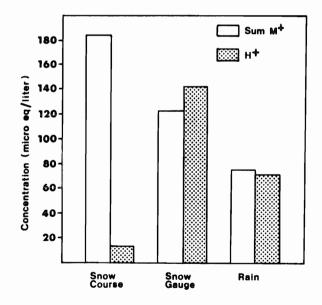


Figure 3. Ionic Composition of snow course, snow gauge, and rain samples.

Figure 3 shows that the metal cation concentrations of the snowpack were higher than those of the snow collected by the gauges. The opposite was true for hydrogen; it decreased dramatically between snow gauge and snow course measurements. Comparison of snow and rain data show that precipitation samples collected by both snow and rain gauges were of similar ionic composition, although the snow samples had somewhat higher concentrations. The data in Table 2 generally follow the pattern illustrated by Figure 3, with the exception of potassium which undergoes a particularly large decrease in concentration between snow course and gauge values.

Since the snow gauges' concentrations were weighted by the amount of snow collected during a sampling interval, a rough correspondence between gauge and snow course concentrations would be expected. The fact that this does not occur can be accounted for by two possible explanations. One is that the snow pack is a more efficient collector of particulate matter than the gauges, and the other is that reactions occurring within the snow pack, prior to sampling, altered its chemical composition.

Since only one of the snow gauges was under dense forest cover it seems possible that the gauge collected data may not have been spatially representative of the actual snowpack. As a result the gauges probably underestimated the quantity of particulate matter entering the snowpack which was derived from the forest canopy. Also, the particulate matter and aerosol catch of the gauges must have been limited by aerodynamic factors. The snow gauges are an obstacle to horizontal air movement. Air striking them is deflected upward, thereby increasing turbulence near the gauge orifice (Larson and Peck 1974) and limiting their catch of particulate matter. The alter shields surrounding the gauges would improve the catch somewhat, but they are not very efficient even for snow (Goodison 1978), which would have a much greater settling velocity than most particulate matter. It therefore seems certain that the gauges must undercatch particulate matter, and aerosols, relative to what actually hits the ground and is incorporated into the snowpack.

The actual organic and inorganic particulate matter concentrations of the snow were not measured, but observations showed that almost all snow cores contained particulate matter, especially organic particulate matter. Since potassium is readily leached from organic matter (Attiwill 1968, Eaton et al. 1973) the potassium concentration of the snowpack was greatly increased relative to the snow gauge data (Table 2). Hornbeck and Likens (1974) obtained similar results which also appeared to be caused by organic leaching within the snowpack.

The leaching of potassium from organic matter within the snowpack may have been overestimated to a certain extent since it was impossible to remove this material prior to

TABLE 2. COMPARISON OF THE IONIC CONCENTRATIONS OF PRECIPITATION COLLECTED AS RAIN AND SNOW

	Concentration (micro eq/liter)								
Precipitation Type	Water mm	Hydrogen	Calcium	Magnesium	Sodium	Potassium	Sum Metals	Chloride	
Snow (course) 1	43.8	11.84	138.22	15.63	16.53	14.83	185.21	32.72	
Snow (Gauge) 2	37.8	144.24	91.98	10.92	17.13	3.17	123.20	29.36	
Rain ³	193.4	72.17	42.87	5.87	24.87	2.23	75.84	9.50	
Percent change between snow gauges and snow course	15.9	- 91.79	50.27	43.13	-3.50	367.82	50.33	11.44	

l Mean values for entire watershed

 $^{^2}$ Average of weighted mean concentrations from 3 gauges under differing vegetation

Weighted mean concentrations

melting a snow sample. The organic matter was, therefore, suspended in the melt water for several hours before it was removed by filtration, which may have led to enhanced leaching relative to what would occur under actual field conditions. It was originally thought that the differences in ionic concentrations found by the snow course might simply be due to the leaching of greater concentrations of organic matter in snow from wooded areas. This hypothesis was rejected since potassium, the most mobile of elements, showed no difference in concentration.

The snow course samples had higher calcium and magnesium concentrations relative to the snow gauge samples also as a result of the snowpack's apparently greater efficiency at collecting particulate matter. In this case it seems likely that the leaching of calcareous dust was of greater importance than organic leaching. The acidic snow found here would be especially effective at bringing carbonates into solution.

This reaction with carbonates and ion exchange reactions with organic matter provides one explanation of the reduced hydrogen concentration in the snow course samples. However, this can only be of limited importance since the increase in metal cations is much less than the decrease in hydrogen (Fig.). The most probable process leading to such a large reduction in hydrogen concentration would be the leaching of hydrogen from the snowpack during minor snowmelt episodes. Prior to the snow course sampling no snowmelt occurred which was significant enough to cause runoff, but there were several rain-on-snow events and short periods of above freezing temperatures. These would likely have led to a sequence of thawing, leaching, and refreezing, which would result in significant translocation of hydrogen ions from the snowpack to the soils below (Johannesson and Henriksen 1978). Johannes et al. (1980) have documented seasonal decreases in snowpack hydrogen concentration for, what appears to be, similar seasons.

Sodium and especially chloride are both conservative elements being present in calcareous rock (Pettijohn 1957, Johns and Huang 1967) and vegetation (Gosz et al. 1973) in relatively small quantities. Particulate matter incorporated into the snowpack would, therefore, have little influence on the snows sodium or chloride concentrations, which explains the similarity of snow course and snow gauge concentrations for these elements.

CONCLUSIONS

Predictions of snowpack ion concentration based on gauge collected bulk precipitation samples, in many cases deviated greatly from the actual snowpack concentrations, measured by peak snow course sampling. Such discrepancies can be attributed to several factors:

- Gauge inefficiency in sampling aeolian ion inputs, especially those associated with sedimentation and impaction processes,
- Autocthonous contamination of the snowpack. Organic ion sources seem to be particularly important in this regard,
- Translocation of ions out of the snowpack by small snowmelt events which were minor in hydrologic terms.

Spatial comparisons of snowpack samples collected from open and wooded areas indicates that the forest canopy enhances ion input, by providing a large surface area which effectively intercepts aerosols.

The results of this study suggest that snow sampling programs which include chemical analyses, should be thoughtfully taylored to the objectives of the investigation. Using hydrogen as an example to illustrate this point, it is clear that the results obtained will depend largely on the sampling regime. If hydrogen inputs to an area are of interest it would be best to sample with bulk precipitation gauges. On the other hand, if the influence of spring snowmelt on stream or soil chemistry is to be determined, then peak snowpack sampling would be most appropriate.

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