

## The Hydrological and Hydrochemical Response of A Small Canadian Shield Catchment to Late Winter Rain-on-Snow Events

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### ABSTRACT

A study was undertaken during the winter of 1990/1991 in a small (3.7 ha) Canadian Shield catchment to examine the hydrological and hydrochemical response during rain-on-snow events. This paper presents the results of two large (37.9 and 34.6 mm) rain-on-snow events occurring in early and late March, 1991. Peak and total runoff, and groundwater response from the two events are significantly different. Hydrologic data indicate that these differences can be attributed to a combination of meteorological (temperature) and physical conditions (antecedent snowpack ripeness, soil moisture and groundwater levels). An immature snowpack (low temperature and density) combined with low antecedent soil moisture conditions significantly reduced the magnitude of the net hydrologic input and runoff from the catchment during the early March event, whereas a much more mature snowpack and high antecedent soil moisture conditions led to a large runoff event during late March.

During both rain-on-snow events a significant portion of the pre-event snowpack chemical load was lost. Based on the maximum snowpack chemical load measured prior to the events, the two large rain-on-snow events and a brief mid-March warm period during which there were two much smaller rain-on-snow events removed 78% of the hydrogen ion and 63% of the sulphate and nitrate load from the snowpack, while only reducing snowpack water equivalence by 7%. A two component (rain and snowmelt) isotopic ( $\delta^{18}\text{O}$  SMOW ‰) separation of snowmelt lysimeter water during the two events indicated that snowmelt was an important (50 and 65%

respectively) water source available for infiltration and runoff at the snow-soil interface. Considering the high hydrogen ion loadings to the catchment during these two events (3.3 and 3.0 meq  $\text{m}^{-2}$  respectively) streamflow pH was not significantly reduced due to an increase in the discharge of well buffered groundwater. A two component isotopic hydrograph separation of peak stream discharge during the March 2-3 event indicated that 75% of the total flow was groundwater. In mid latitude acid sensitive catchments, winter rain-on-snow events are an important hydrological occurrence due to their ability to elute much of the chemical load ( $\text{H}^+$ ,  $\text{SO}_4$ ,  $\text{NO}_3$ ) from the snowpack prior to the onset of spring melt when the maximum annual hydrologic input typically occurs.

**KEYWORDS:** rain-on-snow, snowmelt, groundwater, forested catchment, stream flow, preferential elution

### INTRODUCTION

While the effects of spring snowmelt on watershed hydrology and hydrochemistry have been the subjects of numerous studies in eastern North America (e.g. Bottomley, 1984, 1986; English *et al.*, 1986; Kerekes *et al.*, 1986; Nichols and McRoberts, 1986; Semkin *et al.*, 1988; Wels, 1991) and throughout Europe (e.g. Wieting, 1986; Tranter *et al.*, 1986; Tsiouris *et al.*, 1985) the interaction between snowmelt, infiltration, and runoff quantity and quality remain poorly understood (Price *et al.*, 1978; Goodison *et al.*, 1986). The presence of rain during the period of

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main snowmelt is regarded as a further complicating factor due to the difficulty in predicting runoff, as well as in interpreting snowmelt chemistry. One particularly complex winter phenomena which commonly occurs in the region of central Ontario are mid to late winter rainfall events over relatively thick snowpacks. For any given catchment stream runoff from a rain-on-snow event can range from zero increase to very large floods (Gerdel, 1945; Colbeck, 1975). Analyses of twelve rain-on-snow events in the forested areas of the Sierra-Nevada showed that, in over half the events, the water equivalent of the snowpack (SWE) either stayed the same or increased (Kattelman, 1987).

The physical variables which control the magnitude of runoff from a mid to late winter rain-on-snow event: the amount and intensity of rainfall input, the ambient air temperature, the depth and maturity (density, temperature) of the snowpack, and the antecedent soil moisture conditions in the catchment, need to be clearly understood to determine the hydrologic response of catchment (Colbeck, 1975). In catchments where groundwater discharge and perennial streamflow occur throughout the year, variable antecedent soil moisture conditions may be a crucial factor in determining the hydrologic response to rain-on-snow events. The ability of the groundwater flowsystem to respond to any rain/snowmelt infiltration can also be limited by the presence of ground frost, or ice lens in the snowpack which can divert meltwaters downslope through the snowpack (English *et al.*, 1986). The timing of groundwater and stream response to a rain-on-snow event is highly dependent on the maturity of the snowpack. Colbeck (1975) illustrated that the lag time for water exiting the base of a 1 m thick immature snowpack during an intensive 36 mm/hr<sup>-1</sup> input of rain at the snow surface was 2 hours, whereas lag time for the same depth of ripe snowcover was only 8.8 minutes.

The hydrochemical response of a catchment to a rain-on-snow event can be equally, if not more, complex due to the highly variable hydrologic response and the potential effect of preferential elution of ions from the snowpack. The preferential elution of major ions, especially sulphate, nitrate and H<sup>+</sup> from the snowpack during the early stages of snowmelt can greatly enrich runoff waters (Johannessen *et al.*, 1975; Tsiouris *et al.*, 1985). Up to 80% of the chemical

load of the snowpack can be released during the first 20 to 30% of melt (Johannessen *et al.*, 1975; Johannessen and Henriksen, 1977). Sulphate, nitrate and hydrogen ions have the fastest removal rates from a snowpack (Tsiouris *et al.*, 1985; Tranter *et al.*, 1986). Sulphate is a surface-adsorbed aerosol on the snow grain, thereby making it readily available to infiltrating snowpack meltwater (Jones and Stein, 1990). Jones and Stein (1990) report that in the first 5% of snowpack melt the ionic concentration of meltwaters is five times that of the bulk snowpack, while Semkin and Jefferies (1988) reported initial meltwaters containing ten times the concentration of the bulk snowpack. Jones and Bedard (1987) suggest that the initial meltwaters from a snowpack of pH 4.5 may produce meltwater pH's as low as 3.7. The chemical enrichment of surface runoff waters (i.e. increased specific conductance and decreased pH) during early periods of snowmelt is often observed in catchments underlain by shallow soils and glacial tills, or poorly buffered soils (Morris and Thomas, 1985; Barry and Price, 1987).

The impact of rain-on-snow events on snowpack and meltwater chemistry is unclear. Jones and Stein (1990) indicate that rain events can contribute to the total chemical load of the snowpack, whereas Dewalle (1987) suggests that rain-on-snow events would reduce the snowpack chemical load due to percolation of rainfall through the snowpack and snowmelt. Schemenauer *et al.* (1985) presented data that clearly show how an early February rain-on-snow event rapidly diluted the chemical composition of the snowpack by washing out much of the sulphate, nitrate, and hydrogen ions. In a study of a shallow till basin in northern Ontario four rain-on-snow events which accounted for only 18% of total meltwater runoff resulted in 50% of the hydrogen and sulphate, and 37% of the nitrate ions exported from the snowpack (Semkin and Jefferies, 1986). During two of the rain-on-snow events stream alkalinity was reduced by 40 and 57%.

The impact of enriched snowmelt/rain water infiltrating the soils and tills of a Canadian Shield catchment with deeper glacial tills and an unconfined aquifer contributing to streamflow is not fully understood. Bottomley *et al.* (1984, 1986) suggest that in catchments where groundwater discharge plays a large role in generating stream runoff it is the chemical

composition of groundwater, not the snowmelt and rain water that exerts the primary influence over stream runoff chemistry during spring melt. To model stream runoff chemistry during a rain-on-snow event it is essential to understand the chemical changes that occur within the snowpack, and the hydrologic processes and antecedent conditions that determine the sources of water and the hydrologic flowpaths of stream discharge.

To address the hydrological and hydrochemical effects of rain-on-snow events a study was undertaken in a small catchment located in central Ontario. In this paper two large rain-on-snow events are analysed to address two specific objectives: 1) determine the key hydrological and hydrochemical processes operating in a first order catchment during rain-on-snow events, and 2) examine the role of variable antecedent snowpack and soil moisture conditions on catchment response.

## 2. STUDY SITE

The study was conducted in a small headwater catchment (Harp 4-21, 3.7 ha) located within the Harp Lake watershed (45° 25' N 79° 10' W) in the Muskoka-Haliburton region of central Ontario (Figure 1). This extensively instrumented and monitored catchment has been the focus of considerable research on groundwater-surface water interactions and streamflow generation (Dankevy, 1989; MacLean, 1992; Hinton *et al.*, 1993, 1994). All of the basins and catchments located within the Harp Lake watershed are currently being monitored and sampled by the Ontario Ministry of Environment and Energy's (MOEE) (Dillon *et al.*, 1978; 1988). An automated meteorological station is situated approximately 1 km from the Harp 4-21 catchment. The mean annual precipitation of the region is 1033 mm (1976-89) (MOEE unpublished data), with approximately 26% falling as snow.

The topography of the catchment is characterised by a long northeasterly facing hillslope which comprises the majority of the total catchment area (Figure 1). Bedrock geology in the Harp Lake region consists of granitized biotite and hornblende gneiss (Jefferies and Snyder, 1983). A relatively thick layer of glacial overburden was deposited over the bedrock throughout much of the area. Geophysical surveys conducted in the Harp 4-21 catchment identified overburden depths ranging from 1 to 3 meters in near-stream areas to 15 meters in the

upper reaches of the catchment. The overburden is composed of a heterogeneous mixture of medium to fine sands, and silty sand (Dankevy, 1989).

An unconfined aquifer in the glacial overburden maintains perennial flow to the stream in the lower reaches of the catchment. A detailed description of the hydrogeology can be found in Dankevy (1989) and Hinton *et al.* (1993). The maximum depth to water-table in the hillslopes of the basin generally occurs in late summer - early fall. The water-table in the near-stream areas generally exhibits low seasonality and is usually within 0.80 m of the soil surface.

The soils of the Harp 4-21 catchment are of the Podzolic order, with soil development limited to the upper 0.70 - 1.00 m of surficial material. A typical soil profile in the catchment consists of a thin (5 cm) organic horizon (L, F, H), a humic-rich Ah mineral horizon which averages 10 cm in thickness, and a sandy to silty loam Bhf/Bc horizon which averages 55 cm in thickness. In lower slope areas adjacent to the stream, the B horizon soils exhibit a gleyed or mottled appearance. The B soil horizon is sporadically underlain by a highly compact (densipan) C horizon.

The catchment is entirely covered with a mixed deciduous and coniferous forest including Sugar Maple (*Acer saccharum*), Yellow Birch (*Betula alleghaniensis*), Eastern Hemlock (*Tsuga canadensis*), and Balsam Fir (*Abies balsamea*).

## MATERIALS AND METHODS

### 1. Meteorological and snowpack data

Hourly rainfall, air temperature, and bulk (wet and dry) precipitation chemistry data for the Harp 4-21 catchment were obtained from the automated meteorological station (MOEE unpublished data). The water equivalent of the snowpack (SWE), and detailed measurements of snow layering and density were determined at several sites within the Harp 4-21 catchment. Using the time profile site technique (Adams and Barr, 1974; English *et al.*, 1987) measurements of total snow depth, snow layer depth and density, and total SWE were obtained at a centrally located site in the catchment (Figure 1). In addition to the data collected at the time profile site, SWE data was also available from three snow survey sites (HPST14, HPST16, HPSZ07) in the Harp 4-21 catchment (MOEE, 1993). At these snow survey sites the mean SWE was determined by extracting

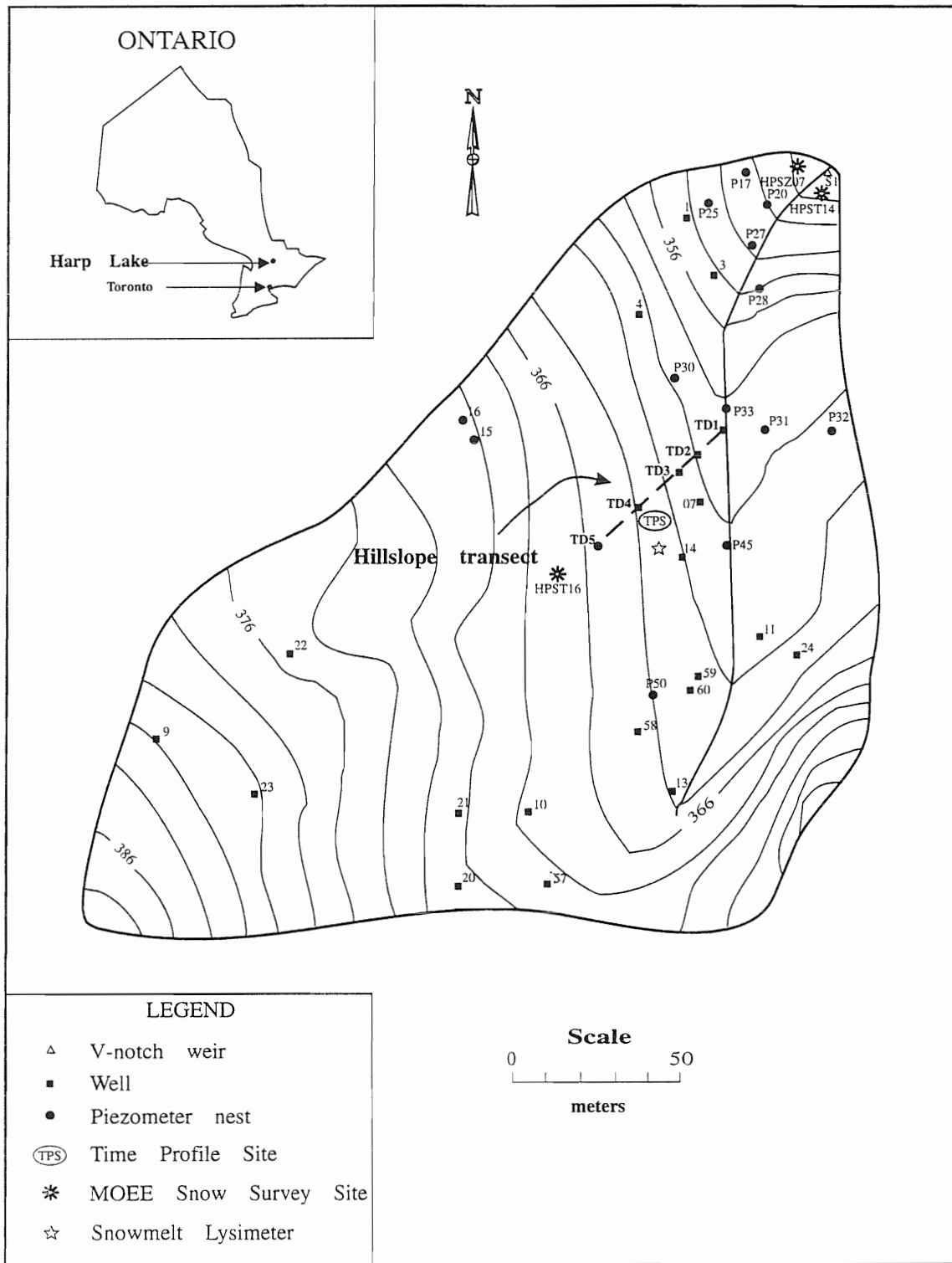


Figure 1. Instrumentation of the Harp 4-21 basin.

three vertical cores of snow using a Utah snow corer (7 cm I.D.), and weighing the samples in the field with a calibrated spring scale. Before and after event SWE measurements from the time profile site (TPS) and the three MOEE sites, and rainfall data from the meteorological station are used to derive a snowpack water balance. The results of the snowpack water balance were used to identify the positive or negative SWE change, and the net amount of water available for infiltration/runoff at the soil surface.

## 2. Discharge

Total runoff from the Harp 4-21 catchment was measured at a heated v-notch weir (90°) located at the basin outflow (site S1, Figure 1). Stage was measured in a stilling well using a Stevens Model F-1 water level recorder. Throughout each runoff event manual measurements of discharge were taken to verify the accuracy of the rating curve for this weir.

## 3. Groundwater levels and soil moisture

The response of the groundwater flow system in the Harp 4-21 catchment was determined at a number of wells and piezometers distributed throughout the basin (Figure 1). A detailed record of water-table fluctuations and soil moisture data was obtained from five stations located along a hillslope transect, that extended from the stream edge to a point approximately midway up the north easterly facing hillslope. Based on water-table measurements throughout the 1990-1991 hydrological year the mean depth to water-table along this transect ranges from 0.30 m (n=94) at station TD2 to 1.69 m (n=144) at station TD5. These stations represent the vadose zone boundary conditions, as defined by the depth to water-table and soil moisture content, within which typical precipitation event inputs (10 - 50 mm) result in measurable water-table responses. In the higher hillslope reaches the vadose zone is sufficiently thick that most individual precipitation events do not lead to significant water-table responses.

Water levels in the groundwater wells and piezometers were measured before, during and after each rain-on-snow event using either an electronic water level tape or calibrated ping-pong ball floats similar to those used by Abdul and Gillham (1989). The frequency of measurement was especially critical in the lower slope and near-stream areas where rapid water-table response

occurs due to the capillary fringe effect (Gillham, 1984; Novakowski and Gillham, 1988).

Soil temperature measurements in the Harp 4-21 basin were obtained from an instrumented soil pit located approximately half way up the hillslope transect near groundwater/soil moisture station TD4 (Figure 1). Soil temperatures at three different points in the soil/glacial till profile (0.15, 0.40, 0.85 m) were measured using Campbell Scientific 107 temperature probes connected to a 21X datalogger. Temperatures were measured every hour, averaged and recorded every four hours. The soil/till temperature data made it possible to determine the presence or absence of ground frost, which in turn can be very useful in interpreting water-table response data.

Soil moisture conditions along the hillslope transect were determined at each of five stations located adjacent to groundwater wells (Figure 1). Time domain reflectometry (TDR) was used at each hillslope groundwater/soil moisture station to determine the *in situ* soil volumetric water content ( $\theta$ ) at specific depths in the upper 0.80 m of vadose zone before, during and after each rain-on-snow event. At each station three twin wire waveguide pairs (l=300 mm) were inserted horizontally at different depths into the upslope face of an excavated soil pit. Horizontal installation of waveguide pairs was chosen so that the calculated soil water contents ( $\theta$ ) would be representative of a specific depth in the soil profile (Topp *et al.*, 1982; Baker and Lasano, 1989). Furthermore, the saturated water content ( $\theta_{sat}$ ) from any waveguide pair could be accurately determined when water level data from the adjacent groundwater well indicated that the water-table had risen over top of the specific waveguide pair.

The waveform trace from each of the waveguide pairs was obtained using a Tektronix 1502C cable tester (TDR). Using an IBM compatible computer program (WCGR, 1989) the waveform trace was transferred from the 1502C, via the SP232 serial interface to a portable computer. The waveform trace from each of the waveguide pairs was later analyzed for the dielectric constant, and the volumetric water content ( $\theta$ ) using the Topp *et al.* (1980) calibration equation. Repeatability of the analysis procedure for any given waveform trace was within  $\pm 0.015$  ( $\theta$ ). As pointed out by Baker and Allmaras (1990) the analysis of waveform traces by a computer can reduce the potential human error and/or bias

involved in the determination of the initial and reflected pulse (start and end point).

#### 4. Hydrochemistry

Chemical and isotopic analyses were performed on samples of snow, snowmelt runoff, and streamwater. Bulk snowpack chemistry samples were collected at the same time snowpack water equivalent was determined at each of the MOEE snow survey sites in the Harp 4-21 catchment (MOEE, 1993). Snow samples obtained in a clean plexiglass coring tube were melted and then analysed for major ions, pH and specific conductance at 25 °C (COND25) using standard methods of the Ontario Ministry of Environment and Energy (Janhurst, 1993). Bulk snowpack samples extracted from the time profile site before and after each rain-on-snow event were melted and analysed for  $\delta^{18}\text{O}$  SMOW (‰).

Samples of snowmelt/rain exfiltrating the base of the snowpack during the rain-on-snow events were obtained from a snowmelt lysimeter located at the midway point of the hillslope transect (Figure 1). The small snowmelt lysimeter (2.5 m<sup>2</sup>) with 15 cm high walls was constructed of wood and lined with plastic sheeting. The plastic sheeting was cleaned with deionized water prior to accumulation of the winter snowpack in early December. The lysimeter drained by gravity into a clean one litre collection bottle. Samples were collected throughout the period of rainfall and snowpack drainage, and were analysed for pH, specific conductance and  $\delta^{18}\text{O}$ .

Streamwater samples were collected from S1 prior to each of the March 1991 rain-on-snow events, and throughout the runoff hydrographs. All samples were field-filtered using a 100 micron NITEX filter to remove larger suspended sediment and organic matter. With the exception of NO<sub>3</sub> streamwater samples were analysed for the same chemical and isotopic parameters as the snow and snowmelt lysimeter.

Isotope ( $\delta^{18}\text{O}$ ) results will be used in two ways. Firstly, data from the snowpack, rainfall and snowmelt lysimeter will be used to calculate the proportions of rain and snowmelt in water exiting the base of the snowpack:

$$x_{\text{snow}} = [(Cl - Cr)/(Csb - Cr)] \times 100 \quad (1)$$

where:

$x_{\text{snow}}$  = is the percentage of snowmelt water in snow lysimeter

$Cl$  = is the  $\delta^{18}\text{O}$  of snowmelt lysimeter sample, or calculated from isotopic mass balance of snowpack  
 $Cr$  = is the  $\delta^{18}\text{O}$  of rainfall  
 $Csb$  = is the  $\delta^{18}\text{O}$  of the antecedent snowpack

The second use of isotope data is to calculate the groundwater component of peak stream flow using a two component flow separation model:

$$Qg = Qs[(Cs - Ce)/(Cg - Ce)] \quad (2)$$

where:

$Qg$  = is the discharge of old water (groundwater & soil water) in the stream at S1  
 $Qs$  = is the discharge of the stream at S1  
 $Cs$  = is the  $\delta^{18}\text{O}$  of streamflow at S1  
 $Ce$  = is the  $\delta^{18}\text{O}$  of the snowmelt lysimeter  
 $Cg$  = is the  $\delta^{18}\text{O}$  of old (groundwater) water, the value of stream baseflow at S1

## RESULTS AND DISCUSSION

### 1. Hydrology

The snowpack water balances resulting from the March 2-3 and March 27-28, 1991 rain-on-snow events are summarised in Table 1. While Table 1 identifies considerable SWE variation within and amongst the four sites on any given sampling date, the data clearly show that the snowpack reacted very differently to the two rain-on-snow events. Following the March 2-3 rain-on-snow event three of the four snow survey site indicated an increase in SWE, (mean of 4.7 mm, n = 4), whereas the March 27-28 balance identifies a 19.0 mm SWE loss. Even though the total rainfall inputs for the March 2-3 and March 27-28 events were similar (37.9 and 34.6 mm respectively) the net amount of water calculated to be available for infiltration (rainfall ± change in SWE storage) is quite different (33.2 and 53.6 mm respectively). This difference can be directly attributed to the air temperature associated with each of the two events, and, perhaps more importantly the antecedent snow density and thermal characteristics (i.e. maturity of the snowpack). Prior to March 2, the snowpack in the Harp 4-21 basin had not been subjected to any significant warming periods or rain-on-snow events.

**Table 1. Water balance of the snowpack (mm) resulting from the March 2-3 and March 27-28, 1991 rain-on-snow events.**

Event	Snow Survey Site	(a) Before (Feb 20)	(b) Before (Feb 27)	(c) After <sup>1</sup> (March 4)	SWE Change (c-b)
March 2-3, 1991	HPST14	143.9 (± 2.6)	148.5 (± 7.4)	136.6 (± 14.3)	- 11.9
	HPST16	164.5 (± 3.5)	164.5 (± 4.8)	170.6 (± 8.3)	+ 6.1
	HPSZ07	153.8 (± 3.5)	161.5 (± 6.1)	166.1 (± 17.3)	+ 4.6
	TPS <sup>2</sup>	163.8 (± 2.9)	167.9 <sup>3</sup> (na)	187.8 <sup>4</sup> (± 2.5)	+ 19.9
	Mean	156.5 (± 8.4)	160.6 (± 7.3)	165.3 (± 18.4)	+ 4.7 (± 11.3)
	Water available for infiltration = Rainfall -/+ change in SWE = 37.9 - 4.7 = 33.2 mm ± 11.3				
March 27-28, 1991	Snow Survey Site	Before (March 21)	Before (March 25)	After <sup>5</sup> (March 28)	SWE Change (c-b)
	HPST14	172.2 (± 13.0)	170.6 (± 11.5)	137.8 (± 11.3)	- 32.8
	HPST16	160.7 (± 13.4)	151.5 (± 20.8)	128.6 (± 19.8)	- 22.9
	HPSZ07	156.1 (± 20.8)	168.3 (± 2.3)	155.4 (± 7.0)	- 12.9
	TPS	na	182.7 (± 4.3)	175.4 (± 1.5)	- 7.3
	Mean	163.0 (± 6.8)	168.3 (± 11.1)	149.3 (± 17.9)	-19.0 (± 9.7)
	Water available for infiltration = Rainfall -/+ change in SWE = 34.6 + 19.0 = 53.6 mm ± 9.7				

\* ± is equal to one standard deviation

<sup>1</sup> After a total rainfall of 37.9 mm

<sup>2</sup> Time profile site

<sup>3</sup> Estimation based on average (HPST14, HPST16 and HPSZ07) SWE increase of 4.1 mm between Feb 20 and March 2

<sup>4</sup> Measured on March 3, 1991 @ 17:00

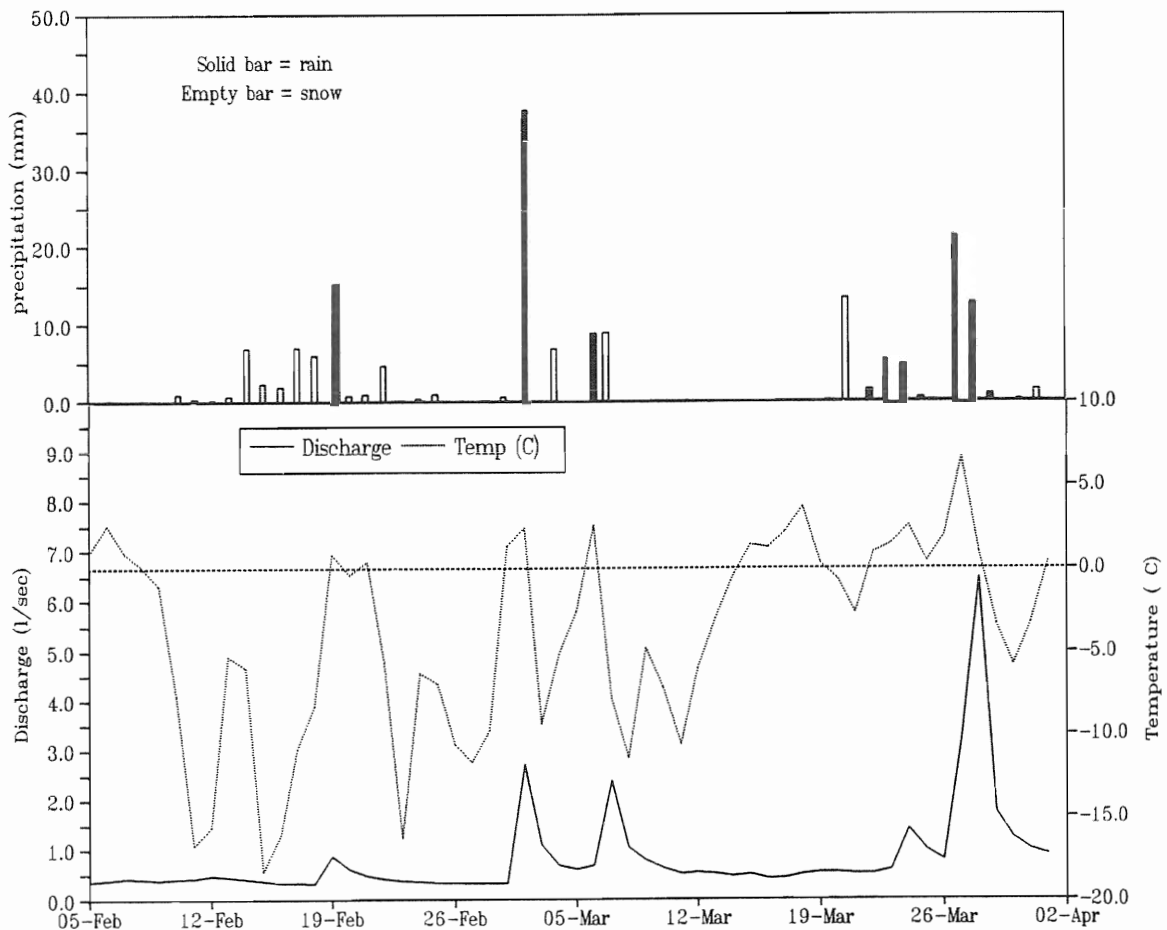
<sup>5</sup> After a total rainfall of 34.6 mm

The snow densities within the snowpack at the time profile site were considerably lower than those normally associated with a state of 'ripeness'. While ripe snowpacks are usually defined as isothermal at 0 °C with densities greater than 0.35 g/cm<sup>3</sup> (Gray and Male, 1970), data from the time profile site on February 20 indicate densities ranging from 0.21 g/cm<sup>3</sup> in the upper layer to 0.28 g/cm<sup>3</sup> in the bottom layer. Furthermore, the mean temperature of the snowpack was probably well below zero due to

the predominantly cold daily mean temperatures throughout most of February (Figure 2). Gerdel (1945) points out that immature snowpacks with their characteristic low snow density and smaller crystal size are much more capable of absorbing liquid water from a rain event onto the surface of the crystals, and within the capillary and non-capillary voids between snow crystals.

Immediately prior to the March 27-28 event the snowpack was more mature. There was little distinction amongst the three layers of the





**Figure 2.** Daily precipitation, mean temperature and stream discharge in the Harp 4-21 catchment.

snowpack and the mean ( $n=6$ ) snowpack density of  $0.35 \text{ g/cm}^3$  showed little variation ( $\pm 0.03 \text{ g/cm}^3$ ). Rainwater can quickly infiltrate a snowpack containing densities above  $0.30 \text{ g/cm}^3$ , and the associated increase in snow crystal size (Colbeck, 1976). In addition, the mean temperature of the snowpack would have been closer to  $0^\circ\text{C}$  due to the warm daily mean temperatures leading up to the event (Figure 2). A warmer snowpack is much more likely to melt during a rain-on-snow event since very little heat is required to bring the snowpack temperature to

$0^\circ\text{C}$ , thereby permitting the remainder of the heat added by the infiltrating rain to melt snow (Gerdel, 1945). Furthermore, in a warm snowpack, the heat added from infiltrating rain has a greater potential for being transmitted down to the bottom snow layers. These conditions clearly show that having knowledge of the antecedent snow pack physical characteristics is essential in determining the amount of water which can become available for infiltration/runoff at the soil surface during a given rain-on-snow event.



The ambient air temperatures associated with each of the rainfall events play a role in determining the total amount of water available for infiltration at the soil surface. During the March 2-3 event the relatively moderate air temperatures (maximum of 5 °C) occurred for less than 24 hrs and may not have supplied the energy necessary to initiate snowmelt throughout the snowpack. During the March 27-28 event the ambient air temperature was much higher (maximum of 11 °C) and persisted for nearly 48 hrs. Furthermore, the bulk of the rainfall in the March 2-3 event was preceded by less than 13 hrs of above zero temperature, whereas for the March 27-28 event, the air temperature was well above zero for more than 30 hrs before the initiation of rainfall.

The hydrologic response of the Harp 4-21 catchment to the March 2-3 and March 27-28 rain-on-snow events was markedly different (Figures 3 & 4). Peak discharge and total runoff during the March 27-28 event was considerably larger than the March 2-3 event. Peak discharge on March 28 was nearly three times higher than that occurring on March 2 (15.5 vs 5.4 l/sec), whereas total runoff was 2.44 times greater (29.0 mm vs 11.9 mm respectively). With the exception of spring snowmelt, the March 27-28 rain-on-snow event was the largest single runoff event monitored in the Harp 4-21 basin during the 1989-1991 period. The relative differences in peak and total runoff between the two events can be partially explained by the respective volumes of water available for infiltration (Table 1). The water available for infiltration during the March 27-28 event (53.6 mm) was more than one and one half times that of the March 2 event (33.2 mm).

A particularly interesting aspect of the hydrological response during the two events, especially the March 2-3 event, was the lack of a time lag between the input of rainfall and the response of the water-table and stream discharge. Even though the 0.65m thick snowpack prior to the March 2-3 event was immature, the water-table and stream responded very quickly to the initial pulse of rainfall. A similar response was recorded by Semkin and Jefferies (1986) during a large rain event falling on a deep snowpack (228 mm SWE) with a low antecedent density of 0.23 g/cm<sup>3</sup>.

Soil temperature data obtained from the three temperature probes indicates a distinct reduction

in temperature associated with the infiltration of 0 °C rain/snowmelt waters during both events. The rapid water-table response observed in the Harp 4-21 catchment during the March 2-3 event suggests that the combination of warm ambient air temperatures and the amount of heat introduced into the snowpack by the rain quickly brought the snowpack to a state where infiltration occurred at the soil surface. Gray and Male (1970) provide an example snowpack energy balance suggesting that by distributing a 10 mm rainfall throughout a 1 m thick snowpack of 0.34 g/cm<sup>3</sup> the energy released by refreezing would raise the average snowpack temperature from -5 °C to 0 °C.

The rapid response of the water-table during the March 2-3 and March 27-28, 1991 events can be explained by four main points: firstly, there is a relatively large amount of water available for infiltration (33.3 and 53.6 mm respectively); secondly, the antecedent soil moisture conditions in the vadose zone indicate a high level of saturation (Figure 3 & 4); thirdly the soils in the Harp 4-21 basin were not frozen (the 0.15 m soil temperature probe indicated 1.5 °C throughout February/March); and fourthly, the possibility of flow fingering through the snowpack can rapidly move rain/meltwater down to the soil surface (Wankiewicz, 1978; Marsh and Woo, 1984).

Soil moisture content data from TD2 and TD4 indicates that the respective vadose zones were nearly saturated, hence resulting in a low specific yield. Under conditions where nearly saturated soils extend to the ground surface a small addition of water at the soil surface can result in a rapid and significant water-table response ('the capillary fringe effect') (Gillham, 1984). Given the detailed information on antecedent water-table depths and soil moisture content in the vadose zone it is possible to calculate the amount of storage available prior to the two rain-on-snow events (Figure 5). The amount of storage available in the vadose zone, combined with the water-table depths may well be the best indicator of antecedent basin saturation for the Harp 4-21 catchment. The calculation of available soil moisture storage involves determining the maximum amount of water (mm) that the vadose zone can hold under full saturation (i.e. if the water-table were at the ground surface), and subtracting from this the actual amount of stored water. At sites TD2 and TD4 the saturated water content ( $\theta_{sat}$ ) values from all soil probes was

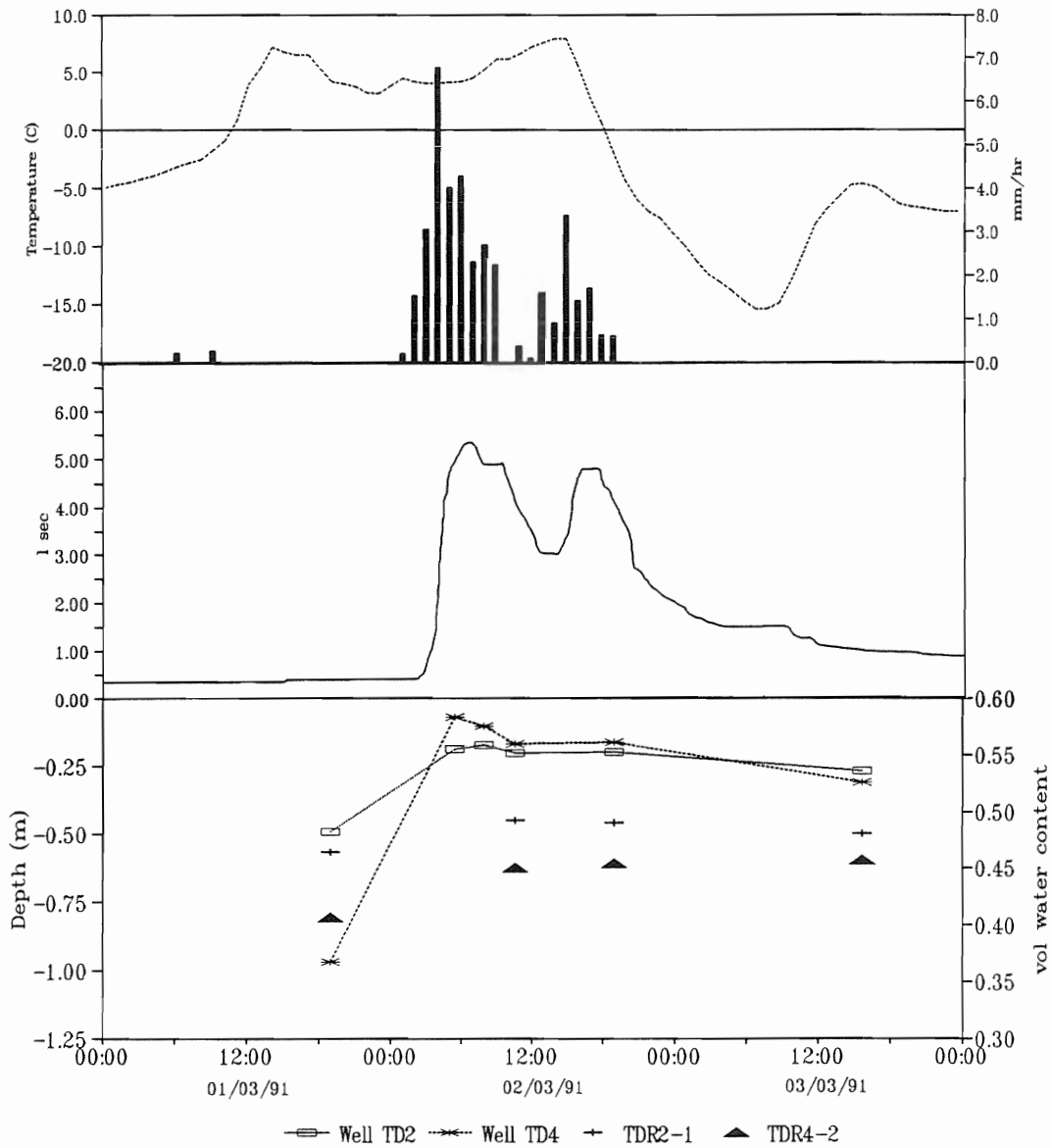


Figure 3. Hourly precipitation, mean temperature, stream discharge (S1), water-table and soil moisture<sup>1</sup> response in the Harp 4-21 catchment during the March 2-3, 1991 rain-on-snow event.

<sup>1</sup> soil moisture probes TDR2-1 and TDR4-2 are -0.08 m and -0.48 m respectively, below the ground surface

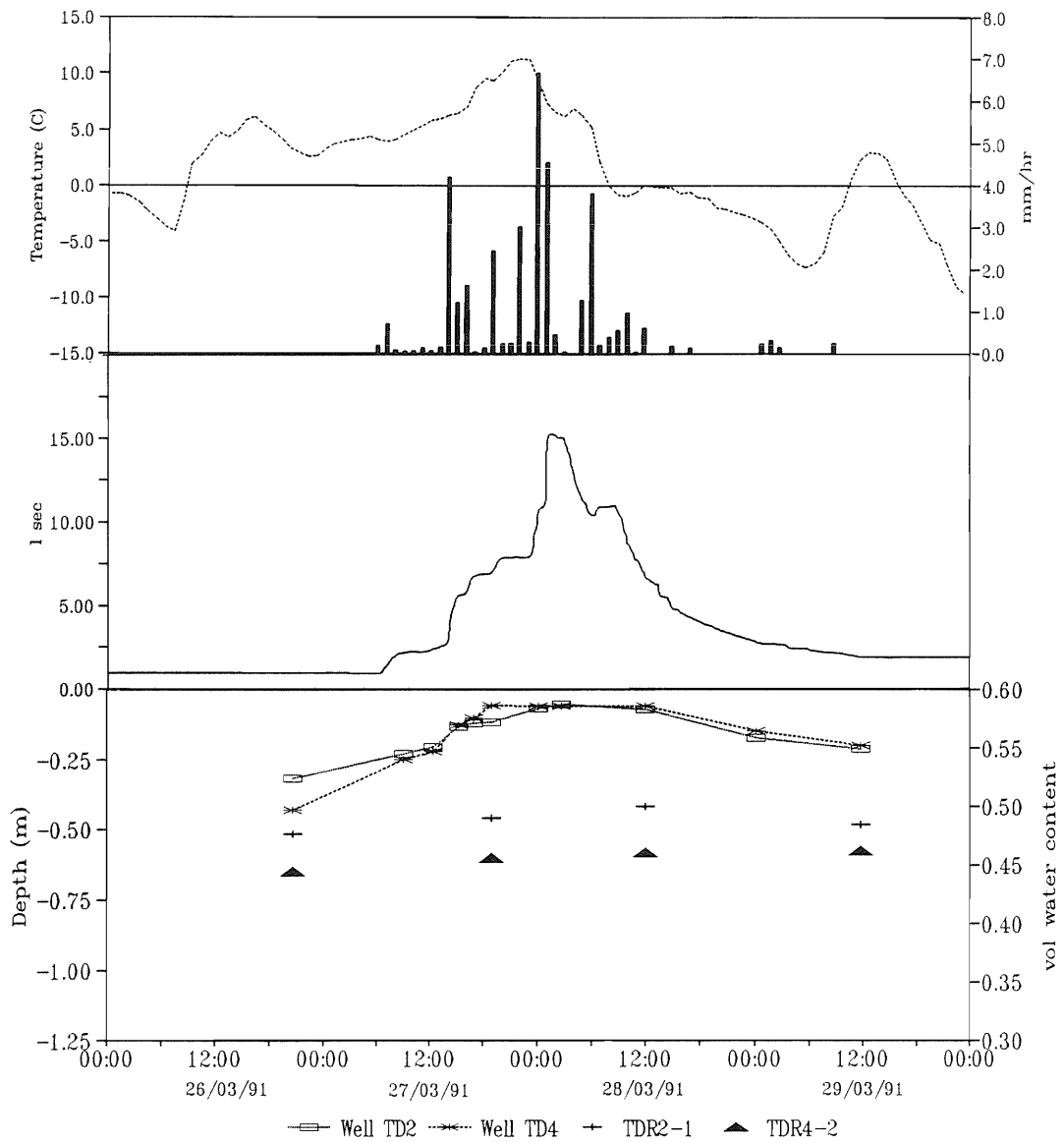
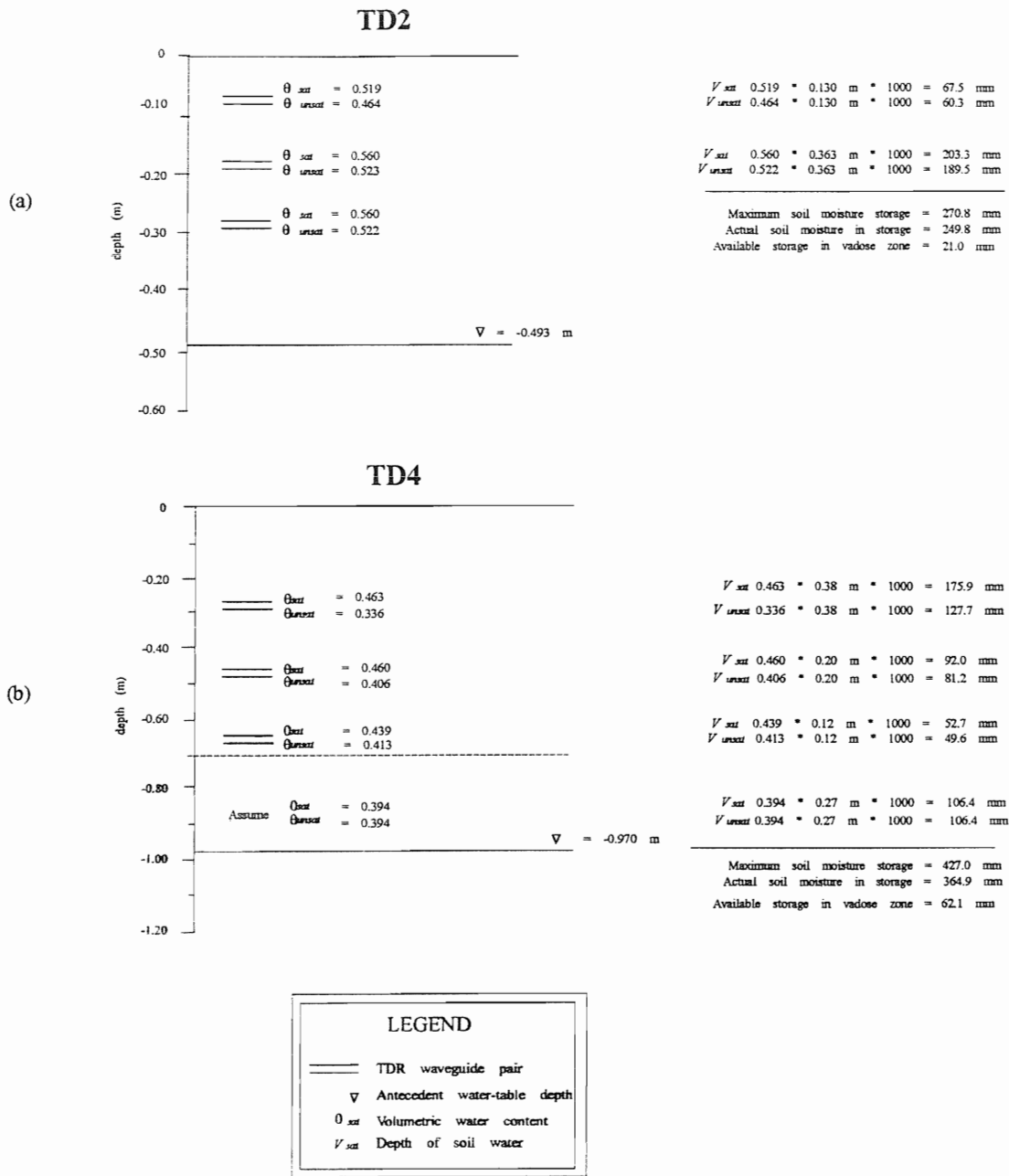


Figure 4. Hourly precipitation, mean temperature, stream discharge (S1), water-table and soil moisture<sup>1</sup> response in the Harp 4-21 catchment during the March 27-28, 1991 rain-on-snow event.

<sup>1</sup> soil moisture probes TDR2-1 and TDR4-2 are -0.08 m and -0.48 m respectively, below the ground surface



**Figure 5.** Determination of available soil moisture in the vadose zone at sites TD2 and TD4 prior to the March 2-3, 1991 rain-on-snow event.

obtained during periods in which the water-table is above the probe. The unsaturated water content ( $\theta_{\text{unsat}}$ ) of the soil prior to each rain-on-snow event was then measured from the three TDR soil probes at sites TD2 and TD4. Maximum and actual soil moisture storage (mm) were determined by dividing the vadose zone into representative sections based on the spacing of the TDR waveguide pairs, depth range of soil horizons, differences in soil porosity, and moisture gradients (see Figure 5).

The available storage calculated for sites TD2 and TD4 prior to the two rain-on-snow events indicates that the antecedent soil moisture and water-table conditions were considerably different. Prior to the March 2-3 event there was 21 and 62 mm of storage available at TD2 and TD4 respectively, whereas prior to the March 27-28 event there was only 11 and 34 mm of storage at TD2 and TD4 respectively. While assumptions concerning soil moisture gradients and representative sections in the calculation of available storage can lead to potentially large errors it is, however, clear that antecedent soil moisture conditions prior to the March 2-3 event were drier than those before the March 27-28 event.

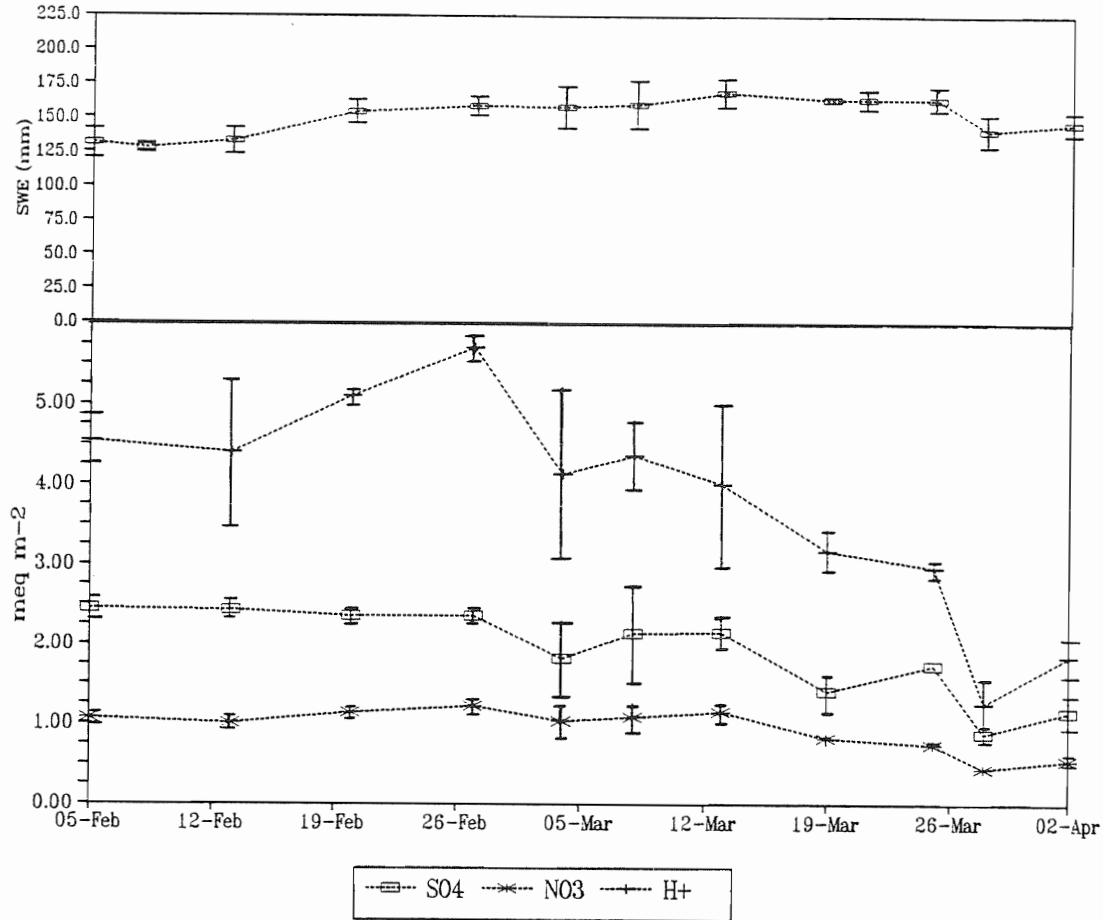
The combination of a mature snowpack, warmer ambient air and snowpack temperatures, higher groundwater levels, and reduced available storage in the vadose zone all helped to produce significantly greater runoff during the March 27-28 rain-on-snow event. In comparing the March 27-28 and March 2-3 events the proportionate increase in total runoff ( $29.0/11.9 \text{ mm} = 2.44$ ) was greater than the respective increase in water available for infiltration ( $53.6/33.3 \text{ mm} = 1.61$ ). While it is difficult to accurately quantify the relative importance of antecedent soil moisture versus snowpack conditions, the antecedent maturity of the snowpack likely exerts the strongest control over the production of runoff during a rain-on-snow event. While antecedent soil moisture conditions are critical in determining the response of the groundwater flow system, and ultimately stream runoff, if the antecedent snowpack conditions are such that most of a typical rainfall event ( $< 30 \text{ mm}$ ) is retained/frozen within an immature snowpack, stream runoff will be small regardless of soil moisture conditions.

## 2. Hydrochemistry

The mean ionic load ( $\text{meq m}^{-2}$ ) of the snowpack in the Harp 4-21 catchment was clearly depleted with respect to sulphate, nitrate and hydrogen ion as a result of the March 2-3 and March 27-28 rain-on-snow events (Figure 6). The March 2-3 event led to a significant reduction in the hydrogen ion and sulphate load of the snowpack, with a somewhat smaller loss in the nitrate load. The reduced chemical load resulting from this event is interesting considering: 1) there was no loss (actually a 4.7 mm gain) in SWE, and 2) the rain contained some sulphate, nitrate and hydrogen ion. These data suggest that either there was a displacement of snowpack water, or an enrichment of the portion of rainfall which moved through the snowpack and infiltrated the soil.

The chemical mass balance of the snowpack during the two rain-on-snow events is presented in Table 2. The percentage of chemical load removed from the pre-event snowpack during the March 27-28 event was approximately twice that of the March 2-3 event. The loss of hydrogen ion from the snowpack, coupled with the load from the rainfall, lead to a significant loading to the soil and tills of the Harp 4-21 catchment, particularly during the March 2-3 event. The higher hydrogen ion loading during the March 2-3 event can be explained by the high combined load of the rain and snowpack ( $7.46 \text{ meq m}^{-2}$ ), and the subsequent elution of hydrogen ion from the snowpack. To put the hydrogen ion loadings into perspective a 75 mm spring/summer/fall rainfall event with a pH of 4.35 (mean average annual pH @ Harp 4-21) would be required to produce the loading ( $3.33 \text{ meq m}^{-2}$ ) calculated for the March 2-3 rain-on-snow event.

Isotopic data ( $\delta^{18}\text{O}$ ) from the antecedent snowpack, rainfall and snowmelt lysimeter provides further explanation of the significant reduction in snowpack ionic loads (Table 3). The high proportion of snowmelt water present in the water draining through the base of the snowpack during the March 2-3 and March 27-28 events clearly shows that snowmelt was an important water source available for infiltration/runoff at the snow-soil interface. Given the large snowmelt component in the snowmelt lysimeter water the large reduction in snowpack chemical loads during these events is not surprising. It is important to note here that the isotopic signature of water exfiltrating the base of a snowpack receiving



**Figure 6.** Snow water equivalent (SWE) and chemical load (SO<sub>4</sub>, NO<sub>3</sub>, and H<sup>+</sup>) of the snowpack from MOEE sites HPST14, HPST16 and HPSZ07.

\* Error bars indicate ± one standard deviation (n=3)

rainfall may be highly transient, thereby creating a considerably different snowmelt/rainfall ratio through time. In a laboratory study where isotopically heavy rainwater was introduced to a column of homogeneous isotopically light melting snow at 0.55 g/cm<sup>3</sup> the δ<sup>2</sup>H (‰) of the outflow water became rapidly heavier during the period of rain, but quickly returned to the original snow signature as the rain ceased (Herrmann *et al.*, 1981). A hydrological mass balance of the snow core indicated that 65% of the total outflow was snowmelt, with 35% rainfall. Given the transient

response of the rain and snowmelt components exfiltrating the base of the snowpack during a rain-on-snow event, and the fact that the calculated snow lysimeter (CI) oxygen-18 value represents the total runoff volume, it is not surprising that the measured and calculated CI values are different (Table 3).

Given the calculations of hydrogen ion load available for infiltration at the soil surface, and the total amount of water available for infiltration (Table 1) it is possible to approximate the pH of

**Table 2. Chemical mass balance (meq m<sup>-2</sup>) of the snowpack<sup>1</sup> resulting from the: i) March 2-3, and ii) March 27-28 rain-on-snow events.**

ION	(a) Before Event i) Feb 27 ii) Mar 25	(b) Rain <sup>2</sup>	(c) Total Load (a+b)	(d) After Event i) Mar 4 ii) Mar 28	(e) Total Available for infiltration (c-d)	(f) Lost from snowpack (a-d)	(g) Per Cent lost from snowpack (f/a×100) (%)
i) March 2-3, 1991 rain-on-snow event							
SO <sub>4</sub>	2.36	1.10	3.46	1.82	1.64	0.54	22.9
NO <sub>3</sub>	1.22	0.18	1.40	1.04	0.36	0.18	14.7
H <sup>+</sup>	5.69	1.77	7.46	4.13	3.33	1.56	27.4
ii) March 27-28, 1991 rain-on-snow event							
SO <sub>4</sub>	1.73	1.73	3.46	0.88	2.58	0.85	49.1
NO <sub>3</sub>	0.74	0.23	0.97	0.45	0.52	0.29	39.2
H <sup>+</sup>	2.95	1.26	4.21	1.25	2.96	1.70	57.6

<sup>1</sup> Snowpack chemical load derived from mean of MOEE snow survey sites HPST14, HPST16 and HPSZ07.

<sup>2</sup> Rainfall load determined from total depth of liquid precipitation (mm) multiplied by the concentration of specific ion obtained from MOEE wet/dry precipitation chemistry collector

**Table 3. Relative proportion of snowmelt and rainfall in snowmelt lysimeter water using δ<sup>18</sup>O data.**

Event	Antecedent Snowpack (Csb) (‰)	Rainfall (Cr) (‰)	Snowmelt lysimeter (Cl)		Percentage of snowmelt <sup>3</sup>		Percentage of rainfall	
			meas. <sup>1</sup> (‰)	calc. <sup>2</sup> (‰)	meas. (%)	calc. (%)	meas. (%)	calc. (%)
March 2-3	-19.9	-13.1	-16.5	-19.4	50	91	50	9
March 27-28	-18.9	-6.1	-14.6	-15.9	67	77	33	23

<sup>1</sup> lysimeter sample taken during period of maximum rainfall intensity/stream discharge

<sup>2</sup> calculated from isotopic mass balance of snowpack during rain-on-snow event

<sup>3</sup> equation 1 in material and methods section



the infiltrating water at the base of the snowpack during each of the events:

$$\text{ipH} = -\log (C \times 10^{-3}/H) \quad (3)$$

where:

- ipH* = the pH of the infiltrating water  
*C* = the hydrogen ion load available for infiltration (meq m<sup>-2</sup>)  
*H* = the water available for infiltration at the base of the snowpack (mm)

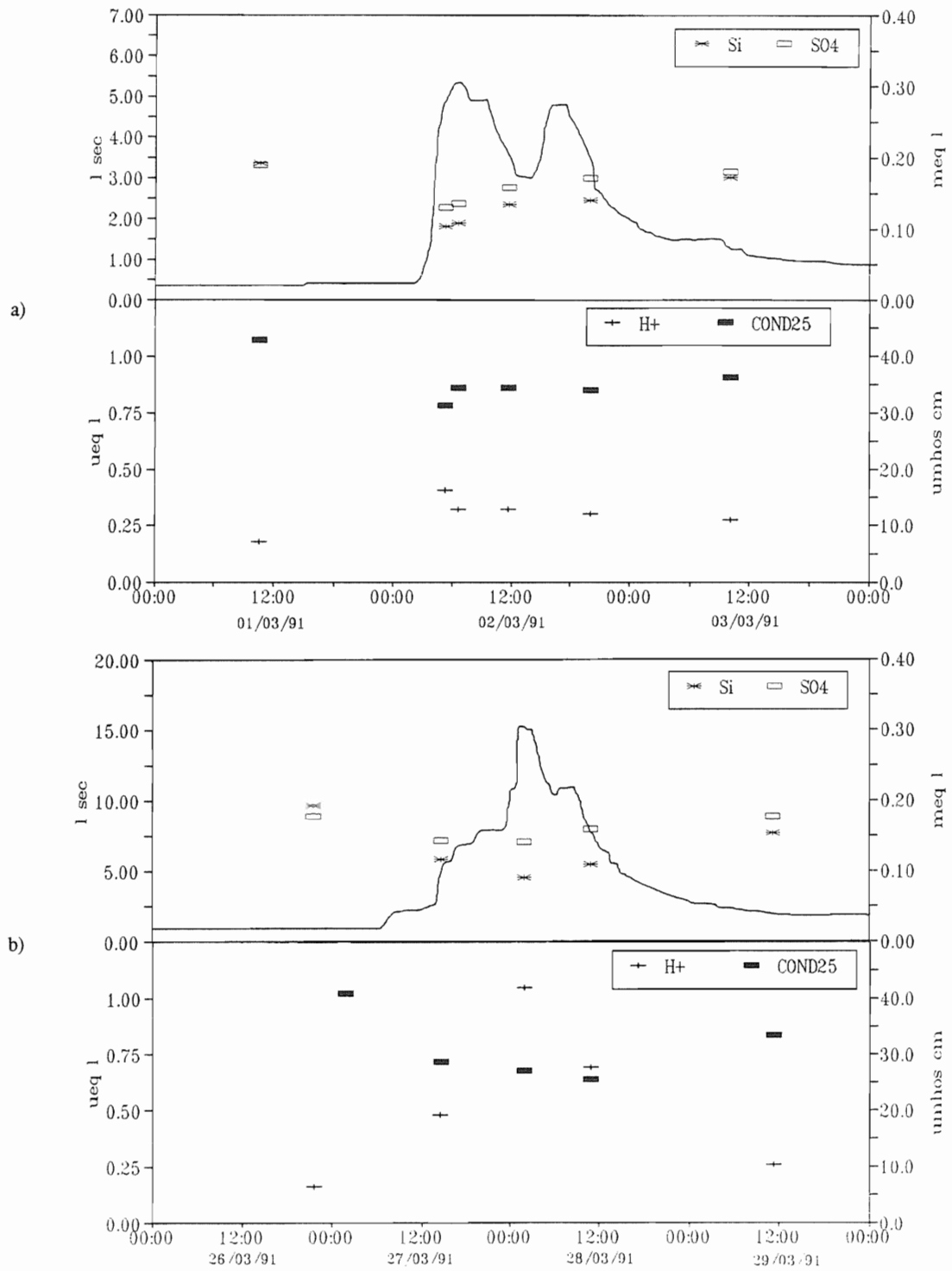
Based on eqn. 3, and the respective *C* and *H* for the March 2-3 and March 27-28, 1991 rain-on-snow events, the pH of water infiltrating through the pack and into the soil would have been 4.00 and 4.26 respectively. Both of these values are more acidic than the average (4.32) precipitation pH in the Harp 4-21 catchment during the September 1990 - April 1991 period (MOEE unpublished data). The pH of rain/snowmelt runoff obtained from the snowmelt lysimeter in the Harp 4-21 catchment during the March 27-28 rain-on-snow event varied from 4.04 during the initial stages of rainfall, to 4.29 during peak rainfall intensity. The net effect of the two large rain-on-snow events, as well as the mid-March warm period and two significantly smaller rain-on-snow events (9.0 mm on March 8, and 10.3 mm on March 23-24) was to remove a significant portion of the total chemical load from the snowpack well in advance of the main period of snowmelt in early April. Based on the maximum snowpack chemical load measured on February 27, the two large rain-on-snow events and a brief mid-March warm period during which there were two much smaller rain-on-snow events effectively removed 78% of the hydrogen ion and 63% of the sulphate and nitrate load from the snowpack, while only reducing snowpack water equivalence by 7%.

The hydrochemical response of the Harp 4-21 stream during the March 2-3 and March 27-28 rain-on-snow events was also very different (Figure 7). Considering that the two events exhibited large differences in the amount of water available for infiltration/runoff, the magnitude of peak and total runoff, the ionic load of the snowmelt/rain, and the antecedent soil moisture and depth to water-table conditions, it is not surprising that the chemical response of the stream is also different. Specific conductance (COND25) data presented in Figure 7 clearly shows that the stream water was more dilute

during the March 27-28 event than during the March 2-3 event. During the March 2-3 event the decline in stream specific conductance and increase in hydrogen ion was small even though over 30 mm of highly acidic (100 µeq l<sup>-1</sup>, equivalent pH of 4.00) rain/snowmelt recharged the catchment over a relatively short period. The maximum pH decline in the stream during peak runoff of the March 2-3 event was only 0.36 units (6.75 - 6.39). The stream concentration of sulphate during the event did decrease during peak flow (from 0.189 to 0.130 meq l<sup>-1</sup>) but did not approach the concentration (calculated at 0.049 meq l<sup>-1</sup>) of the rain/snowmelt runoff.

Based on the stream hydrochemistry data from the Harp 4-21 catchment it would appear that, even with the preferential elution of ions from the snowpack during rain-on-snow events, runoff chemistry is largely controlled by groundwater discharge. If ionically enriched rain/snowmelt water did comprise a significant fraction of stream runoff there should have been a significant increase in stream hydrogen ion. An isotopic (<sup>18</sup>O) hydrograph separation of pre-event (groundwater) and event water (value of snowmelt lysimeter) during the March 2-3 event indicates that 75% of peak stream discharge was comprised of groundwater discharge. The results of the March 2-3 rain-on-snow event hydrograph separation at peak discharge is comparable to a previous study where results indicated that the groundwater portion of total runoff from a June thunderstorm (36 mm) and an October (19 mm) rainfall was 80 and 77% respectively (Hinton *et al.*, 1994).

Examination of the hydrogen and sulphate ion mass balance during the two March rain-on-snow events sheds additional light on the hydrochemical response of the Harp 4-21 catchment (Table 4). The data clearly show that the actual mass of hydrogen ion exported from the catchment during the March 27-28 event was over five times that exported during the March 2-3 event. A comparison of the respective hydrologic input versus chemical export for the two events shows that even though the increase in hydrologic input between the two events was only 1.6 times (53.6/33.2 mm), and the respective increase in total runoff was 2.44 times (29.0/11.9 mm), there is a fivefold increase in the H<sup>+</sup> load exported from the basin (1.97 x 10<sup>-2</sup>/3.59 x 10<sup>-3</sup>) during the March 27-28 event. Hydrologic flowpathways became shallower, thereby producing groundwater discharge and surface runoff of reduced pH.



**Figure 7.** Response of selected ions (Si, SO<sub>4</sub>, H<sup>+</sup>), and specific conductance (COND25) in stream runoff during: a) March 2-3, and b) March 27-28, 1991 rain-on-snow events.

**Table 4.** Hydrogen and sulphate mass balance ( $\text{meq m}^{-2}$ ) in the Harp 4-21 catchment during the March 2-3 and March 27-28, 1991 rain-on-snow events. (Export calculated by multiplying stream (S1)  $\text{H}^+$  and  $\text{SO}_4$  data by corresponding section of the runoff hydrograph).

ION	INPUT Total load available for infiltration/runoff		EXPORT Total load exported from catchment during runoff event		Relative increase in export for March 27-28 event
	March 2-3	March 27-28	March 2-3	March 27-28	
$\text{H}^+$	3.33	2.96	$3.59 \times 10^{-3}$	$1.97 \times 10^{-2}$	5.49
$\text{SO}_4$	1.64	2.58	1.92	4.48	2.33

## CONCLUSIONS

The amount and quality of runoff resulting from rain-on-snow events in the Harp 4-21 catchment are controlled through the interaction of several important processes operating with variable antecedent conditions. With respect to average size and intensity (up to 30 mm,  $6 \text{ mm hr}^{-1}$ ) rain-on-snow events, total stream runoff is largely controlled by the thickness and antecedent maturity, or ripeness of the snowpack, and the antecedent soil moisture conditions in the hydrologically/hydrogeologically responsive near-stream and lower slope areas. Low runoff potential exists when the antecedent snowpack is of low density and low mean temperature and when the antecedent soil moisture conditions in the vadose zone are such that a significant fraction of the precipitation infiltrating the soils is taken up in storage. High runoff potential exists when the antecedent snowpack is mature (high snow densities with large crystal/particle size, isothermal temperature close to  $0^\circ\text{C}$ ) and the antecedent soil moisture conditions are such that there is little available vadose zone storage for infiltrating event water in the near-stream and lower slope areas.

Both of the rain-on-snow events monitored in this study clearly depleted the ionic load ( $\text{H}^+$ ,  $\text{SO}_4$ ,  $\text{NO}_3$ ) of the snowpack. Snowpack chemical mass balance results indicate that for the March

2-3 event the percentage of the  $\text{H}^+$ ,  $\text{SO}_4$ , and  $\text{NO}_3$  loads removed from pre-event snowpack was 27%, 23% and 15% respectively, whereas for the March 27-28 event the respective figures were 58%, 49% and 39%. Based on the maximum winter snowpack chemical load measured on February 27, the two large rain-on-snow events and a brief mid-March warm period during which there were two much smaller rain-on-snow events effectively removed 78% of the hydrogen ion and 63% of the sulphate and nitrate load from the snowpack, while only reducing snowpack water equivalence by 7%. The high  $\text{H}^+$  loadings to the basin during the rain-on-snow events created highly acidic (calculated  $\text{pH}=4.00$  on March 2) water available for infiltration and surface runoff. A two component (rain and snowmelt) isotopic separation of snowmelt lysimeter water during the March 2-3 and March 27-28 events indicated that snowmelt was an important water source (50 and 67% respectively) exiting the base of the snowpack. This information, combined with the rapid hydrologic response of the basin during the events suggests that latent heat released by refreezing of rain in the snowpack, and the subsequent melting of snow, was the physical process responsible for much of the water infiltrating the soils.

The hydrochemical response of the Harp 4-21 stream during the rain-on-snow events was

dominated by a large contribution of groundwater. A two component (groundwater and snowmelt lysimeter water) isotopic separation of peak stream discharge during the March 2-3 rain-on-snow event indicated that groundwater comprised 75% of the total discharge. Even though there was a significant  $H^+$  loading to the basin during the March 2-3 event, the large component of well buffered groundwater present in the stream during maximum discharge helped mitigate any significant reduction in stream pH. However, when a high flux of  $H^+$  enriched rain and snowmelt water is coupled with a high hydrological flux, such as occurred during the March 27-28 event, several processes occur which eventually lead to greater hydrogen ion export from the catchment. Firstly, the high hydrological flux raises the overall level of basin saturation via increased lower and middle slope groundwater levels and increased vadose zone soil moisture content. These conditions lead to shallower hydrologic flowpaths in the soils which consequently begin to discharge soil and groundwater of reduced alkalinity. The increased level of saturation in the catchment also promotes more overland flow of event water in the near-stream and lower slope saturated areas.

It appears that mid to late winter rain-on-snow events are a hydrochemically important occurrence because of their ability to elute much of the chemical load from the snowpack prior to the main period of spring snowmelt. Given a sufficient time lag between the rain-on-snow event(s) and the spring snowmelt, the soil and groundwater may have the necessary residence time to reacquire depleted alkalinity, thereby increasing the catchment's ability to neutralize the residual load of hydrogen ion in the snowpack during the annual maximum hydrologic flux of spring snowmelt. One factor which can greatly affect this process is the magnitude of the hydrologic flux through the catchment during the previous fall. If the fall has been relatively dry then the residence time of shallow soil and groundwater will be greater and the acid neutralizing capacity of the catchment may be even greater during both the ensuing rain-on-snow events and the spring melt. It is clear that climatic variability can exert a large influence on the eventual hydrological and hydrochemical response of a watershed during winter rain-on-snow events and spring snowmelt.

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## REFERENCES

- Abdul, A.S. and R.W. Gillham, "Field Studies of the Effects of the Capillary Fringe on Streamflow Generation." *J. of Hydrology*, 112: 1-18. 1989.
- Adams, W.P. and D.R. Barr, Techniques and equipment for measurement of snow cover. Occasional paper 3. Dept. of Geog, Trent University, Peterborough, Ontario. 1974.
- Baker J.M. and R.R. Allmaras, "System for automating and multiplexing soil moisture measurement by time-domain reflectometry." *Soil Sci. Soc. Am. J.*, 54: 1-6. 1990.
- Baker J.M. and R.J. Lascano, "The spatial sensitivity of time-domain reflectometry." *Soil Sci.*, 147: 378-384. 1989.
- Barry, P.J. and A.G. Price, Short term changes in the fluxes of water and dissolved solutes during snowmelt. in *Seasonal Snowcovers: Physics, Chemistry, Hydrology* ed H.G. Jones and W.J. Orville-Thomas, NATO ASI series Vol. 211, 1987.
- Bottomley, D.J., D. Craig, and L.M. Johnston, "Neutralization of acid runoff by groundwater discharge to streams in Canadian Precambrian Shield watersheds." *J. of Hydrology*, 75: 1-26. 1984.
- Bottomley, D.J., D. Craig, and L.M. Johnston, "Oxygen-18 studies of snowmelt runoff in a small precambrian shield watershed: implications for streamwater acidification in acid sensitive terrain." *J. of Hydrology*, 88: 213-234. 1986.

- Colbeck, S.C., Analysis of hydrologic response to rain-on-snow, *Res. Rep. 340*, U.S. Army Cold Reg. Res. and Eng. Lab., Hanover, N.H., 1975.
- Colbeck, S.C., An Analysis of water flow in dry snow, *Water Resour. Res.*, 12(3), 523-527, 1976.
- Dankevy, S., Groundwater flow and chemistry in a small acid-stressed sub-catchment of the Canadian shield. Unpublished Masters project, University of Waterloo. 1989.
- DeWalle, D.R., Review of snowpack chemistry studies. in Seasonal Snowcovers: Physics, Chemistry, Hydrology ed H.G. Jones and W.J. Orville-Thomas, NATO ASI series Vol. 211, 1987.
- Dillon, P.J., D.S. Jefferies, Y. Snyder, R. Reid, N.D. Yan, D. Evans, J. Moss and W.A. Scheider, "Acidic precipitation in south central Ontario: recent observations." J. Fish. Res. Board. Can., 35: 809-815. 1978.
- Dillon, P.J., M. Luis, R. Reid, and D. Yap, Ten year trends in sulphate, nitrate and hydrogen deposition in central Ontario." Atm. Envir., 22: 901-905. 1988.
- English, M.C., D.S. Jeffries, N.W. Foster, R.G. Semkin and P.W. Hazlett, "A preliminary assessment of the chemical and hydrological interaction of acidic snowmelt with the terrestrial portion of a Canadian Shield catchment." Wat. Air Soil Pollut. 31: 27-34. 1986.
- English, M.C., R.G. Semkin, D.S. Jeffries, P.W. Hazlett and N.W. Foster, Methodology for investigation of snowmelt hydrology and chemistry within an undisturbed Canadian Shield watershed. in Seasonal Snowcovers: Physics, Chemistry, Hydrology ed H.G. Jones and W.J. Orville-Thomas, NATO ASI series Vol. 211, 1987.
- Gerdel, R.W., "The dynamics of liquid water in deep snowpacks" *Eos Trans. AGU*, Vol 26: 83-90, 1945.
- Gillham, R.W., "The effect of the capillary Fringe on water-table response." J. of Hydrology, 67: 307-325. 1984.
- Goodison, B.E., P.Y.T. Louie and J.R. Metcalfe, "Snowmelt acidic shock study in South Central Ontario." Water, Air, and Soil Pollution, 31:131-138, 1986.
- Gray, D.M. and D.H. Male, Handbook of Snow: Principles, Processes, Management and Use Pergamon Press. 1970.
- Herrmann, A., M. Lehrer and W. Stichler, "Isotope input into runoff systems from melting snowcovers." Nordic Hydrology 12:309-318, 1981.
- Hinton, M.J., S.L. Schiff and M.C. English, "Physical properties governing groundwater flow in a glacial till catchment." J. of Hydrology, 142: 229-249, 1993.
- Hinton, M.J., S.L. Schiff and M.C. English, "Examining the contributions of glacial till water to storm runoff using two- and three-component hydrograph separations." Water Resour. Res. 30(4): 983-993, 1994.
- Janhurst, S., 1991 Performance Report, Water Quality Section. Laboratory Services Branch, Ontario Ministry of Environment and Energy, Etobicoke, Ont. 394 pp., 1993.
- Jefferies, D.S. and W.R. Snyder, Geology and geochemistry of the Muskoka-Haliburton study area. Dorset Research Centre, Ontario Ministry of the Environment, Data Rep. DR 83/2. p. 101. 1983.
- Johannessen, M. Dale, T., Gjessing, A., Henriksen, A., and R.F. Wright, Acid precipitation in Norway: the regional distribution of contaminants in snow and the chemical concentration processes during snowmelt. Proc. Isotopes and Impurities in Snow and Ice Symposium, Grenoble. IAHS Publ. No. 118, 1975.
- Johannessen, M. and A. Henriksen, Chemistry of snow meltwater: change in concentration during melting. Water Resour. Res. 14: 615-619, 1978.
- Jones, H.G. and Y. Bedard, The dynamics and mass balance of NO<sub>3</sub> and SO<sub>4</sub> in meltwater and surface runoff during springmelt in a boreal forest. in Forest Hydrology and Watershed Management IAHS Publ. No. 167., pp. 19-31. 1987.
- Jones, H.G. and J. Stein, Hydrochemistry of snow and snowmelt in catchment hydrology. in Process studies in Hillslope Hydrology. ed M.G. Anderson and T.P. Burt. 1990.

- Kattelmann, R., Water release from a forested snowpack during rainfall. in Forest Hydrology and Watershed Management IAHS Publ. No. 167., pp. 265-272. 1987.
- Kerekes, J., S Beauchamp, R. Tordon, C. Tremblay and T. Pollock, "Organic versus anthropogenic acidity in tributaries of the Kejimikujik Watersheds in Western Nova Scotia." Water, Air, and Soil Pollution, 31:165-174, 1986.
- MacLean, R.A. The role of the vadose zone in the generation of runoff from a headwater basin in the Canadian Shield. Unpublished M.A. thesis, Wilfrid Laurier University, Waterloo Ontario. 1992.
- Marsh, P. and Ming-Ko Woo, "Wetting front advance and freezing of meltwater within a snow cover 1. Observations in the Canadian Arctic." Water Resour. Res., 20(12):1853-1864, 1984.
- Morris, E.M. and A.G. Thomas, Preferential discharge of pollutants during snowmelt in Scotland. J. of Glaciology, 31: 190-193, 1985.
- Nichols, D.S. and R.E. McRoberts, "Relations between sulphate deposition in northern Minnesota, Wisconsin and Michigan." Water, Air, and Soil Pollution, 31:197-206, 1986.
- Novakowski, K.S. and R.W. Gillham, "Field investigations of the nature of water-table response to precipitation in shallow water-table environments." J. of Hydrology, 97: 23-32. 1988.
- Ontario Ministry of Environment and Energy (MOEE), Biogeochemistry project update: Snow cores 1989-1993 Plastic Lake and Harp Lake. 1993.
- Price, A.G., L.K. Hendire and T. Dunne, Controls on the production of snowmelt runoff. in Proc. Modelling of Snowcover and Runoff. ed S.C Colbeck and M. Ray. CRREL, 1978.
- Semkin, R.G. and D.S. Jeffries, "Storage and release of major ion contaminants from the snowpack in the Turkey Lakes Watershed." Water, Air, and Soil Pollution, 31:215-221, 1986.
- Semkin, R.G. and D.S. Jeffries, Chemistry of atmospheric deposition, the snowpack, and snowmelt in the Turkey Lakes watershed. Can J. Fish. Aquat. Sci. 45: 38-46, 1988.
- Schemenauer, R.S., Summers P.W., Wiebe H.A., and K.G. Anlauf, Spatial and temporal variability of surface snowfall and snowpack chemistry in central Ontario. J. of Glaciology, 7: 185-190, 1985.
- Topp, G.C., J.L. Davis and P. Annan, "Electromagnetic determination of soil water content: measurements in coaxial transmission lines." Water Resour. Res., 16(3): 574-582. 1980.
- Topp, G.C., J.L. Davis and P. Annan, "Electromagnetic determination of soil water content using TDR, I, applications to wetting fronts and steep gradients." Soil Sci. Soc. Am. J. 46(4): 672-678. 1982.
- Tranter, M., Brimblecombe, P., Davies, T.P., Vincent, C.E., Abrahams, P.W. and I. Blackwood. The composition of snowfall, snowpack and meltwater in the Scottish Highlands: evidence for preferential elution. Atmospheric Environment, 20: 517-525. 1986.
- Tsiouris, S., C.E. Vincent, T. D. Davies and P. Brimblecombe, "The elution of ions through field and laboratory snowpacks." Annals of Glaciology 7:196-201. 1985.
- Wankiewicz, A.C., "A review of water movement in snow" in Proceedings of the modelling of snowcover runoff, Edited by S.C. Colbeck and M. Ray. pp. 336-350, CRREL., Hanover, N.H., 1978.
- WCGR, Software for obtaining and analyzing TDR traces. Waterloo Centre for Groundwater Research (WCGR). Dept. of Earth Sciences, University of Waterloo. 1989.
- Wels, C., C.H. Taylor, R.J. Cornett, and B.D. Lazerte, "Streamflow generation in a headwater basin on the Canadian Shield." Hydrological Processes, 5: 185-199. 1991.
- Wieting, J., "Water acidification by air pollutants in the Federal Republic of Germany." Water, Air, and Soil Pollution, 31:247-256, 1986.

