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Hydrological Response Patterns and Solute Flux in Canadian Shield Basins: Role of Different Physical Features and Antecedent Moisture Conditions

Jessica Mueller
Wilfrid Laurier University

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Jessica Mueller

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Abstract

Patterns of stream flow in relatively undisturbed Canadian Shield basins are closely linked to their physical and vegetative characteristics and meteorological conditions. The physical characteristics include topography, soil-till composition, depth and structure, slope morphology and bedrock geology. Hydrological flowpaths through, and *in-situ* chemical processes in the soil-till matrix are influenced greatly by the composition of these features and by the antecedent hydrological conditions preceding a given storm or snowmelt event.

A long term data set, collected by the Dorset Environmental Science Centre, is used to examine eight forested basins within the Muskoka-Haliburton region of south-central Ontario. The basins have a range of physical characteristics representative of this part of the Canadian Shield.

Statistical analysis of streamflow from all basins for approximately 20 years indicates that the response of basins with shallow till is significantly more variable than basins with deeper till. For this data set, streamflow patterns were assessed relative to ambient temperature and precipitation meteorological conditions. This analysis quantifies the differences between annual responses in shallow and deeper tilled basins.

A new approach is taken to quantify antecedent moisture conditions in the study basins. These antecedent moisture conditions are related to precipitation magnitude and basin runoff coefficients. Regression equations quantify these relationships for the study basins and demonstrate significant differences which are related to the physical characteristics of the basin. A daily time series of antecedent moisture conditions constructed for four study basins for four consecutive years explains runoff coefficient patterns in basins with shallow and deep till.

Temporal patterns of dissolved ions, sulphate (SO_4^{2-}) chloride (Cl^-), calcium (Ca^{2+}) and dissolved silica (SiO_2) and alkalinity export in surface water were assessed to examine the distribution of these solutes across the range of annual storm events at each site. Storm and spring melt events that are exceeded 20 % of the time during the course of a year are responsible for the majority of solute export during a year; however, the relative importance of storm events on solute export differs between deeper and shallow tilled basins and during dry and wet years.

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Chapter 1

1   Introduction

Water is a mobile medium within the hydrosphere. As such, it plays key role in ecosystems as it is the primary transport medium for dissolved solids. Rainfall on its way to the stream percolates through the soil thereby changing its chemistry many times. Once the water enters the top layer of the soil column its chemistry changes further and becomes enriched in organic acids derived from decomposing vegetation. Precipitation on its way to the stream leaches soil minerals of the A-horizon, some of which are then re-deposited in the B-horizon. From there, with increasing depth, soluble cations are leached away in soil water and transmitted to the underlying groundwater reservoir, enriching this saturated zone with base cations.

Clearly, precipitation is one of the most crucial driving forces for geochemical and hydrological processes and the different chemical properties of soil horizons are an important tool for hydrologists to infer about streamflow generation. Local topography, vegetation type, soil characteristics, underlying geology, antecedent soil moisture conditions, rainfall input patterns (frequency and intensity of rainfall) and other climatic variables account for differing spatial and temporal runoff responses of a catchment. Saturation of areas depends on different physical characteristics of basins such as converging slopes, their shapes and/or variations of till thickness. These factors in turn determine water flow pathways, flow rates, storage capacities and elevation of groundwater tables throughout the basin.

Over the past few decades, scientists have dedicated much effort into revealing the mechanisms and sources of stormflow in small forested catchments. When in the mid 1970's scientists started to use hydrochemistry to explain stream flow generation, they discovered that it was pre-event water rather than new event water that dominated the storm hydrograph (Sklash and Farvolden, 1979). The use of hydrochemistry integrates biological, geochemical, and physical processes in small catchments and couples hydrology to terrestrial processes, including soil cation exchange, chemical weathering and mineralization. The dominance of pre-event water in storm runoff is well documented (Rice and Hornberger, 1998). Scientists use a number of stream flow mechanisms to explain the rapid delivery of water to the stream such as saturation overland flow (Dunne and Black, 1975), translatory flow (Bishop, 1991), groundwater ridging (Sklash and Farvolden, 1979), and macropore flow (McDonnell, 1990, Beven and Germann, 1982). All of these processes can coexist within a catchment and may vary spatially and temporally at various times as a function of rainfall intensity and duration, and catchment antecedent wetness. Each catchment may be dominated by a particular mechanism depending on climatic conditions and physical attributes of the catchment.

1.1 Research background

To generate streamflow, a variety of hydrological processes are involved. Over the past few decades, several hypotheses have been recognized that describe the mechanisms and pathways by which streamflow is generated. These include the following:

a) *Direct channel precipitation* usually makes up a small percentage of the total streamflow during storms and is only considered important where large areas of wetlands or lakes make up a big proportion of the basin; however, channel precipitation always occurs.

b) *Hortonian overland flow* is direct surface runoff generated over the entire basin across dry or saturated soils, when the rainfall rate exceeds the rate of infiltration. In humid areas Hortonian overland flow primarily occurs only after long duration rains or if wet antecedent soil moisture conditions keep the soil saturated, or if the soil is frozen, on steep slopes with shallow soils, compacted soils or bare soils.

c) *Saturation overland flow* (Hewlett and Hibbert, 1967), whereby the infiltration capacity of soil is exceeded by rainfall inputs that are higher than soil storage capacity resulting in a rising water table intersecting the ground surface. The spatial extent of saturated areas varies greatly with time and is dependent on initial soil wetness, storage capacity, and rainfall intensity reflecting the overall wetness of the basin. The process of varying contributing areas is known as the *variable source area concept* (Hewlett and Hibbert, 1967) and can develop wherever flow convergence occurs on the hill slope or valley bottom.

d) To describe the movement of soil water, Hewlett and Hibbert (1967) hypothesized the mechanism of *translatory flow*, whereby the lateral through flow of "old" (pre-event) water stored in the soil is released to streamflow by a process of displacement by "new" (event) water, and each new increment of rainfall infiltrates and displaces all of the preceding increments. Translatory flow

is controlled by the decrease in saturated hydraulic conductivity with soil depth (Bishop, 1991) and most likely if soil moisture conditions are close to saturation. This process is also known as transmissivity feedback and was tested and studied by Bishop (1991). The decrease in hydraulic conductivity with depth may also be reason for subsurface storm flow from the development of perched water tables if infiltration rates exceed the capacity of an underlying horizon with low hydraulic conductivity to percolate water vertically. However, it is now generally accepted that the occurrence of lateral subsurface storm flow is too slow to produce significant volumes of quickflow without the assistance of some other mechanism (Bonell, 1993).

e) Based on the work of Ragan (1968), Sklash and Farvolden (1979) support the concept of *groundwater ridging* to explain high contributions of subsurface storm flow. This mechanism is associated with near-stream areas, where the capillary fringe or tension-saturated zone is close to the ground surface. The capillary fringe is located immediately above the water table as a result of capillary forces, which hold water in the void spaces between sediment particles. Only very small amounts of infiltrating water are necessary to rapidly convert the near-surface, tension saturated capillary fringe into a saturated zone or groundwater ridge (Sklash and Farvolden, 1979). The concept proposes that where the capillary fringe adjacent to the stream extends to the ground surface the water table rises rapidly, which subsequently steepens the hydraulic gradient, thus allowing significant amounts of subsurface water to contribute to the storm hydrograph. However, this mechanism does not occur farther upslope where

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infiltration is stored in the unsaturated zone above the capillary fringe (Hinton et al., 1993). Therefore, the groundwater ridge cannot explain increases in subsurface runoff that are generated in midslope and upslope portions of the catchment. Buttle and Sami (1992) tested the groundwater ridging process during snowmelt in a forested catchment located in south central Ontario. However, they found no evidence of the groundwater ridge mechanism and stress the fact that alternative explanations are required to elucidate runoff production.

f) *Macropore flow* is the rapid movement of water via systems of large interconnected pores within the soil that transmit water much more rapidly than the soil matrix. They may be a result of animal activity (earthworms, burrowing animals), old plant roots, natural soil pipes or due to cracks caused by freezing and melting or drying and wetting. Usually macropores only make up a relatively small fraction of the soil's total porosity. Nevertheless, they can have a disproportionate effect on the soil's infiltration properties allowing infiltrating water to bypass the soil matrix and reach specific depths ahead of water moving via soil micropores (Buttle et al., 2000). Macropore flow occurs when high rainfall intensities exceed the rate at which water is abstracted through the macropore walls into the soil's matrix (Beven and Germann, 1982) and can result in large pre-event water contributions to storm flows (McDonnell, 1990; Peters et al., 1995). Under dry soil conditions macropores are not filled with water and do not contribute to flow and under moderate infiltration macropores will be rapidly emptied by flow through the walls in response to the capillary potential gradients to the surrounding soil matrix (Rodhe et al., 1991). Models of

macropore flow suggest that event water infiltrates forest soils via vertical preferential flow paths to an underlying impermeable layer, where a perched water table forms, resulting in mixing of event and a larger volume of stored pre-event soil matrix water. This saturated layer which consist mainly of pre-event water is displaced rapidly downslope via preferential flow paths along the impermeable bedrock interface (Hill et al., 1999). Buttle and Peters (1997) revealed that water inputs to the slope surface reached the bedrock as preferential flow through soil macropores, which is indicated by dissolved silica and oxygen 18/16 ratios. Macropore flow is not simply a delivery process of event water *per se* but can result in pre-event water displacement as studies suggest (McDonnell, 1990; Peters et al., 1995).

Although findings and concepts regarding streamflow generation have been evolving since Horton's overland flow hypotheses, there are still unanswered questions remaining.

For example, forested catchments on the Canadian Shield often exhibit variable depths of soil cover. Studies conducted in the Dorset area, Muskoka region of south central Ontario (Devito, 1995; Devito and Hill, 1997; Devito et al., 1999; Hinton et al., 1994) highlight the fact that differing till thickness within a catchment influences runoff processes within the basin. Typically, in this region, the till depths ranges between < 1 m to ~10 m whereas the Precambrian bedrock acts as impermeable layer. According to Peters et al., (1995) most of the runoff from areas with deeper soil occurred concentrated as a thin layer above the soil bedrock interface providing > 90 % of total slope runoff

during rainfall events. Catchment areas with thin soil/till cover (< 1m) generate mostly subsurface stromflow if the overburden is relatively uniform (Buttle et al., 2000). In contrast, slopes covered by thicker till (up to 15 m) primarily deliver runoff to the riparian zone via groundwater flow moving through the glacial till (Hinton et al., 1994). Research examining patterns of export of dissolved constituents from the Muskoka-Haliburton basins indicates strong relationships with shifting dry-wet antecedent conditions in some basins and little pattern in others (Devito and Hill, 1997; Devito et al., 1999; Eimers and Dillon, 2002). The contradictory results raise questions about how basin structure, physical features, and climate variables play a role in governing the export of dissolved constituents.

In order to understand the hydrological processes and solute sources of a catchment, it is crucial to identify hydrological flow pathways within a basin. Hydrochemical properties of runoff have widely been used to elucidate runoff processes and sources. Variations in hydrologic and chemical response within a catchment are affected by variations in the antecedent wetness, soil thickness and texture, vegetation, size, ratio between wetland size and basin, topography of the catchment, and the ability of the catchment to store, cycle and release various types of chemical constituents. Thus, catchments with different physical and hydrological characteristics show different chemical responses for the same precipitation input. Variations of chemical concentrations during storm or snowmelt events are attributed to changing water routes in the subsurface caused by alterations from micropore to macropore flow (Wilson et al., 1991) or changing contributions from various soil horizons (Swistock et al., 1989; Mulder et al., 1990).

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In general, water with high concentrations of weathering products, such as base cations (Ca^{2+}, Na^+, K^+, Mg^{2+}), dissolved silica and high alkalinity bear the signature of deep soils whereas soil water is characterized by acidic storm flow (Robson and Neal, 1990). At baseflow conditions, water is more alkaline and has higher silica and base cations concentrations resulting from bedrock weathering reactions. In small catchments, especially in small basins with steep slopes and thin soils, stream discharge can be rather quick with rapid flow during prolonged heavy rain or snowmelt. Runoff generally diminishes rapidly once precipitation ceases. In relation to these events, the chemical composition of streamwater can vary substantially. Several studies (Neal et al., 1990; Robson et al., 1992) observed a sharp decline in alkalinity and SO_4^{2-}, Ca^{2+}, Mg^{2+} and Na^+ with increasing flow. In contrast, concentrations of dissolved organic carbon (DOC) and Al tend to increase (Hooper and Shoemaker, 1985; Sullivan et al., 1986; Neal et al., 1990). These patterns are not a result of rainfall or snowmelt passing directly to the stream outlet providing the major volume of water contributing to storm flow during the event, but can be linked to water routing through catchment sources picking up different chemical signatures before entering the stream. However, although interpretations of flow paths through catchments can be derived from stream chemistry analysis, the mechanisms underlying the varying chemical concentrations of pre-event water contributing to storm flow still remain poorly understood. Soil moisture conditions prior to an event play an important role in the hydrological and chemical response to a given rainfall input and it is well-known that runoff is sensitive to antecedent moisture conditions (Whipkey 1967; Lynch et al., 1979; Uchida et al., 1999).

There are several methods to estimate antecedent moisture conditions, such as the Soil Conservation Service (SCS) curve number (CN) approach, where total runoff is estimated from total rainfall assuming that the ratio of actual storage to potential storage is equal to the ratio of actual runoff to potential runoff (Ponce and Hawkins, 1996; Jacobs et al., 2003), or the usage of an antecedent precipitation index (API) (Kohler and Linsley, 1951). Soil moisture loss rates using the API are calculated by assuming a decay rate over time; however, there is no physical basis for the API loss rates (Singh, 1989; Jacobs et al., 2003). Estimating soil moisture using remote sensing data is useful, especially because of the often sparse instrumentation network in a catchment; however, dense vegetation cover can obstruct the radiative flux from the ground. Antecedent moisture is difficult to quantify since preceding rainfall is not the only parameter determining soil moisture conditions. Variables such as temperature, wind speed, daylight hours and relative humidity affect antecedent moisture by impacting evaporation rates, which depending on the region will change seasonally. Vegetation cover influences evapotranspiration rates and has an additional effect on soil moisture within a basin. Therefore, defining antecedent moisture conditions temporally and determining their role in the hydrological processes governing streamflow generation continues to be a challenge.

1.2 Research objectives

The overall objective of this study is to assess the effects of annual and seasonal variations in precipitation inputs on hydrological processes that control the movement and solute composition of basin discharge. This research aims to identify how physical

characteristics, such as topography, soil types, and surficial geology of Canadian Shield basins in central Ontario couple with climatic/hydrological antecedent moisture conditions and how variations in water routes result in different chemical concentrations entering streams in forested watersheds. The specific goals that will support the overall objectives of this thesis are:

i) To quantify climatic variability and to characterize the hydrological regime at the regional scale by analyzing eight small forested catchments in order to identify long and short term spatial and temporal patterns of hydrological responses between and within basins and to define the structure of the climatic and hydrological system.

ii) To analyze the hydrological response under varying antecedent moisture conditions in catchments differing in their physical make-up by examining a range of storm events to quantify the strong and controlling link between climate and basin hydrological processes.

iii) To determine seasonal controls on runoff patterns in relation to differing physical attributes of a basin.

iv) To examine temporal variability of chemical export in basins with differing physical make-up.

1.3 Study design

Chapter 2 discusses frequency-curve analysis for precipitation, flow-duration analysis, standardized departure statistics and timing or dynamics of runoff from eight differing basins within the Muskoka-Haliburton region, Ontario, Canada to characterize the hydrological regime.

Chapter 3 examines the predictability of hydrological responses in relation to varying antecedent moisture conditions in eight differing basins. Relationships between runoff coefficients and antecedent moisture conditions are discussed. Antecedent moisture conditions are defined by baseflow conditions and meteorological characteristics, such as storm duration, magnitude, frequency and season of occurrence.

Chapter 4 describes the relationships between climate variability and basin hydrology and discusses temporal patterns of streamflow response, baseflow and antecedent moisture conditions in four small forested study basins with respect to their physical make-up. A statistical analysis is employed to test for the homogeneity of precipitation inputs throughout the study years.

Chapter 5 compares temporal variations of chemical concentrations in streamwater of four consecutive years in two similar sized basins. Patterns of solute mass export in relation to high/low discharge patterns are examined.

Chapter 6, the final chapter, provides a summary of the major findings of this research and the overall conclusions.

Chapter 2

Variability of hydrological patterns in forested catchments in Canadian Shield basins

2 Introduction

The relationship between precipitation inputs and streamflow outputs characterizes the hydrological regime within a basin. In response to the dominant climate factors, the annual flow regime is, in part, determined by the seasonality of precipitation and snowmelt events. Within each catchment, temporal and spatial response of streamflow to precipitation inputs is connected to variations in hydrologic connectivity between upland and riparian zones, which in turn are linked to antecedent soil moisture conditions; this results in temporally variable water flow pathways. The heterogeneity of basin attributes, such as soil thickness, slope morphology and wetland proportion, thereby influence spatial variability of streamflow response. Temporal variations of runoff are also affected by the geobotanical properties of a basin and by the timing, duration and intensity of rainfall. Central to the physical make-up of the Canadian Shield basins are wetlands and terrestrial areas forested by deciduous and coniferous vegetation established in soil-till matrices of ablation and basal till, which exhibit significant two-dimensional spatial variability in hydrogeological characteristics including hydraulic conductivity and gradient.

Hydrological functions of catchments are influenced by a range of till depth and/or soil-till matrix, and vary with differences in climate and antecedent soil moisture conditions (Winter and Woo, 1990). The selected catchments have been monitored since the mid-1970s as part of the Acid Precipitation in Ontario Study (APIOS) to determine the impacts of acid precipitation on several streams and lakes in the region. In this chapter, frequency-curve analysis for precipitation, flow-duration analysis, standardized departure statistics and timing or dynamics of runoff are discussed to characterize and to explain the variations in hydrological responses in eight physiographic differing basins located in Muskoka-Haliburton region of south central Ontario and to relate variations in climate input and basin attributes.

2.1 Data and study sites

The study sites are in the southern portion of the Canadian Shield (Figure 1), where the climate is described as cool continental with cold winters (Köppen Climatic Classification System). Impermeable Precambrian metamorphic, plutonic and volcanic silicate bedrock underly the catchments, generally overlain with varying thicknesses of ablation and basal till (~0-20 m) deposited during the Pleistocene. Lowland areas can exhibit notable peat deposits. The Plastic Lake watershed has an area of 88.6 ha and is comprised of seven basins, two of which will be examined in this study. The largest, Plastic 1 (PC 1, 23.3 ha) drains a *Sphagnum*-conifer swamp that covers about 7 % of the basin area. Soil-till deposits are generally shallow with 83 % less than 1 m. Plastic 1-08 (PC 1-08, 3.4 ha) drains into PC 1 and contains no wetland. Till cover throughout the

basin is less than 1 m. Average slopes of the PC 1 basin measure about 6 % compared to 13 % in the PC 1-08 basin (Table 1) (Dillon et al., 1991).

The Harp Lake watershed is also divided into several basins. For this study Harp 3A, 4, 5 and 6 (HP 3A, HP 4, HP 5 and HP 6) are examined. The basins of Harp Lake display considerable variability in till thickness and topography. Soil-till cover ranges between 0 to ~ 20 m. Till deposits in the lowermost area of HP 3A are up to 4 m deep, while those on the valley slopes measure just above 1 m (Hinton, 1998). Average slopes range from 3 – 13 %, whereby the HP 5 (3 %) has the most gentle slope gradients and HP 4-21 the steepest with an average of 13 %. HP 5 is the largest of these Harp basins, followed by HP 4, HP 3A, HP 6 and HP 4-21. Harp 3A and Harp 5 contain wetlands, which cover 3 % and 13 % of the catchment area, respectively (Table 1).

The Paint Lake watershed is also comprised of several basins; however, only one, Paint 1 (PT 1), is gauged, and has an area of 23.1 ha. Soil-till deposits, similar to the Harp and Plastic catchments are shallow, whereby 52 % of the catchment is covered with minor till > 1 m and 43 % with thin till < 1 m thick (Table 1). A pond within the Paint 1 basin covers about 5 % of the catchment. Average slopes measure about 9 %.

Data records for temperature, precipitation and streamflow varied among the catchments. Temperature records provided by the Dorset Environmental Science Centre (DESC), located within the Muskoka - Haliburton region and in close proximity within 30 km of the study basins, spanning from 1976 to 2002 were used to obtain estimates of seasonal and annual temperatures. The average July and January temperatures are 18.4°C and –10.5°C, respectively, and the mean annual temperature over the 26-year period was 4.7°C (range 3.1 – 6.1°C).

Precipitation (daily total in mm) from 1977 to 1998 was measured at five meteorological stations, which were used to obtain precipitation inputs for individual basins. The five stations are: Dorset Environmental Science Centre (DOR2; 45°13'N, 78°56'W), Harp Lake (HPP2; 45°23'N, 79°08'W), Heney Lake (HYP2; 45°08'N, 79°06'W), Plastic Lake (PCP2; 45°11'N, 78°50'W), and Paint Lake (PTP2; 45°13'N, 78°57'W). In the case of missing data for a basin, values were used from the appropriate closest station to the basin. Since the stations were operated during different time periods, prior to 1984 precipitation inputs to the Harp and Plastic basins and prior to 1989 inputs to the Paint basin were represented by DOR2 station. From the time the stations of Harp, Plastic and Paint began recording, precipitation data were represented by the closest station for each catchment.

Total annual precipitation for the Harp basins ranged from 1246 mm in the hydrological year 1995/96 (June 1 – May 31) to 741 mm in 1997/98. For the Plastic basins the annual precipitation ranged from to 1213 mm in 1982/83 to 786 mm in 1997/98 and for the Paint basin from 1289 mm in 1978/79 to 767 mm in 1991/92.

Streamflow data were provided from the DESC in daily mean flows (L/s) for the Harp Lake basins for the 1977 – 1998 period, from 1979 – 1998 for the Plastic 1 basin, from 1989 – 1995 for Plastic 1-08 basin, and from 1977 – 1993 for the Paint Lake basin (Table 1).

Detailed information of soil profiles and elevation maps of the study sites are limited. However, comprehensive descriptions of the physiography, geology and geochemistry for the study area can be found in Scheider et al. (1983), Jeffries and Snyder (1983), McDonnell and Taylor (1987) and Fortescue et al.(1973). Topographic

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maps for HP 4-21, HP 3A, HP 4 and PC 1-08 can be found in Hinton et al. (1993, 1998),

Buttle et al. (2004) and McDonnell and Taylor (1987).

Table 1: Characteristics of the examined eight basins of Harp Lake: Harp 3A (HP 3A), Harp 4 (HP 4), Harp 4-21 (HP 4-21), Harp 5 (HP 5), Harp 6 (HP 6); Plastic Lake: Plastic 1 (PC 1), Plastic 1-08 (PC 1-08); and of Paint Lake, Paint 1 (PT 1).

Data partly taken from Dillon et al. (1991), Hinton et al. (1997) and Buttle et al. (unpublished).

Basin	HP3A	HP4	HP4-21	HP5	HP6	PC1	PC1-08	PT1
Mean annual PPT (mm)	1040	1040	918	1040	1040	1019	947	1020
Mean annual Q (mm)	540	553	409	614	612	561	499	469
Size (ha)	21.7	119.1	3.7	190.5	9.97	23.3	3.4	23.1
Slope average (%)	8	5	13	3	8	5.9	13	9
Soil thickness > 1m (%)	97	56	100*	38	45	10	0	52
Soil thickness < 1m (%)	0	41	0	49	55	83	99	43
Wetland proportion (%)	3	0	0	13	0	7	0	0
Pond	0	3	0	0	0	0	1	5
Drainage density (1/m)	0.0039	0.0017	0.0038	0.0001	0.0071	0.0034	0.0061	0.0053
Years of record	21	21	4	21	21	19	8	17

* > 15 m on slopes
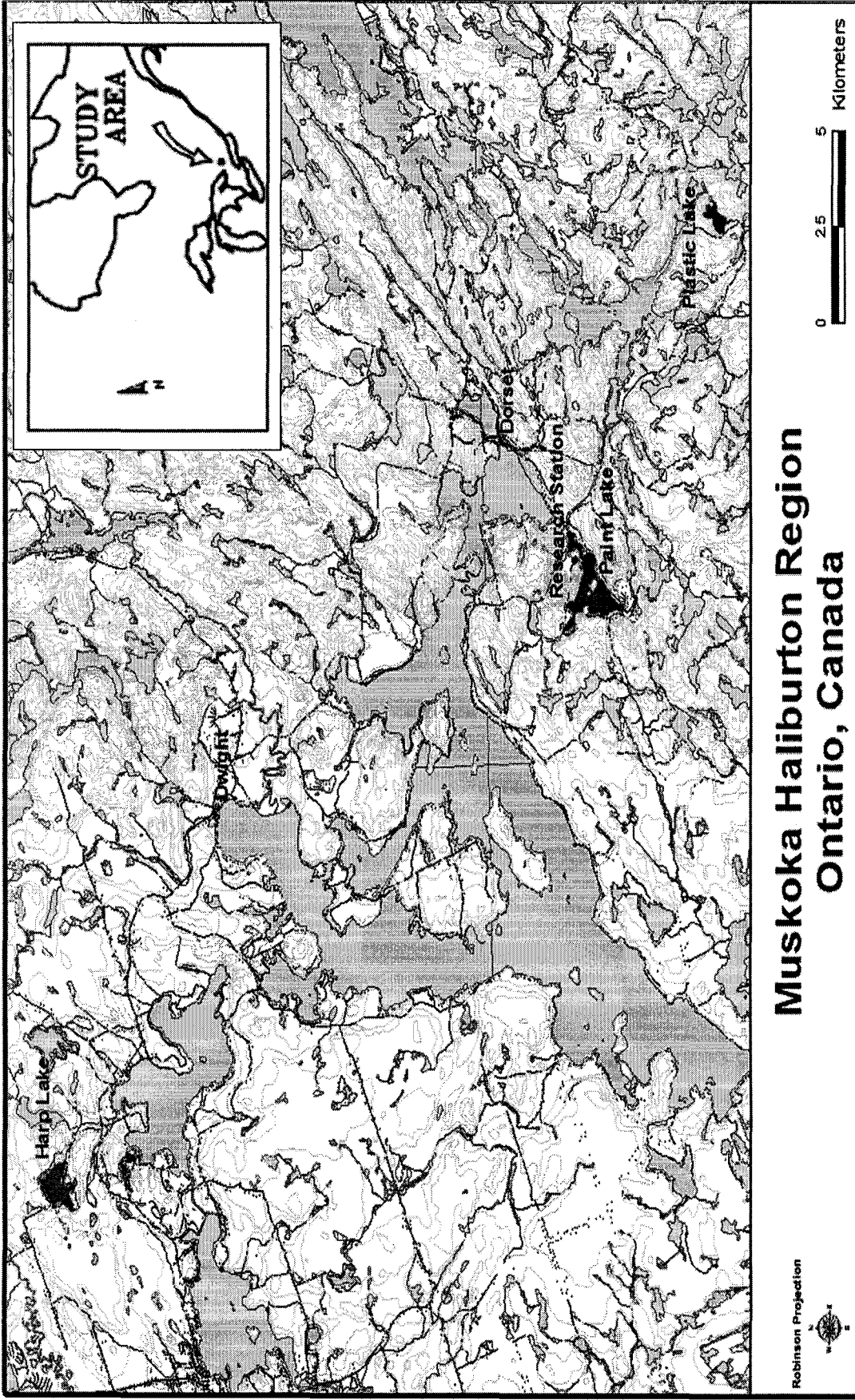
Figure 1: Map of the study sites, Harp Lake, Paint Lake, and Plastic Lake watersheds within the Muskoka-Haliburton Region, South-Central Ontario, Canada.

2.2 Methods

Hydrological trends and variability were analyzed in order to characterize the hydrologic regime of the study basins. The natural flow regime is one of the major factors that drive ecological processes in streams and floodplain areas and is defined by climatic variability.

Comparisons and assessments among and within the different sites were conducted by using statistical approaches to systematically evaluate the relationship between temperature, precipitation and streamflow response.

Flow duration curves were used to characterize streamflow distribution of the basins within the Muskoka-Haliburton region. The shape of a flow-duration curve in its upper and lower regions can be used to evaluate stream characteristics. For example, a very steep curve in the upper limit would indicate that very high discharges, if generated by rainfall only, are infrequent and are not sustained for long periods of time. High flows produced by snowmelt, however, often last for several days, and consequently will result in a much flatter curve near the upper limit (Skelton, 1976). Information on the baseflow component of stream flow can be obtained from the lower limit of the flow duration curve as this part of the curve represents low-flow conditions. Groundwater contributions are considered significant if the curve has a flat slope as this indicates sustained discharge. Steep slopes in the lower limit suggest relatively small groundwater contributions from storages reservoirs (Smakhtin, 2001).

The coefficient of variation (Standard deviation/mean) is used to analyze the variability of temperature, precipitation and streamflow of the DESC basins.

Year-to-year patterns among streams were examined by using the Pearson product-moment correlation coefficient (r). The potential relationship between annual precipitation input and discharge of each individual basin was statistically evaluated using regression analysis.

Standardized departure statistics of annual streamflow, precipitation, and temperature for each site were processed to compare similarity of discharge to precipitation inputs among basins. For this purpose *Z-scores* for different hydrological and climatic variables were calculated in order to provide insight into the deviation from their typical mean and to provide a means to compare temperature, precipitation input, and stream response among the examined basins. According to Chebychev's rule, the *Z-score* of a given observation should be between -2 and 2, provided that approximately 95% of the data follows a normal distribution. Autocorrelations for precipitation and streamflow were performed in order to examine seasonal patterns within the time series and to measure the degree of persistence of these variables.

2.3 Results

The mean annual precipitation amount differs only slightly among the catchments, ranging from 1019 mm for the Plastic catchments to 1040 mm for the Harp catchments (Table 1). Precipitation inputs result in a mean streamflow output of 540 mm for Harp 3A and 553 mm, 614 mm, and 612 mm for Harp 4, 5 and 6, respectively. The Plastic 1 catchment has an average annual discharge of 561 mm, Plastic 1-08 has 499 mm, and Paint 1 basin 469 mm. Correlation coefficients (r) between annual precipitation input and

discharge were generally strong for all examined study basins (Figure 2 and 3), except Harp

4-21 (Table 2), which is due to the short data record of four years.

Table 2: Correlation coefficients (r) for the relationship between annual precipitation and discharge in each of the catchments.

Correlations marked with an asterisks are significant at $p < 0.05$.

Basin	PT 1	HP 3A	HP 4	HP 4-21	HP 5	HP 6	PC 1	PC 1-08
(r)	0.62*	0.85*	0.87*	0.13	0.87*	0.88*	0.84*	0.87*

The variability in annual precipitation and runoff in each basin, and their

relationship to each other on a year to year scale was statistically evaluated using regression

analysis. The spatial and temporal variability of annual precipitation and annual streamflow

differs only slightly between the basins.

Temporal and Spatial Variability
Annual Streamflow vs. Precipitation (1979/80 - 1992/93)
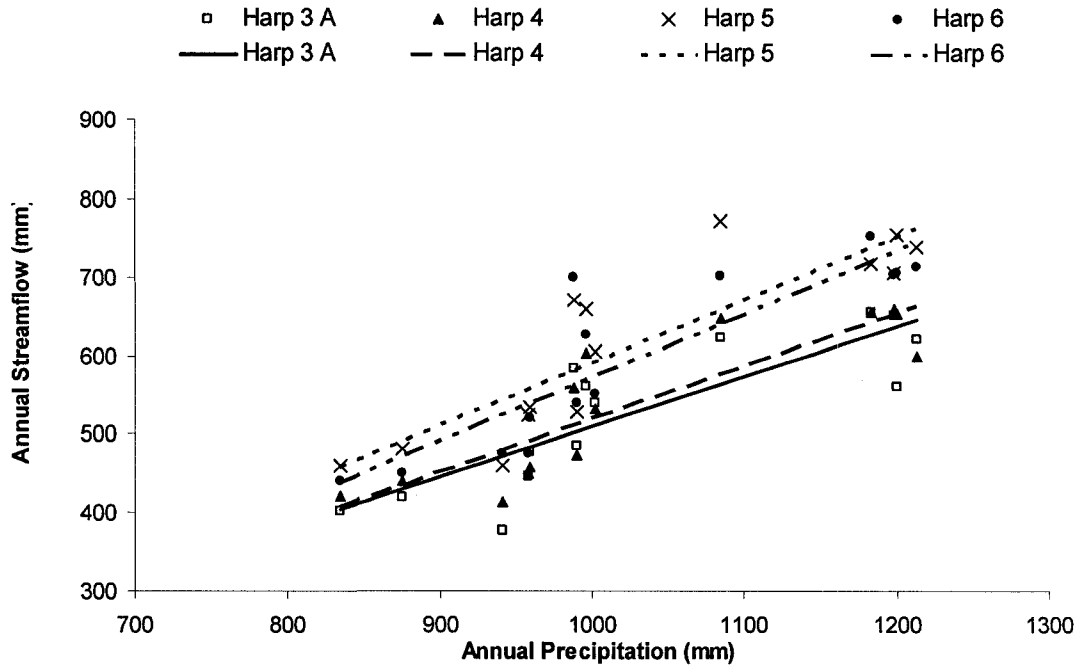
Harp 3A: y = 0.64x - 134.04, r^2 = 0.72, Harp 4: y = 0.67x - 153.97, r^2 = 0.76

Harp 5:   y = 0.80x - 213.51, r^2 = 0.76, Harp 6: y = 0.81x - 237.11, r^2 = 0.78

Figure 2: Illustration of the relationship between precipitation input and discharge of the Harp basins. Regressions are significant at p<0.05.

Temporal and Spatial Variability
Annual Streamflow vs. Precipitation (1979/80 - 1992/93)

◆ Paint 1   ✕ Plastic 1 — — Plastic 1 ——— Paint 1
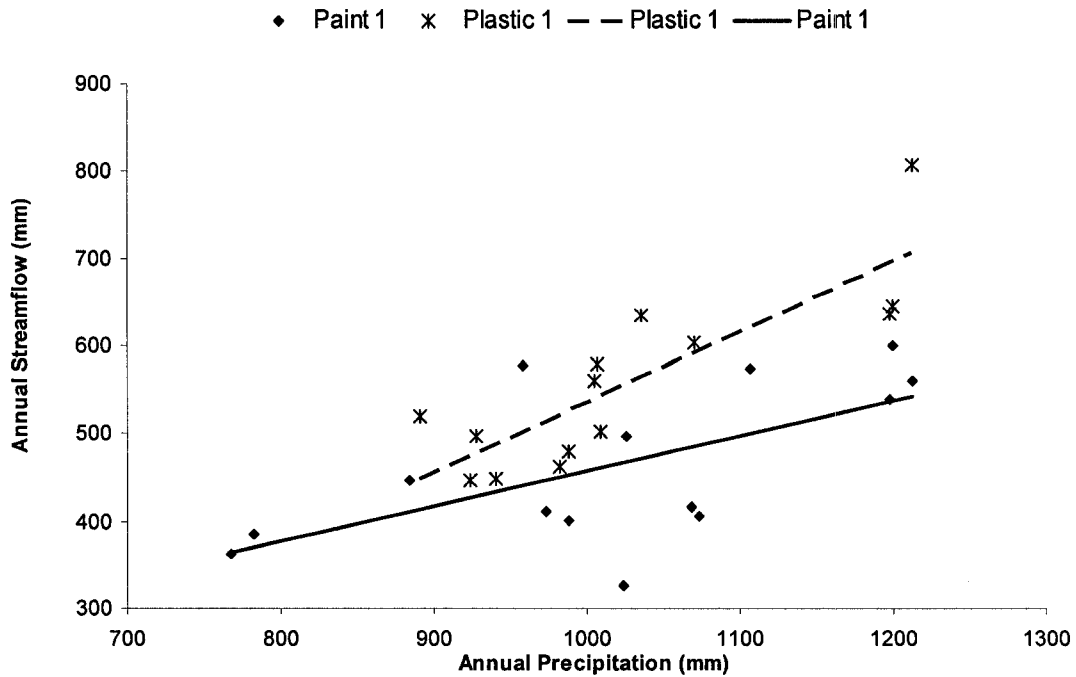
Paint 1   :   y = 0.40x + 58.46, $r^2 = 0.39$

Plastic 1   :   y = 0.80x - 265.56, $r^2 = 0.72$

Figure 3: Illustration of the relationship between precipitation input and discharge of the Paint 1 and Plastic 1 basins. Regression for the Plastic 1 basin is significant at p<0.05.

2.3.1   Runoff characteristics

In small catchments, streamflow reflects the combined result of all climatic and hydrologic processes within a catchment. The shape of the flow duration curve is determined by the size and physical characteristics of a drainage area and can be used to describe the hydrological response of a catchment to precipitation. In this section the flow

duration curves of the different catchments are compared in order to assess runoff patterns

of each individual basin.

Flow duration

◇ HP 3A   ▫ HP 4   △ HP 5   × HP 6   ✕ PT 1   – PC 1
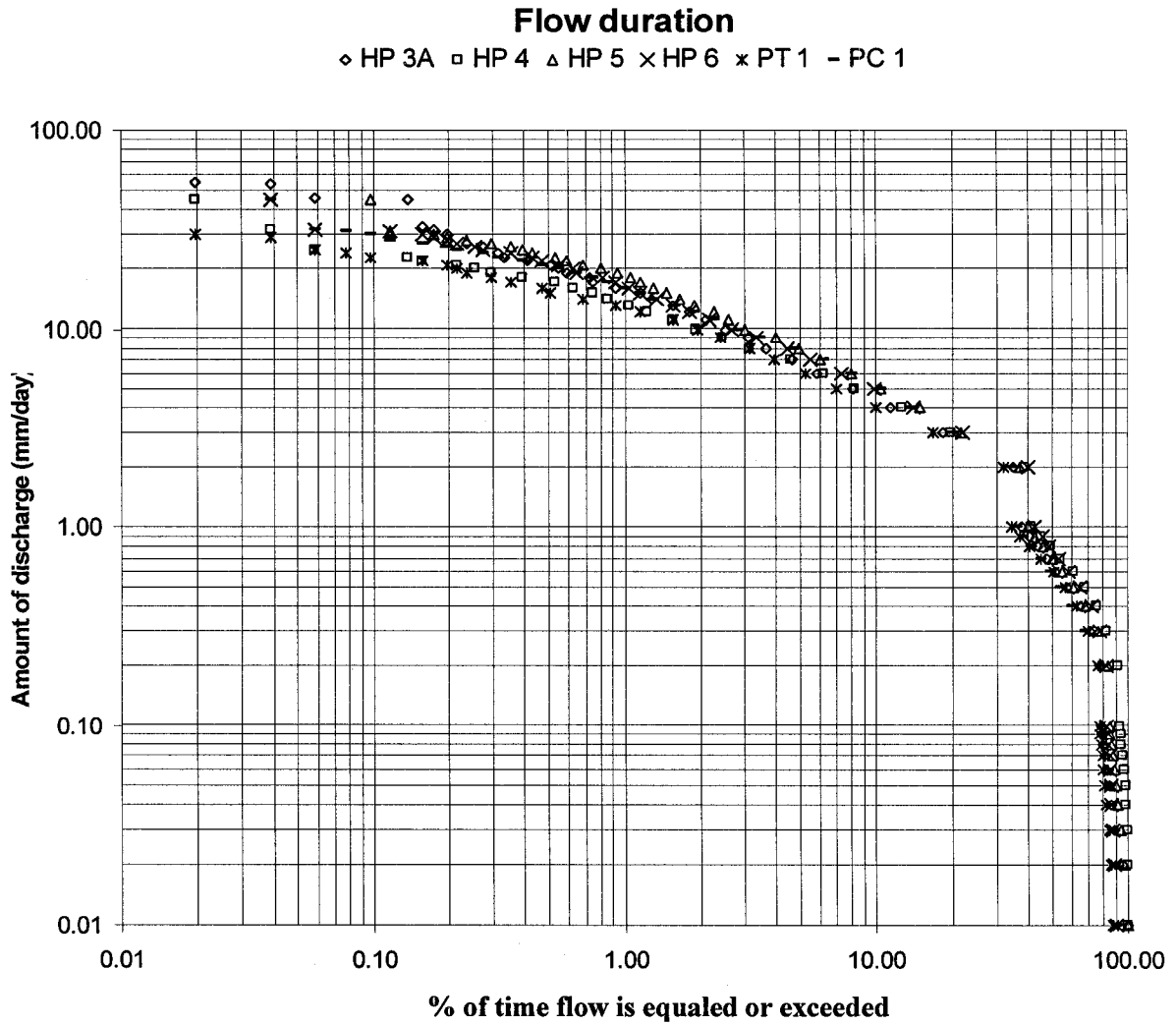
Figure 4: Flow duration curves for Harp 3A, 4, 5, 6, Plastic 1 and Paint 1; 1979-1993

In unregulated streams, the distribution of low flows is controlled mainly by the

geology of the basin. For example, the type, thickness and distribution of surficial soils

determine the hydrologic characteristics of the groundwater storage (Peters and Murdoch,

1985; Peters and Driscoll, 1987). Basins containing deep deposits of till will store more

water and release it more slowly than those containing shallow deposits of till interrupted with outcrops of underlying bedrock (Newton et al., 1987; Peters and Driscoll, 1987). Although the examined basins are underlain by varying percentages of till thickness (Table 1), the distribution of low flow responses suggests similar storage capacities and groundwater dynamics among the basins (Figure 4). The distribution of high flows is governed largely by climate, physiography, such as slope gradients and drainage density patterns, and vegetation cover of the basin (Lane and Lei, 1950). Changing climatic factors throughout the year, such as the type, quantity, intensity and frequency of precipitation, and evapotranspiration rates have considerable effects on flow responses. In order to examine the seasonal influence on the temporal distribution of flows for each individual basin flow duration curves are plotted for each season individually.

a)

HP 3A

✕ Summer ◇ Fall □ Winter △ Spring

% of time flow is equaled or exceeded

b)

HP4

✕ Summer ◇ Fall □ Winter △ Spring

% of time flow is equaled or exceeded

25

c)

HP 5

✳ Summer   ◇ Fall   ▫ Winter   △ Spring

% of time flow is equaled or exceeded

d)

HP 6

✳ Summer   ◇ Fall   ▫ Winter   △ Spring

% of time flow is equaled or exceeded

26

e)

PT 1

✕ Summer ◇ Fall ▫ Winter △ Spring

f)

PC 1

✕ Summer ◇ Fall ▫ Winter △ Spring
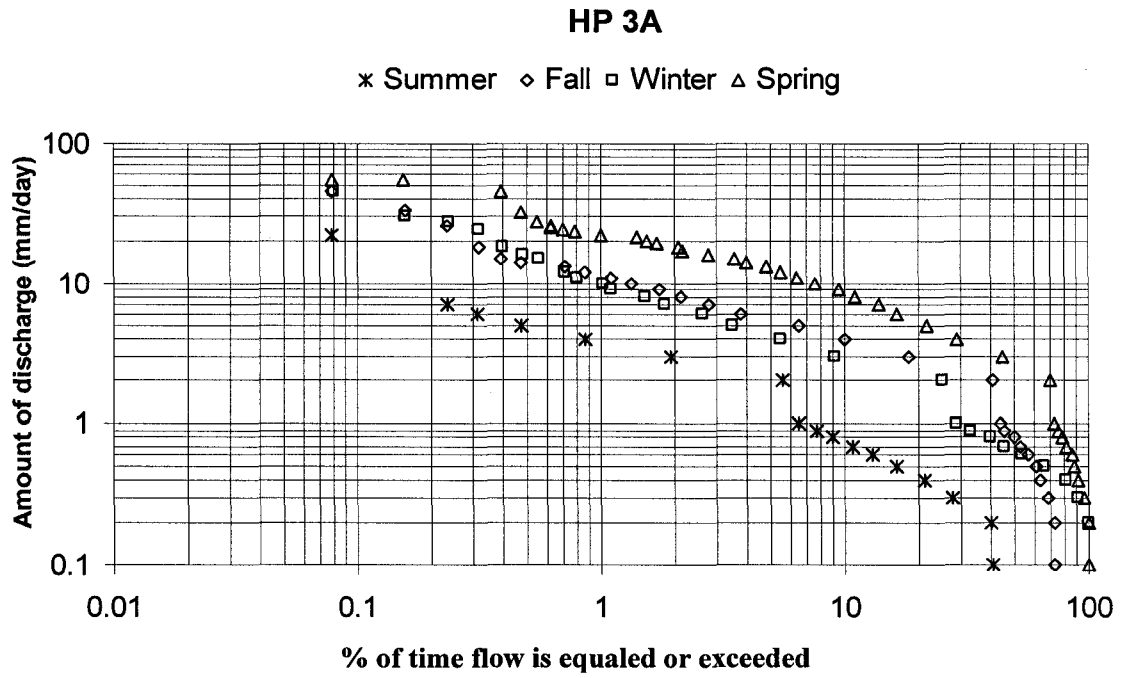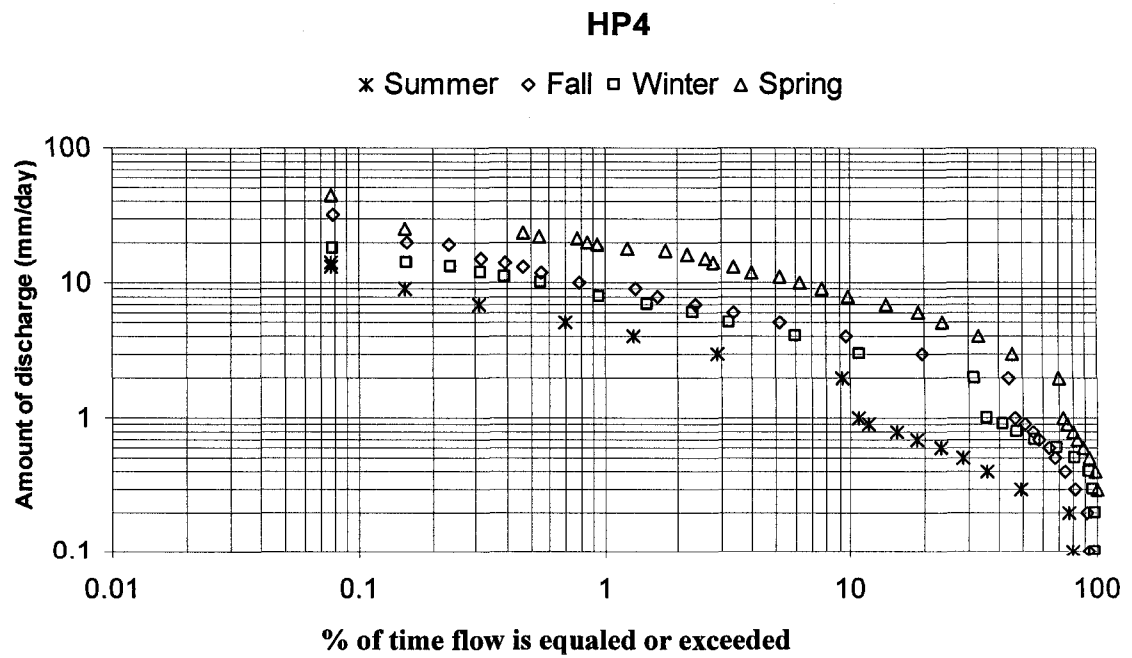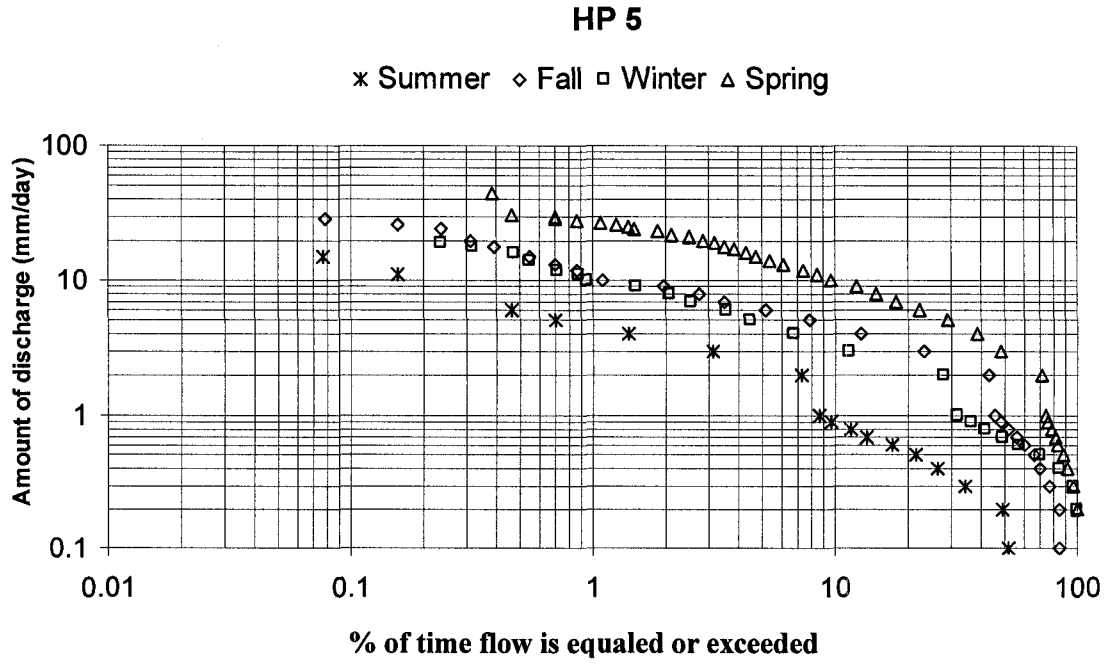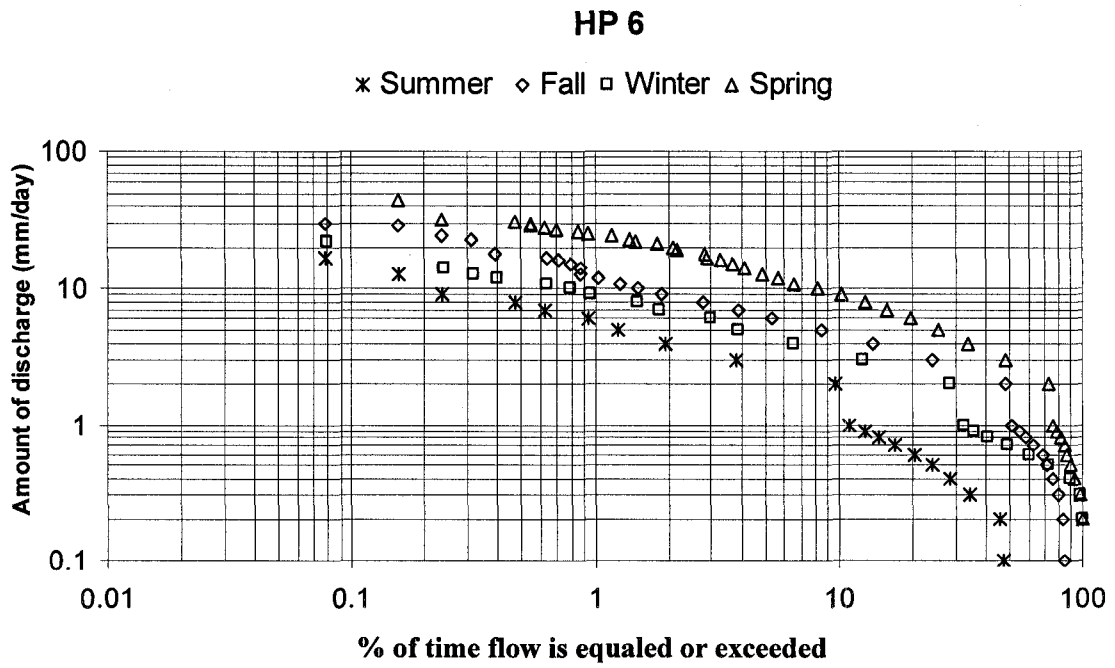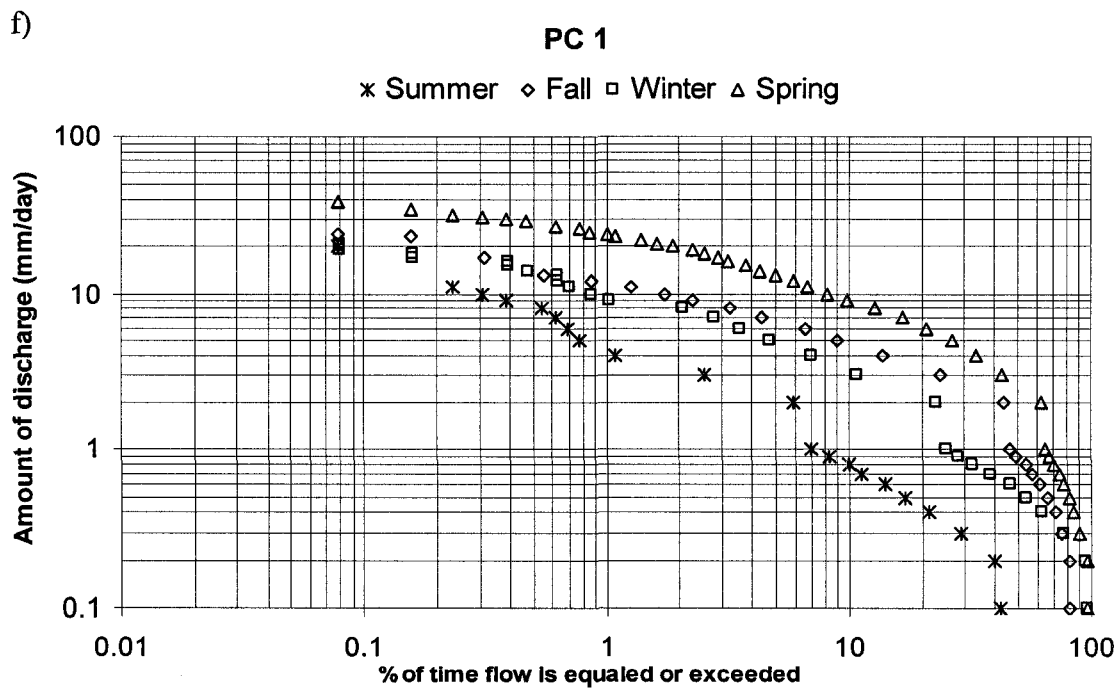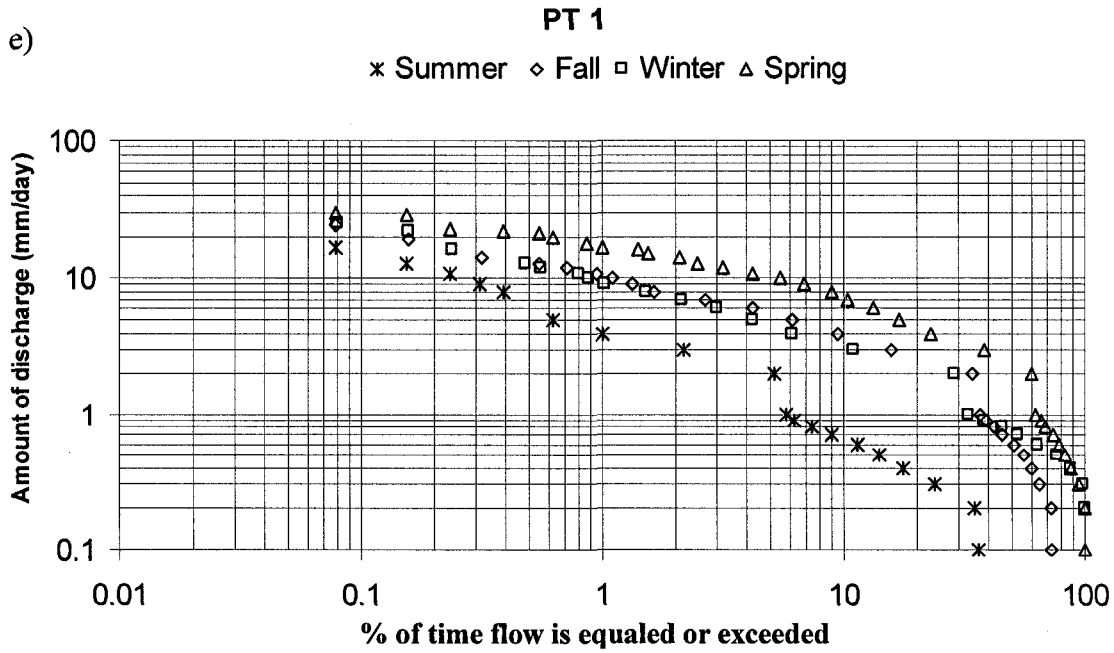
Figure 5a - f: Seasonal flow duration curves for study sites: Harp 3A (a), 4 (b), 5 (c), 6 (d), Paint 1 (e) and Plastic 1 (f).

Flow duration curves differ only slightly among basins (Figures 5a - f). The wettest conditions prevail in spring (March 1 – May 31). The flow duration curves for spring show fairly flat slopes at the upper limit of the curve suggesting sustained flows due to water inputs during snowmelt and rainfall on wet soil during this season. This slope increases as the season gets drier indicating a depletion of groundwater storage.

For the summer season (June 1- August 31), water requirements for vegetation growth and evapotranspiration increase significantly resulting in reduced flows. In comparison with the other seasons, summer flow duration curves therefore are somewhat steeper throughout the entire range of flows. Infrequent precipitation events for short periods of time and summer thunderstorms dominate the season resulting in a slightly steeper shape of the flow duration curve.

Fall curves (September 1 – November 30) are again flatter in the upper and mid-range percentiles but become steeper in the low flow range. During this season, growth of vegetation ceases and evapotranspiration rates drop. This increases soil moisture and water tables, which results in larger runoff and consequently in a more horizontal curve. The steepness of the curve in the low flow range indicates that storage capacities in the DESC basins are limited suggesting a fast depletion of groundwater.

In the winter (December 1 – February 28), flows generally decrease due to the accumulation and storage of precipitation as snow, thus are generally lower compared to the spring and fall season. A somewhat flatter curve in the low flow region points to less zero-flow days as product of snowmelt processes resulting in well sustained flows in the low flow range.

In contrast to the Harp and Paint basins the flow duration curve of PC 1 (Figure 5f) shows a somewhat different shape in the mid range percentiles during the summer. The slope of the curve becomes flat at mid flow ranges, which is a result of the wetland proportion acting as a reservoir that gradually releases stored water.

The results show that the range of discharges in each basin and season is fairly similar, which suggests that all basins examined are within a region that is hydrological homogeneous.

2.3.2   *Coefficients of variation*

The coefficient of variation (CV) was used to compare the variability of annual streamflow of the different basins. The CV of annual maximum streamflow quantifies the combined effect of a basin's mechanism to store or release water and is subject to change with varying basin properties, particularly with basin size (Blöschl and Sivapalan, 1997). Small CVs generally indicate low variability and vice versa.
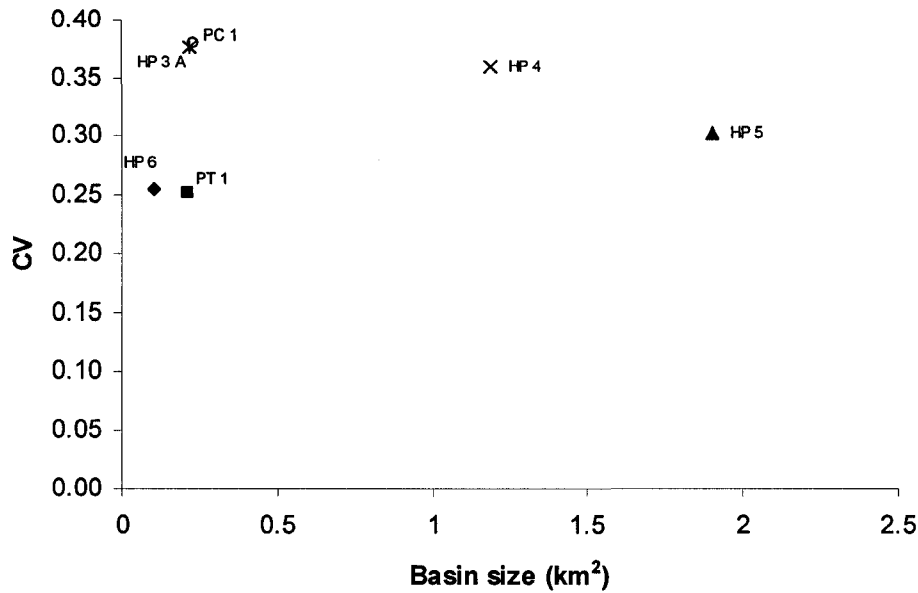
Figure 6: Variation of CVs of maximum annual flows for the basins PC 1, PT 1, HP 3A, HP 4, HP 5 and HP 6 calculated from a time period from 1979/80 until 1992/93.

CVs of maximum annual streamflow vary among the catchments (Figure 6). HP 6 and PT 1 show the smallest CVs suggesting the least variability in maximum streamflow response among the studied basins. HP 3A and PC 1 exhibit the highest CVs, thus indicating the greatest variability in maximum annual streamflow. HP 4 and HP 5, which are the catchments with the largest area, fall between these values. Blöschl and Sivapalan (1997), who analyzed CV data from a number of catchments with differing area sizes in Austria, have shown that CVs increase up to a catchment size of approximately 100 km^2 and decrease thereafter. This pattern within the DESC basins can only be partly observed suggesting that other factors override the influence of basin size on maximum annual response patterns. For example, basin sizes of PT 1, HP 3A and PC 1 are very similar ranging around 0.2 km^2, and thus should result in similar CVs (Table 1). However, the CV

of PT 1 is smaller than those of PC 1 and HP 3A suggesting that yearly maximum runoff responses in PT 1 are more consistent throughout the years. The spatial distribution of tills within the PT 1 provides more evenly distributed runoff responses to precipitation inputs, which results in a lower variability of maximum annual flows.

Greater variability of maximal annual flows results from the wetland proportion within the catchment. The stream of PC 1 can dry up for extended time periods (Figure 5 f) and the water table in the PC 1 swamp drops below the surface due to evaporation and reduction in streamflow. Stream discharge is increased in wetter years as riparian zones and wetlands are extended. Overall the variability of runoff responses is increased.

Higher maximum streamflow variability observed in HP 3A is caused by a different reason. Above approximately 340 m elevation, the HP 3A stream dries out during the summer due to thin soil coverage (< 1.5 m) on the hillslopes (Hinton, 1998), while downstream baseflow is sustained with little flow. After the onset of fall storms when soil moisture is replenished, the water table increases and reaches into the upslope areas of the catchment, thus extending the area contributing to streamflow by re-connecting the upslope area with the valley. Short duration rainfall events would not cause hillslope areas to contribute to streamflow during dry periods (Buttle et al., 2004). Annual maximum streamflows therefore are more variable when compared to PT 1.

Catchments with little storage, such as PT 1 and HP 6, are more consistent in maximum annual runoff patterns, whereas catchments such as PC 1 and HP 3A exhibit more variable responses on a year to year basis implying that annual runoff patterns are highly variable among basins.

2.3.3 Standard departure analysis

In order to compare annual precipitation, streamflow, and temperature, Z-scores
were used to evaluate similarities among catchments. Due to the differences in data record
length for the basins and in order to truly compare each individual basin the analysis was
done for varying lengths of time. Therefore, to compare precipitation and streamflow of the
Harp basins (HP 3A, HP 4, HP 5, and HP 6) and PC 1, a time period from 1979/80 –
1997/98 was used (Figures 8a and b). To perform a comparison between PT 1, PC 1 and the
Harp basins a time frame from 1979/80 – 1992/93 was utilized (Figures 9a and b) and to
compare PC 1-08 and PC 1 a time period from 1987/88 to 1994/95 was used (Figure 10).

Local weather characteristics within the Dorset area prevailing during the study
period were analyzed using mean monthly and annual temperatures. Figure 7 shows
standardized annual deviations of temperature from the long-term annual mean.
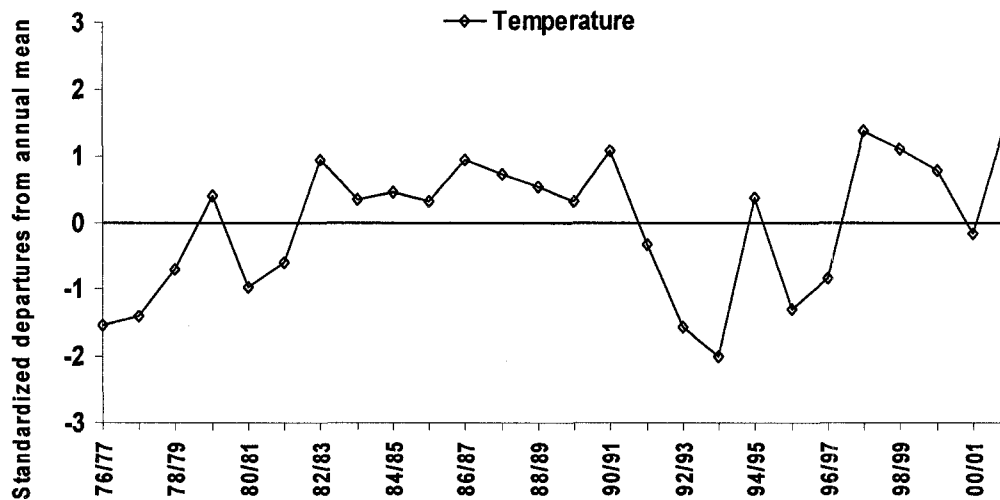
Figure 7: Standard departures of mean annual temperature 1976/77-2001/02 Dorset station.

On an annual scale temperatures greatly deviate from the long term mean. Noticeable is a warm spell during the 1980s, which is suddenly interrupted by colder temperatures just after 1990/91. The time period from 1991/92 to 1996/97 is the coldest period recorded. Warmer temperatures occur from 1982/83 until 1990/91, where departures were consistently elevated, peaking in 1990/91. The greatest positive deviations occur in 1997/98 and 2001/02. Climate is more inconsistent during the time period from 1990/91 to 2001/02, with greater positive and negative departures from the mean.

To obtain deviations from the long-term mean in percentages on a monthly scale all temperatures were shifted to the positive by adding 50°C. Daily values were averaged by month for the period from 1976 to 2002. The long-term mean from the observed monthly value was subtracted and then divided by the long-term mean to standardize the results. On a monthly scale strongest deviations can be observed from December to February. Winter temperatures during the late 1970s and early 1980s frequently show negative deviations from the mean, while winter temperatures during the late 1990s exhibit positive deviations more commonly suggesting milder winters during the latter period.

Table 3: Monthly deviations of long-term mean temperatures in the Muskoka-Haliburton region. Values which deviate more than minus 5% are shaded in darker grey, whereas values deviating more than plus 5% are shown in bold.

	Jun	Jul	Aug	Sept	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May
76/77	1.89	-2.42	-2.32	-2.38	-5.94	-3.76	-11.66	-10.29	-2.08	**6.36**	-1.34	2.66
77/78	-0.82	0.77	-1.55	0.39	0.03	-0.59	-2.74	-7.20	-12.11	-6.79	-4.37	3.60
78/79	-0.98	0.38	2.50	0.27	-1.53	2.02	-0.80	-6.35	-14.32	2.45	-1.79	0.51
79/80	-0.56	1.45	-0.36	2.15	0.88	4.32	4.16	2.63	-7.06	-3.48	1.39	0.74
80/81	-4.81	0.72	3.36	0.15	-2.15	-2.28	-13.43	-13.33	**11.14**	0.35	2.30	-2.50
81/82	0.05	0.43	0.53	-0.01	-1.97	1.52	4.16	-11.31	-4.15	-3.05	-5.04	4.14
82/83	-2.07	0.57	-2.60	1.59	4.26	4.12	**9.72**	**5.17**	**6.04**	2.91	-1.37	-4.93
83/84	0.51	1.74	3.06	4.15	1.41	0.72	-7.41	-4.74	**12.53**	-6.91	3.66	-4.51
84/85	1.08	-0.51	1.76	-2.10	4.30	0.11	**5.65**	-6.48	3.26	0.32	0.41	0.03
85/86	-2.38	-0.96	-1.00	1.96	2.62	-0.24	-5.71	-0.30	-0.60	2.69	**5.52**	3.32
86/87	-1.61	0.60	-2.02	-0.55	0.09	-2.29	**5.39**	**5.67**	0.27	**5.85**	**7.47**	1.62
87/88	2.12	3.41	0.06	2.06	-3.01	-0.06	**6.26**	2.10	-3.83	-1.68	0.53	3.80
88/89	-0.18	4.25	2.12	0.28	-2.96	3.04	0.20	**10.52**	-2.03	-2.21	-2.84	0.26
89/90	0.72	1.71	0.04	0.10	1.58	-3.29	-18.61	**17.37**	4.51	3.18	3.16	-2.75
90/91	0.36	-0.10	1.46	-1.18	0.26	1.22	2.41	0.50	**5.43**	2.75	3.29	4.28
91/92	2.51	0.55	1.60	-1.96	2.09	-0.81	-1.58	0.69	0.07	-6.42	-3.13	-1.05
92/93	-2.80	-4.84	-3.67	-0.87	-4.07	-2.29	2.51	4.38	-10.73	-1.74	-0.26	-1.66
93/94	-1.45	0.32	0.69	-3.76	-3.12	-2.40	-0.80	-20.16	-8.94	-0.54	-0.96	-1.37
94/95	1.11	-0.34	-2.81	0.05	1.22	2.88	**5.49**	**11.54**	-6.18	4.52	-5.62	-0.93
95/96	2.62	0.20	1.61	-2.93	3.31	-6.91	-7.70	-2.77	-2.82	-4.25	-4.77	-2.99
96/97	1.39	-2.54	0.01	1.50	0.08	-5.38	**7.36**	-4.09	1.10	-3.75	-2.98	-6.92
97/98	1.78	-1.02	-2.72	-0.91	-0.46	-2.11	1.84	**9.94**	**13.77**	2.74	2.57	**5.32**
98/99	-0.18	-1.26	1.34	1.51	1.17	1.94	**6.49**	-1.06	**6.70**	0.53	1.69	2.93
99/00	2.34	0.98	-2.08	1.79	-1.09	3.53	1.54	-0.78	3.41	**7.86**	-1.57	-0.46
00/01	-1.97	-2.55	-1.39	-1.35	1.55	-0.18	-3.80	4.33	1.11	0.11	1.90	1.30
01/02	1.35	-1.56	2.38	0.01	1.46	7.16	**11.03**	**14.03**	5.51	-1.80	2.17	-4.43

In general, temperature, and the parameters streamflow and precipitation are inversely related (Figures 8 - 10). Streamflow and precipitation of the Harp catchments exhibit almost alternating deviations from year to year (Figure 8a). The fluctuation of precipitation shows greater amplitude on a year to year basis compared to streamflow for most years. Increased precipitation inputs are offset by increased evapotranspiration. However, in years with little precipitation and above average temperatures (1986/87 –

1989/90) streamflow variability has a greater amplitude than precipitation, which is a result of decreased water levels and reduced hydrological connections within the basins. The highest absolute deviation from the mean occurs in 1997/98, which was an exceptionally warm year indicated by the positive deviation of temperature, and negative deviations of precipitation and streamflow. Positive deviations for streamflow and precipitation are greatest in 1995/96 and 1996/97, which also coincides with cooler temperatures, resulting in the wettest years recorded.

Streamflow and precipitation variability in PC 1 is overall similar to fluctuations in Harp basins suggesting regional climate influences.

One noticeable exception occurs in 1989/90, where precipitation inputs significantly diverge from the average but streamflow shows little deviation. This can be attributed to the fact that PC 1 contains a wetland, which acts as a storage reservoir only slowly releasing water, thus resulting in less variable flow responses. Positive deviations for streamflow and precipitation are greatest in 1982/83 and 1996/97, which also coincides with cooler temperatures in the case of 1996/97. In 1982/83 temperatures are warmer, which may be attributed to global climate influences, such as the El Niño-Southern Oscillation.

a)
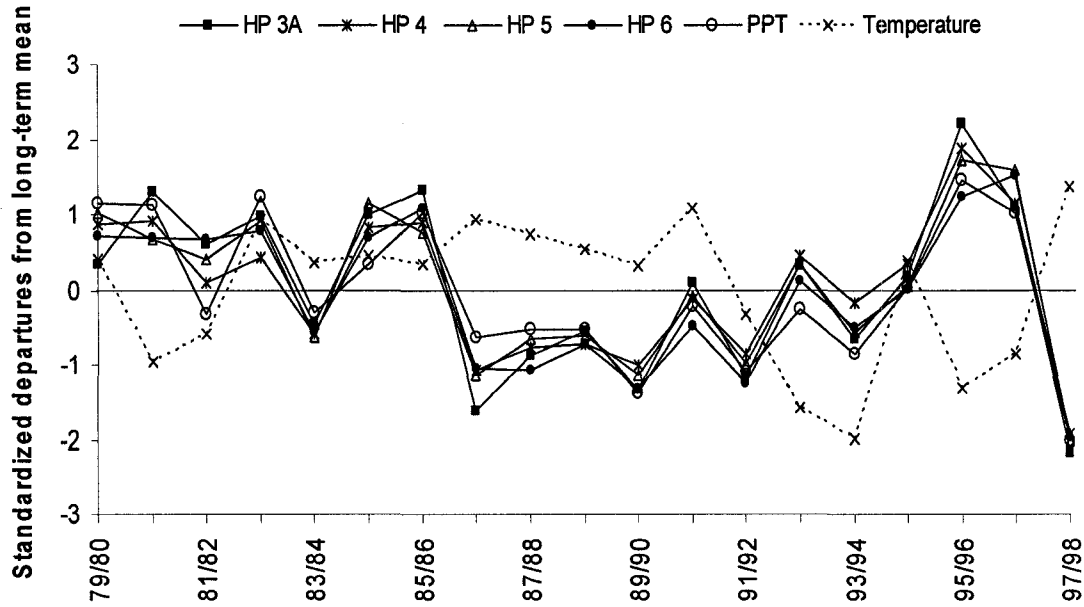
b)
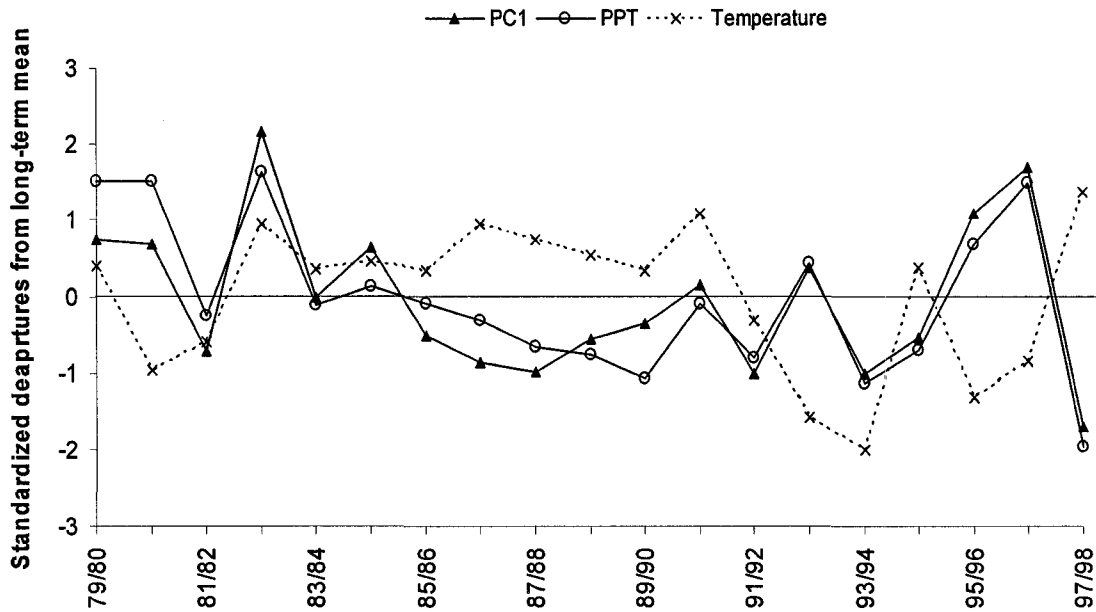
Figure 8a and b: Departures from long term mean for the (a) Harp basins, HP 3A, HP 4, HP 5 and HP 6 and (b) Plastic basin, PC 1 for the time period (1979/80 – 1997/98).

a)
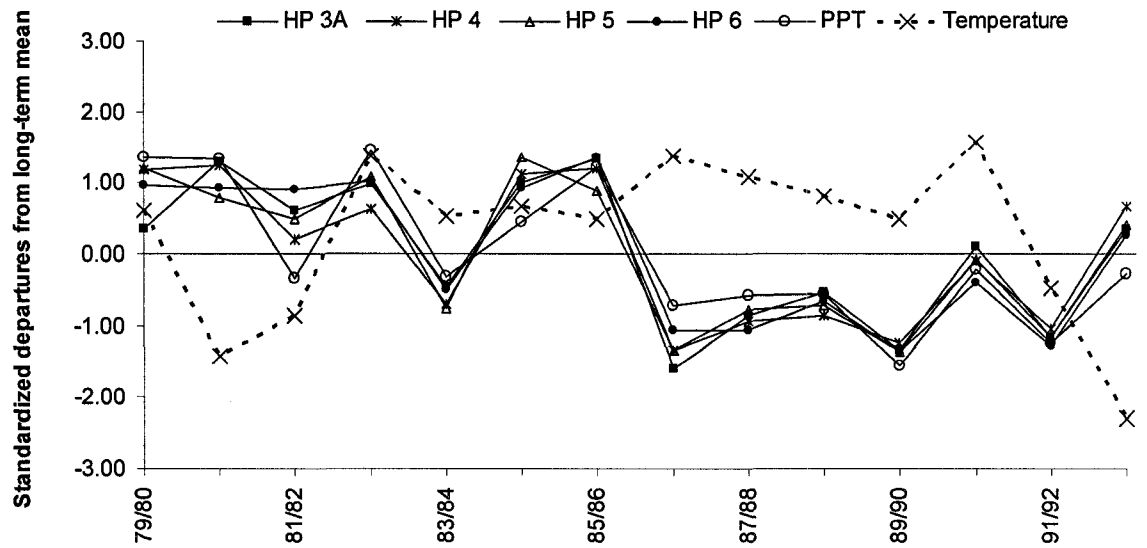
b)
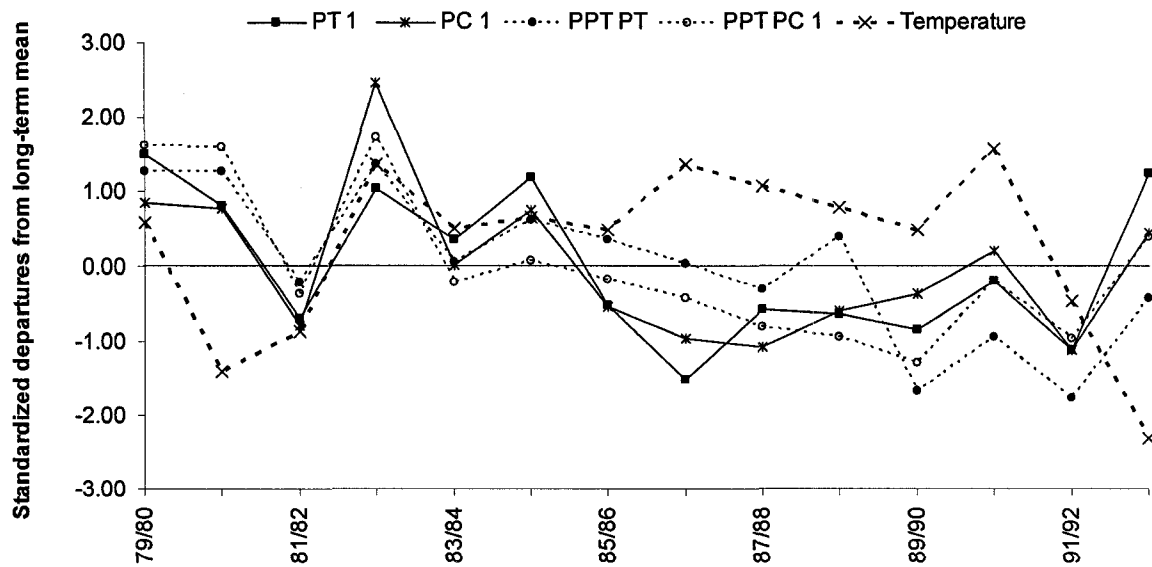
Figure 9a and b: Departures from mean annual stream flow and precipitation for the basins, HP 3A, HP 4, HP 5,HP 6, PC 1 and PT 1 from 1979/80 – 1992/93.

37

In PT 1 streamflow generally follows precipitation inputs until 1985/86 (Figure 9b).

Thereafter, patterns are inconclusive and could indicate problems with the gauge in this

basin. Streamflow compared to precipitation shows greater deviation from the long-term

mean suggesting that precipitation may not be the most important driving process that

affects year to year discharge fluctuations.
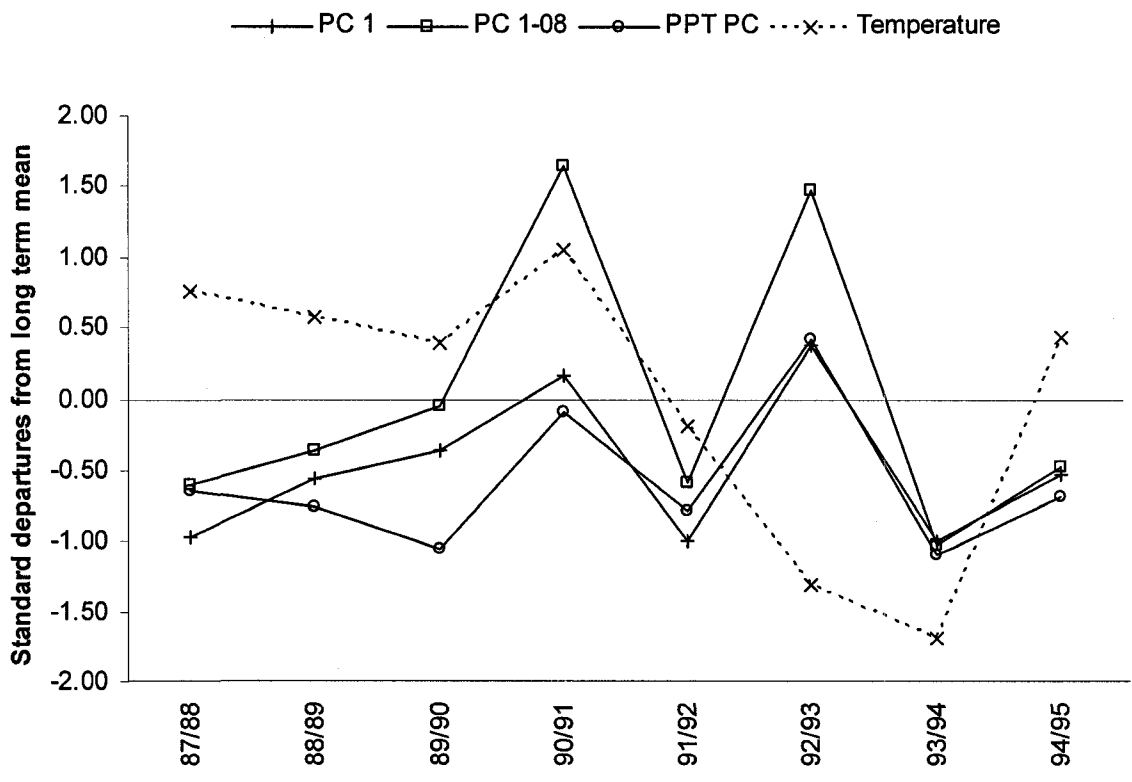
Figure 10: Departures from mean annual precipitation streamflow for PC 1 and PC 1-08, for the time period from 1987/88 – 1994/95.

Streamflow and precipitation of the Plastic basins show alternating year to year

fluctuations (Figure 10) for the most part of the record. High deviations from the mean

occur from 1990/91 to 1993/94. Generally, streamflow deviations in PC 1-08 are greater

compared to PC 1 if precipitation is above or around the average. If there is little annual

precipitation, deviations of streamflow are greater in PC 1 due to the influence of the

wetland proportion within this catchment. Increased storage due to decreased water input

results in a reduction of storm flow responses compared to PC 1-08.

Z-scores of streamflow versus precipitation and streamflow versus temperature

were plotted to evaluate the influence of temperature and precipitation on discharge

(Figures 11 and 12).

× HP 3A ◆ HP 4 ■ HP 5 △ HP 6 × PC 1 ○ PT 1
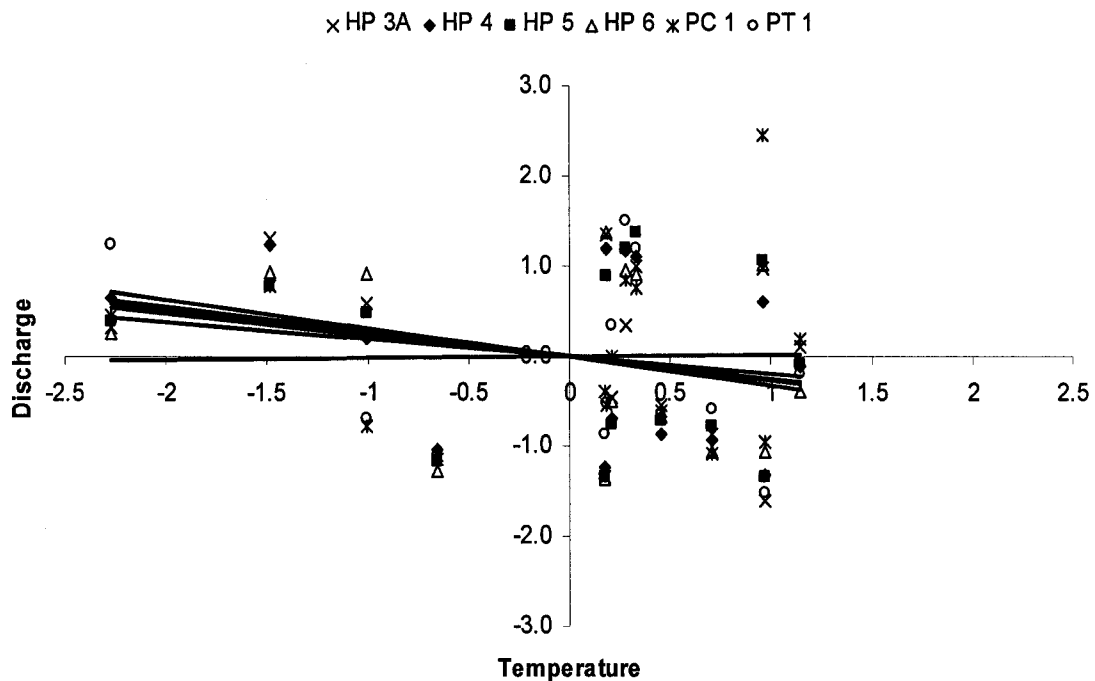
HP 3A; y = -0.27x - 0.00, R^2 = 0.07   HP 4; y = -0.32x - 0.00, R^2 = 0.10
HP 5; y = -0.19x - 0.00, R^2 = 0.04   HP 6; y = -0.24x - 0.00, R^2 = 0.06
PC 1; y = 0.02x + 0.00, R^2 = 0.00   PT 1; y = -0.26x - 0.00, R^2 = 0.07

Figure 11: Z-scores of discharge versus temperature for the period from 1979/80 to 1992/93
for each basin.

Figure 12: Z-scores of discharge versus precipitation for the period from 1979/80 to 1992/93 for each basin.
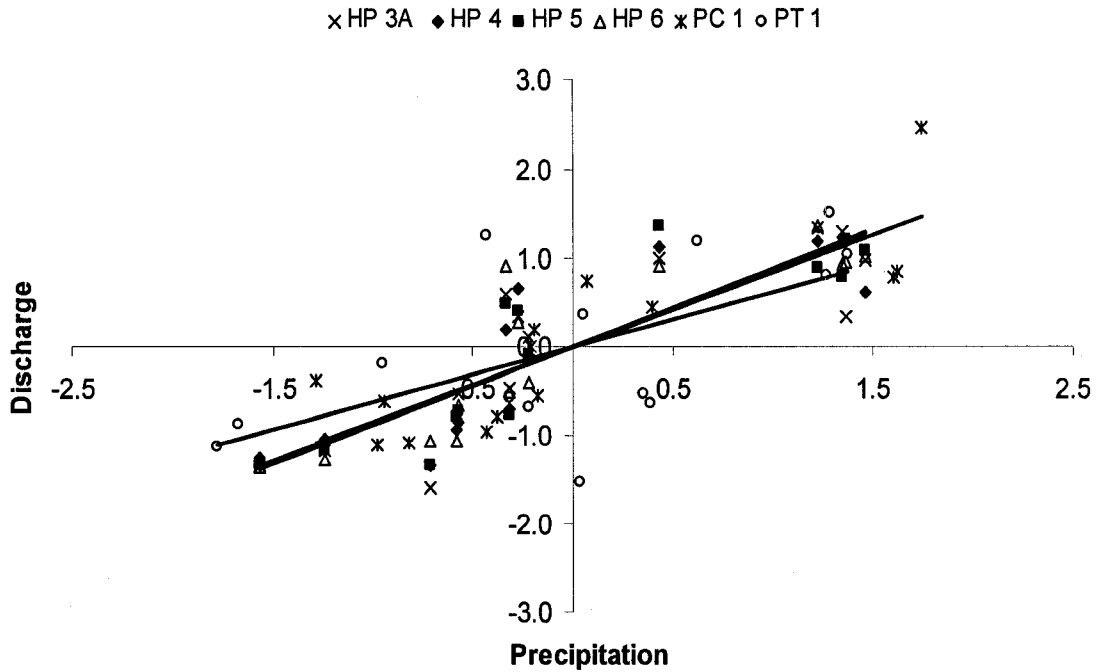
HP 3A; y = 0.85x + 0.00, R^2 = 0.72*   HP 4; y = 0.87x + 0.00, R^2 = 0.76*
HP 5; y = 0.87x + 0.00, R^2 = 0.76*   HP 6; y = 0.88x + 0.00, R^2 = 0.78*
PC 1; y = 0.84x - 0.00, R^2 = 0.71*   PT 1 ; y = 0.62x + 0.00, R^2 = 0.39

* significant at $p < 0.05$

Significant regressions between deviations of precipitation and discharge are

observed in Figure 12. The coefficients show that in most occasions discharge is reduced if

precipitation is decreased and vice versa. The lower regression coefficient for PT 1 is

related to inaccuracies at the stream gauge in this basin. Temperature has no clear effect on

discharge as regression equations show no significant trend.

2.3.4 Autocorrelation

Autocorrelations for monthly precipitation and streamflow totals were performed in order to determine systematic trends among the DESC basins. The autocorrelation function is a statistical description of a time series that measures dependence among adjacent time series values. Autocorrelation is essentially a correlation coefficient. However, instead of two different time series, the correlation is computed between one time series and the same series lagged by one or more time units. The lagged autocorrelations shown in Figures 13 – 18 refers to the correlation between the time series against itself offset in time by one to several months.

Time series that are positively correlated are sometimes referred to as persistent because high values tend to follow high values and low values tend to follow low values. Time series that are characterized by reversals from high to low values or from low to high values from one lag to the next are negatively correlated (Dawdy and Matalas, 1964). Hydrological time series is often autocorrelated because of carryover processes in the physical system. The most common patterns are trends and seasonality. Seasonality is a trend that repeats itself systematically over time.

Autocorrelogram (PT - Precipitation)
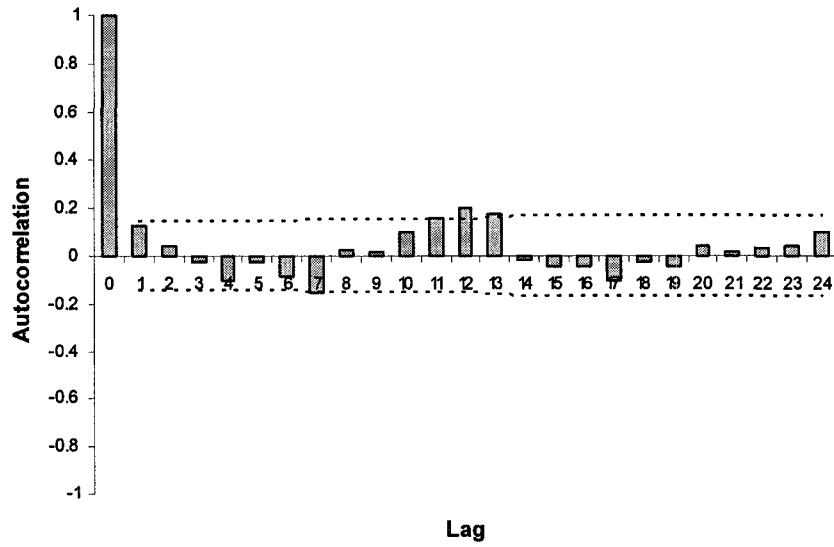
Figure 13: Autocorrelation of the monthly time series (June – May) from 1976/77 – 1992/93 for the Paint catchment.

Autocorrelogram (PC - Precipitation)
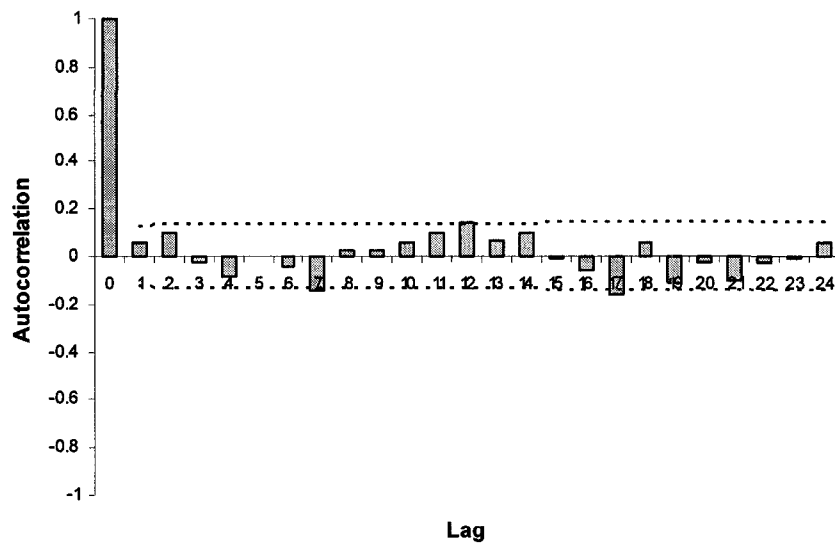
Figure 14 : Autocorrelation of the time series (June – May) from 1979/80 – 1997/98 for the Plastic catchment.

Autocorrelogram (HP - Precipitation)
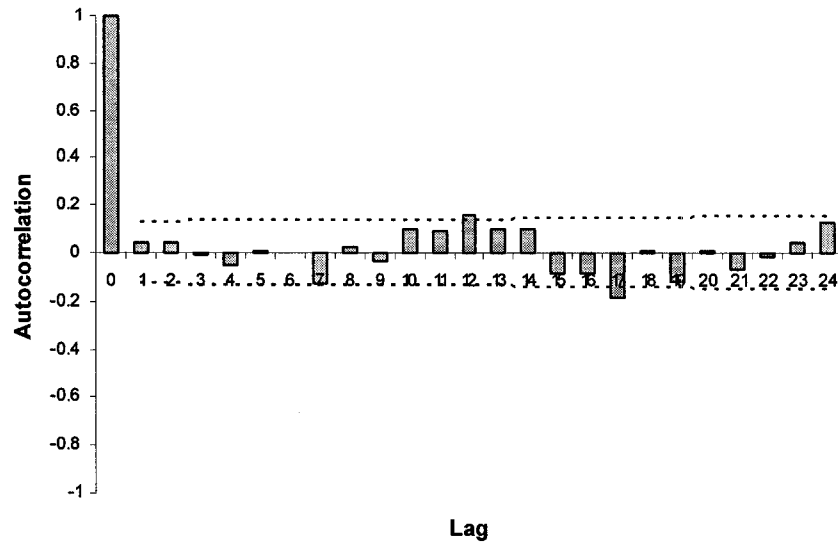
Figure 15: Autocorrelation of monthly time series (June – May) from 1979/80 – 1997/98 for the Harp catchment.

The dashed lines mark the 95% confidence limits. Bars that exceed dashed lines are statistically significant.

Autocorrelation plots show significant correlations at lag seven, twelve and in the case of the Harp and Plastic data also at lag seventeen suggesting the presence of some trend. However, whether or not seasonality exists cannot be detected with confidence. Although by analyzing the raw data set seasonality is implied as precipitation is increased during fall and reduced during the summer, monthly autocorrelations do not show this pattern in a recurring regular stretch of correlations from positive to negative.

a)

Autocorrelogram (HP 3A - Discharge)

b)
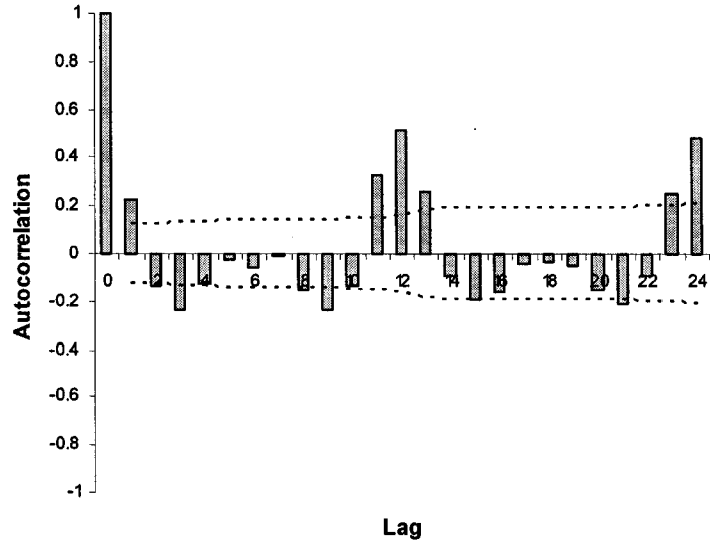
Autocorrelogram (HP 4 - Discharge)

c)

Autocorrelogram (HP 5 - Discharge)

d)

Autocorrelogram (HP 6 - Discharge)
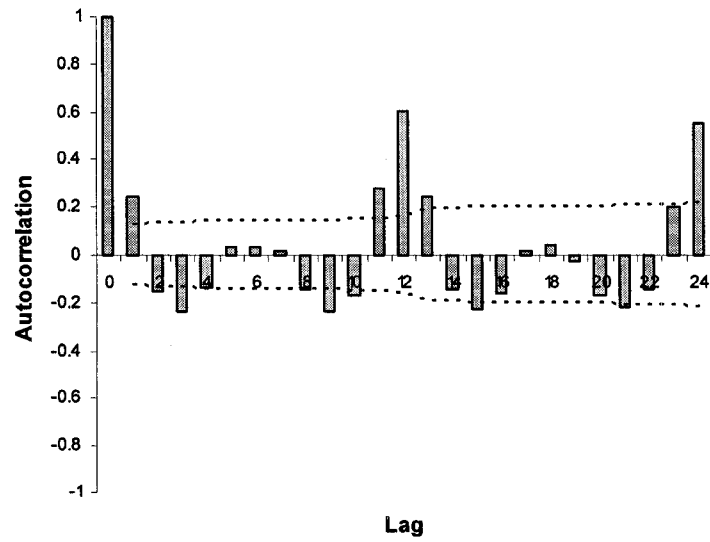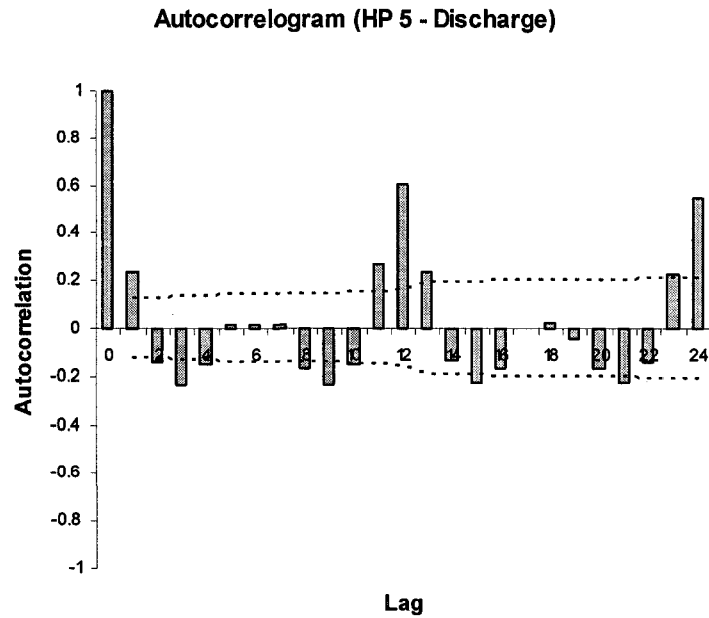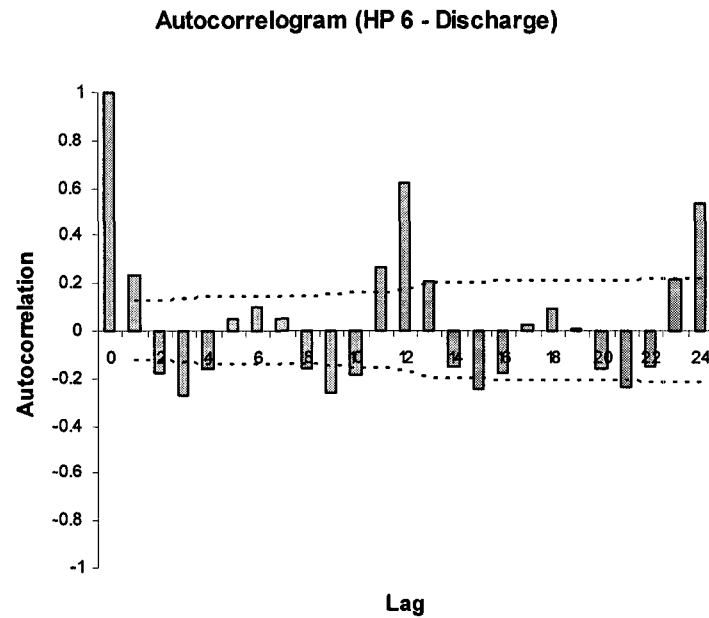
Figure 16a - d: Autocorrelation function of the monthly time series (June – May) from 1979/80 – 1997/98 for the Harp basins, HP 3A (a), HP 4 (b), HP 5 (c), HP 6 (d).

The dashed lines mark the 95% confidence limits. Bars that exceed dashed lines are statistically significant.

a)

Autocorrelogram (PC1 - Discharge)

b)

Autocorrelogram (PC 1-08 - Discharge)
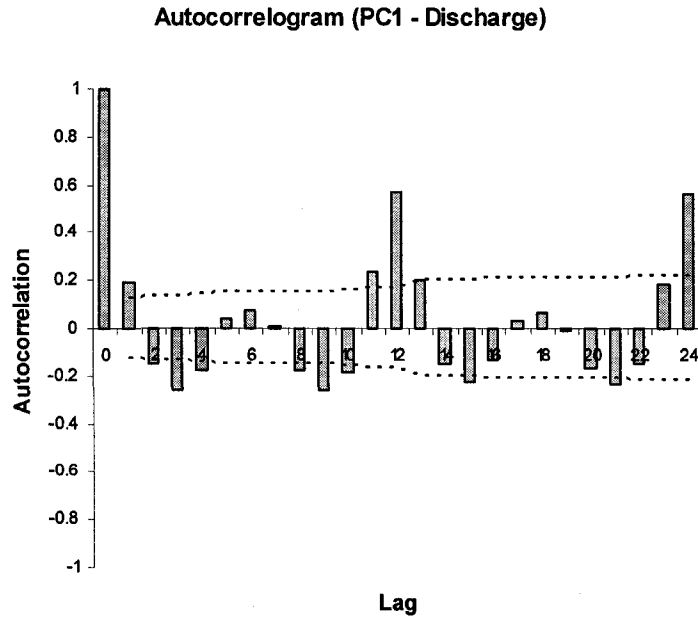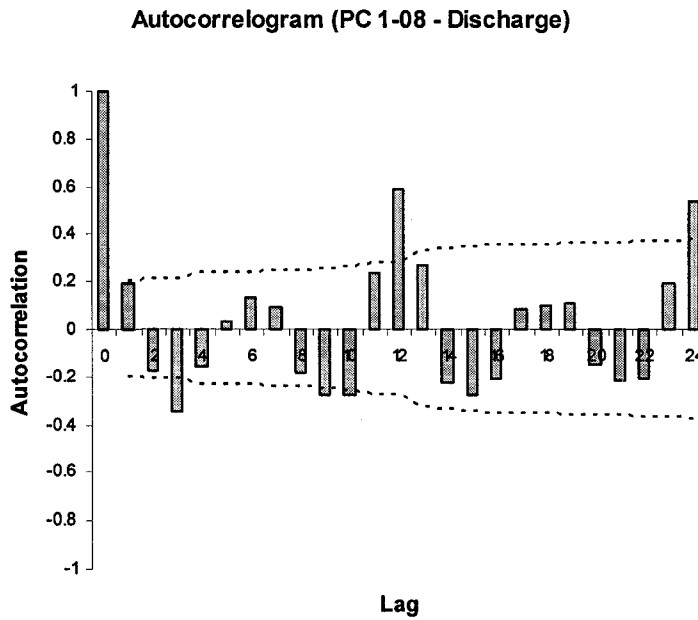
Figure 17a and b: Autocorrelation function of the monthly time series (June – May) from 1979/80 – 1997/98 for the Plastic basin, PC 1 (a) and from 1987/88 to 1994/95 for PC 1-08 (b).

The dashed lines mark the 95% confidence limits. Bars that exceed dashed lines are statistically significant.

Autocorrelogram (PT1 - Discharge)
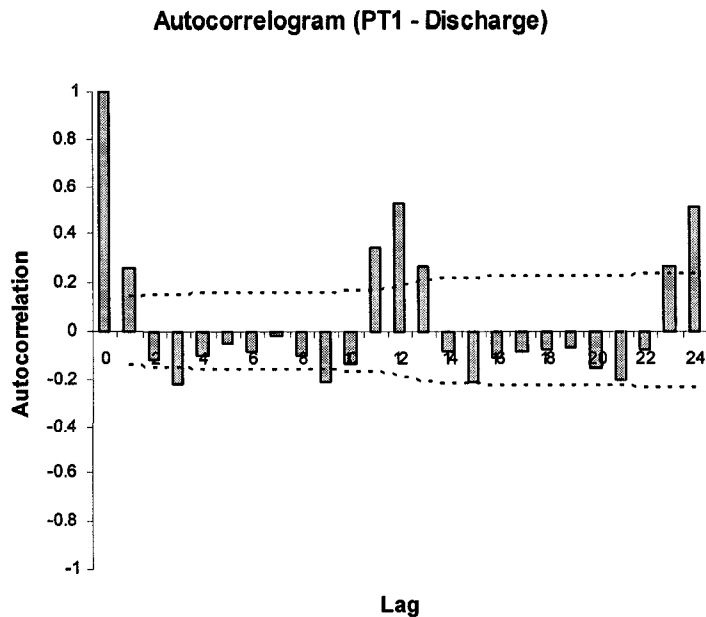
Figure 18: Autocorrelation function of the monthly time series (June – May) from 1976/77 – 1992/93 for the Paint basin, PT 1.

The dashed lines mark the 95% confidence limits. Bars that exceed dashed lines are statistically significant.

Autocorrelograms reveal seasonality for discharge. In Figures 16 -18, there are several residual values that lay more than two standard errors from the zero mean. Spikes show a systematic pattern, shifting in a sequence from positive to negative. This can be an indication of a seasonal pattern that cycles between summer, when there is little discharge, to fall, when discharge is increased, to winter, when discharge is reduced, and to spring, when discharge is at its peak. This is especially evident in the Plastic and in most of the Harp basins. Positive autocorrelation shows that dry or wet months are successive while negative autocorrelation indicates that wet months tend to be followed by dry months or vice versa.

2.4 Discussion and conclusion

Analysis of time series data suggests that patterns of precipitation inputs and streamflow responses within the DESC basin repeat themselves over time (Figures 13 - 18), although recurring cycles of precipitation and streamflow differ. This can be attributed to large-scale climate inputs that affect both precipitation and streamflow. Stream responses show shorter cycles of alternating sequences of positive and negative spikes that are not produced by persistence in the climate system but result from hydrological processes within the catchment.

2.4.1   Impact of temperature on flow

Temperatures were higher than average during the late 1980s and the beginning of the 1990s. Highest positive departure of temperature recorded during the study period occured in 1997/98 and is likely an effect of the global climatic influence caused by El Niño. El Niño and La Niña can greatly affect global precipitation and temperature (McPhaden, 2002). El Niño events seem to cause milder winters in the northern hemisphere, while La Niña events roughly convert to opposite weather variability (McPhaden, 2002). During the period from 1977 to 2001 El Niño events occurred in 1982/83, 1986/87, 1992/93-1994/95 and in1997/98 while strong La Niña periods occurred in 1988/89, 1995/96 and in 2000/01 (Environment Canada, 2002). These events are clearly reflected in deviations of temperature within the study area (Figure 7). All El Niño events resulted in higher than average temperatures, while temperatures during La Niña periods were lower than the mean. The years from 1991/92 to 1993/94 do not follow the pattern of El Niño and La Niña periods, but is rather an effect of the eruption of Mt. Pinatubo in the

Philippines in June 1991 causing global temperatures to drop temporarily overriding the influence of El Niño during this period (Hansen et al., 1996).

On a year to year scale mean temperatures are fairly variable within the study area. Consistently strong deviations on a monthly scale can be observed during the winter months, December to February, while deviations from May to October are less pronounced (Table 3). Winter temperatures therefore may have a pronounced effect on streamflow patterns as milder winters could result in earlier peak-flows during spring. Increased winter temperatures also cause more rain on snow events, causing relatively greater contributions of surface water runoff producing higher runoff magnitudes during spring.

2.4.2 Variations of flow

Overall, precipitation and streamflow vary together throughout the period of record, while temperature varies inversely with both parameters (Figures 8 – 10). There are wet years, where streamflow and precipitation are above average at each of the sites (1982/83, 1984/85, and 1995/96) and dry years, where both parameters are below average (1987/88, and 1991/92 for all catchments, 1986/87 - 1989/90, 1993/94 and 1997/98 for Harp and Plastic 1 basins) (Figures 8a and b). Plotting standard departure values of precipitation versus those of discharge shows that the discharge in Harp is greatly influenced by variations in precipitation. For example, warm years with little precipitation result in below average streamflow (1986/87 – 1989/90) versus warm years with above average precipitation, which result in positive streamflow deviations (1982/83, 1984/85, and 1985/86) (Figure 8a), suggesting that discharge is highly sensitive to a change in precipitation but less effected by an increase in temperature. This is supported by

significant regression coefficients when Z-scores of discharge versus precipitation are plotted (Figure 12). An extensive buffer system due to the slow release of groundwater that would shield year to year fluctuations of discharge cannot be detected among the Harp basins. Buffering or memory from one year to the next would most clearly show if a drier than average year (precipitation falling below the average line) results in above average discharge following a sequence of wet years. The years 1984/85 and 1985/86 would be categorized as wet; however, the following dry year does not reveal buffering as deviations of discharge fall clearly below average. Similarly, PC 1 does not reveal carry-over processes from one year to the next.

Surface-water storage can be critical during the summer season as the slow release of water is responsible for sustaining discharge even when the seasonal water-balance would be negative. Shapes of the flow duration curves of the DESC basins are fairly similar during wetter conditions suggesting that higher precipitation and distribution of till and surface features are not important in terms of flow distribution. Above average winter temperatures and little precipitation during the summer would drastically reduce water storage. If precipitation is reduced and high evapotranspiration occurs during periods of drought wetlands become more important. Wetlands, due to the slow release of stored water, can sustain streamflow in the short term; however, cannot mitigate long-term drought conditions (1985/86 – 1989/90).

Overall results show that the study basins within the Muskoka – Haliburton region are more affected by changes in precipitation than in temperature and that discharge is generally more affected by drought than by increased wetness (Figures 11 and 12).

The results of this study indicate that the DESC basins are located within a hydrologicallly homogenous region. Differences in the range of discharges caused by dry or wet periods in each individual basin were not significant as slopes of all duration curves are relatively similar with steeper incline at the higher range of flows indicating that high discharges are infrequent or not sustained for long periods of time. Baseflows are moderately well sustained in all basins, however variations can be observed in the in the 10 to 90 percentile range pointing to differences in storage capacities between basins. Basins with higher storage potential sustain minimum baseflow for a longer period of time resulting in fewer days with zero flow.

Climate induced shifts as predicted by future climate scenarios (IPCC, 2001) are likely to alter precipitation patterns. General circulation models suggest an increase of summer temperatures of 3°C to 5°C and a minimal increase of summer precipitation across Ontario (Ontario Minsitry of Natural Resources, 1998). This study showed that variations in discharge are largely affected by changes in precipitation as indicated by standard departure analysis and significant relationships between stream discharge and precipitation (Figure 12). Variations of discharge were not significantly related to changes in temperature (Figure 11). This indicates that an increase in temperature alone has little effect on stream discharge in the DESC basins; however, it is clear that climate variables have a combined effect on water availability in forested basins and a warming climate with increased summer temperatures will increase the evaporative demand of forests. Even with no change in precipitation in the Muskoka-Haliburton region water availability for vegetation will decrease and may reduce the productivity of some species.

Chapter 3

Effect of varying antecedent wetness on the hydrological response in forested catchments of the Canadian Shield

3 Introduction

Crucial to the understanding of catchment processes and the ability to predict future changes in the hydrological regime, is the identification of hydrologic pathways within the catchment and the related transit times for water routing through various biological and geological systems. Residence times for water in catchments vary noticeably. They may range from minutes for channel precipitation and water reaching the stream as overland flow to hours or a few days for the shallowest groundwater recharged close to the area where groundwater is discharged to the stream. Water with the longest residence time is typically deep groundwater which can reside in the catchment for several years. The transit times are determined by the velocity and pathways of the water particles which, in turn, are determined by the hydraulic conductivity and the porosity of the soil and bedrock, the rate of groundwater recharge and the topography. Within a given season, short-term variations in streamflow response are related to the variability of storm size (magnitude) and the physical make up of a basin. This study aims to quantify the relationships between climate and basin hydrology and to identify typical patterns of streamflow response to precipitation inputs. Hydrologic functions are influenced by the physical characteristics of a basin, such as depth and texture of soil and till matrix, slope morphology and vegetation, but may also vary temporally with differences in meteorological conditions, all which govern antecedent

hydrological conditions. Antecedent moisture conditions are defined by amount of moisture present in the soil at the beginning of a storm event, soil drainage properties, baseflow conditions, and meteorological characteristics such as storm duration, magnitude, frequency and season of occurrence.

The objectives of this chapter are to examine how differences in the physical make-up of catchments, such as till depth, wetland proportion and topography couple with climatic variability to produce different hydrological responses in surface stream discharge on event basis. A range of storm events is linked to variations in antecedent wetness to quantify the strong and controlling link between climate and basin hydrological response as indicated by basin streamflow.

3.1 Methods

3.1.1 Separation of multiple storms

A complex stream hydrograph is produced during periods of frequent but temporally distinct storm events. In order to determine direct runoff proportion generated by specific precipitation events during these periods hydrograph separation was performed using a digital filtering method (Eckhardt, 2005) based on earlier research by Lyne – Hollick (1979) and Chapman (1991). This separation technique provides an algorithm incorporating a filter that describes an exponential baseflow recession which can be determined by recession analysis and a typical maximum value of the baseflow index. This method provides a valid technique to compare hydrologic responses to individual storm events across the studied basins and is a means to obtain objective and repeatable estimates of baseflow. The following equations are used:

$$b_t = [(1\text{-BFImax}) \, K \, b_{t-1} + (1\text{-K}) \, \text{BFImax} \, y_t] / (1 - K \, \text{BFImax}) \qquad \text{Eq: 1}$$

where: BFI is baseflow index, y is total streamflow, b is baseflow, t is time step number, and K is recession constant.

In order to derive meaningful recession constant (K) recession curves, a range of hydrographs for each season within each basin were analyzed and K calculated as a function of Q_t and Q_{t-1} over a constant time interval, where Q_t is the discharge at the beginning of that interval and Q_{t-1} is the discharge at the end of the interval. The recession constant is calculated on a daily interval by:

$$\text{Recession constant (K)} = Q_t / Q_{t-1} \qquad \text{Eq: 2}$$

Eckhardt (2005) proposed a two parameter based filter using a filter parameter and a BFI_{max} parameter. This second parameter, the maximum value of the baseflow index that can be modeled by the algorithm, is set by the user. To derive meaningful BFI_{max} values and to compare the simulated direct runoff and baseflow values of the varying basins a web-based analysis tool was used to separate quickflow from baseflow. The WHAT (Web-Based Hydrograph Analysis Tool system; http://pasture.ecn.purdue.edu/~what) allows the user to specify filter parameters and representative BFI_{max} values according to physical characteristics, such as aquifer or stream type of a basin. After uploading the data set into the program, WHAT calculates baseflow and direct runoff from the stream flow dataset and provides the results in tabular form. BFI_{max} values for each examined catchment in this

study were optimized by using two different separation methods: 1) the local minimum method; and 2) the one parameter digital filter method, which are both available in WHAT. The local minimum method checks each day of the streamflow record to determine if it is the lowest discharge in a set time interval. If it is, then it is a local minimum and the values are connected by a straight line to adjacent local minimums. Baseflow is then estimated by linear interpolation for each day between the local minimums.

The one parameter digital filter method uses the following algorithm to separate baseflow from stormflow:

$$f_k = a\ f_k\text{-}1 + \frac{(1 + a)}{2}(y_k - y_{k\text{-}1})$$

where f_k is the filtered quick response at the k_{th} time step, y_k is the original streamflow, and a is the filter parameter. Nathan and McMahon (1990) propose a filter parameter of 0.925 based on comparison between automated and manual separation resulting in realistic results of baseflow contribution. The resulting mean BFI_{max} value for each basin was subsequently used to employ Eq: 1 with the two parameter based filter method by Eckhardt (2005) to separate baseflow from streamflow.

Using WHAT the following BFI_{max} values were derived (Table 4):

Table 4: BFI_{max} and filter parameters used to separate baseflow for each basin.

	Harp 3A	Harp 4-21	Harp 4	Harp 5	Harp 6	Plastic 1	Plastic 1-08	Paint
Filter	0.85	0.88	0.87	0.86	0.86	0.85	0.87	0.85
BFI_{max}	0.55	0.65	0.69	0.69	0.65	0.55	0.45	0.55

3.1.2 Defining storm events

In order to calculate the volume contribution of each storm, the start and end of a storm event are defined. The starting point of a storm occurs where the first rising of a storm hydrograph appears. The end of a storm is defined as the intersection point of the falling limb with baseflow calculated by the web-based tool WHAT. The magnitude of each individual rainfall input is defined as the sum of rainfall which occurs just prior to and during the stormflow response. In the case of multiple storms, precipitation falling on the last day of the first storm is attributed to the storm in sequence if at least one dry day of no rain separates them.

3.1.3 Antecedent moisture conditions (AMC)

Estimates of soil moisture conditions are given by an antecedent moisture index (AMC) and are used to define antecedent wetness conditions for the catchments. The AMC is initialized at the beginning of each hydrological year on 1 June. For this computation it is assumed that during spring melt season the storage capacity of soils is equal or close to 0 %; saturation in turn is assumed to be 100 %, which is the base to calculate daily antecedent wetness for each year. Peak spring melt discharge for each individual basin was averaged over 21 years and used as the standard value to calculate each basin's wetness prior to a storm. AMC are given as a fraction of the mean spring melt flow.

3.1.4 Runoff coefficient

The runoff coefficient (RC) is an additional indicator of antecedent wetness and is defined as the ratio of direct runoff to event rainfall, whereby direct runoff equals the total

runoff minus baseflow. Event runoff coefficients can be used to indicate the antecedent wetness of a basin as these ratios are direct result of different hydrological variables such as precipitation intensity, evapotranspiration, infiltration rate, and storage capacity. In general, it is assumed that the higher the RC for a storm event with similar input magnitudes, the higher antecedent wetness within a basin before the event and vice versa. However, high runoff coefficients may also be generated on low antecedent moisture conditions if precipitation intensities are exceptionally high and exceed the basin's infiltration capacity.

3.1.5 *Defining wet and dry conditions*

Streamflow is a better indicator than precipitation for determining whether wet or dry conditions prevail during a year as it is more reflective of wet/dry conditions and is therefore taken to define wetness within a catchment as described above. If deviations from the long term mean of 21 years are less than +/- 10 % conditions are defined as average. A deviation of greater than +/- 10 % from the long term streamflow response was used to define wet and dry stages. The extreme years are defined as those with a deviation from the long-term mean of greater than or equal to +/- 20 %.

3.2 Results

The shape of a hydrograph varies according to a number of governing factors within the catchment, such as basin size, shape, drainage density, soil distribution, and gradient. For example, smaller basins have sharp and narrow peaks while larger basins display wider peaks with a longer time base. In order to identify reasons for variable hydrological responses of the Harp basins hydrographs are plotted to a defined and standardized scale.

This allows a comparison of hydrographs among basins (Figure 19a and b). Streams of the DESC basins have substantial seasonal variation in runoff indicating that discharge is fairly sensitive to climate variables, such as precipitation, temperature and evapotranspiration. Generally, high flows of the Harp basins are caused by snowmelt, as soils are saturated and have low storage capacities resulting in the highest runoff responses during a year. Streamflow in summer and fall originates from rain fed storm events and peaks during this time period are mainly caused by short duration storm events. All Harp basins are in close proximity to one another, which leads to the assumption that precipitation inputs and evapotranspiration among these basins is reasonably similar. Therefore, differences in discharge pattern are caused not only by seasonal changes of precipitation and evapotranspiration but also due to spatial differences in the physical make up of basins. This can be best observed from July until the beginning of October where the times of peaks differ among the Harp basins compared to responses in late fall and spring. For example, from August to September peaks are greatest first for HP 4, then HP 6 followed by HP 5 and HP 3A. In contrast, in October peaks are generally highest for HP 3A, HP 5 and HP 6 followed by HP 4. If we assumed that precipitation and evapotranspiration are very similar among basins then differences observed in the normalized hydrographs can be attributed to physiographical differences among the basins. This is reflective of varying catchment characteristics and is important because the sensitivity of streamflow responses is attributable to changing climatic variables and the physical attributes of a catchment.

To allow for a better examination of the normalized hydrographs the period of data record was split into two periods: June to October and November to May.

Throughout the normalized hydrographs HP 4 responses are less variable and often have a slow recession implying that this stream is comparatively more stable. Drainage

density of this catchment is low and slopes are fairly gentle (Table 1, Chapter 2), which implies that water will take longer to reach the stream resulting in slightly broader hydrographs. In addition, HP 4 has a fairly large area and deeper tills, which contributes to the fact that flow will take longer to recede. HP 5 is the largest basin of the four and has catchment properties which are similar to those of the HP 4 basin (gentle slopes, poor drainage density) (Table 1, Chapter 2). Nevertheless, peaks are flashier and more pronounced in HP 5. The difference between these two basins is that HP 5 has fairly shallow soils, which implies that the thickness of soils is likely more important than drainage density and basin size. In addition, HP 5 contains wetlands that can transmit water rapidly once saturated. HP 6 is the smallest of the four basins and has steep slopes, a high drainage density and shallow soils. All of which explain the fast rise and fall of the hydrographs throughout results. Infiltrating rainwater will saturate soils quickly, which increases the amount of surface runoff, which in turn will result, combined with the high drainage density, in a very fast recession of flow.

Hydrographs of HP 3A exhibit greatest peaks in fall and spring when wet conditions prevail. During summer, hydrographs are consistently lower than those of the other basins suggesting two very different hydrological stages within this catchment. The drainage density of HP 3A is lower and basin size is larger compared to HP 6, suggesting comparatively slower drainage, however slopes are steep, and tills are shallow, both characteristics accounting for a fairly fast rise and fall of discharge, which is evident during the wet periods of the year. However, the consistently low responses during dry periods suggest that evapotranspiration dries up soils, which need to be saturated first before a larger portion of the basin can contribute to stormflow.

a)
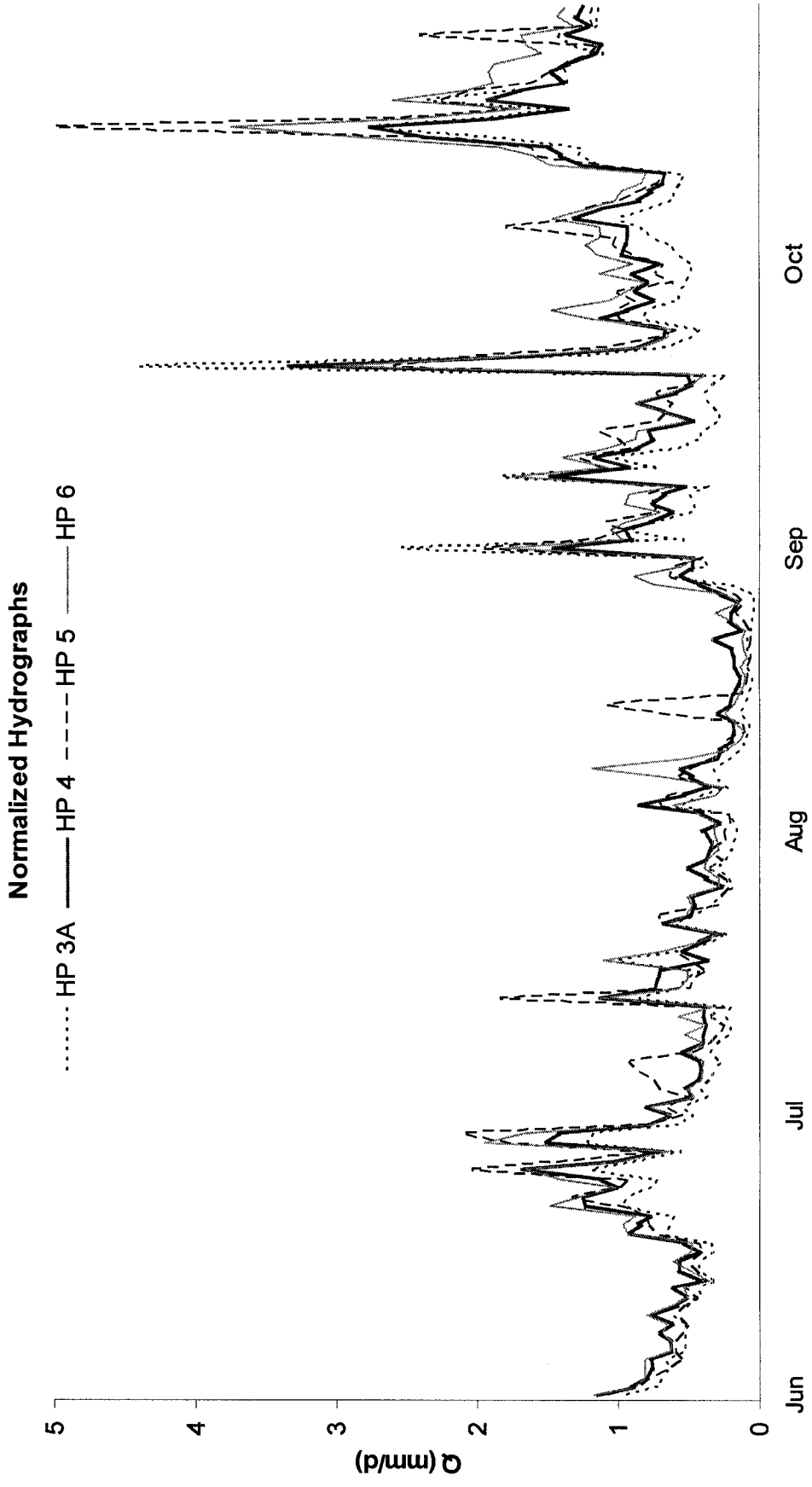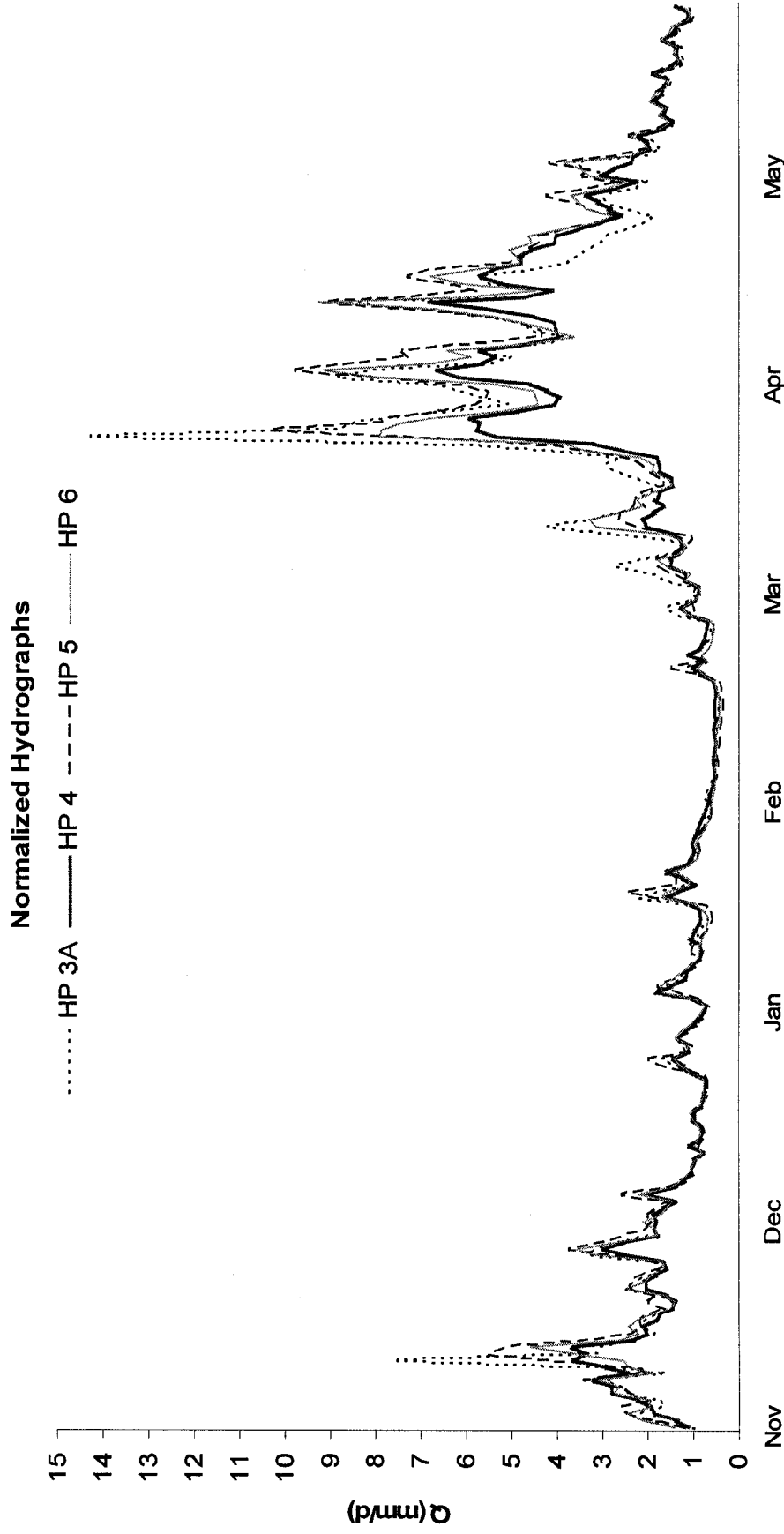
Figure 19a and b: Daily streamflow hydrographs, normalized by drainage area, for the Harp basins, HP 3A, HP 4, HP 5 and HP 6 (Averaged from nine climatic differing years: 1988/89, 1990/91, 1993/94 (average conditions); 1992/93, 1995/96, 1996/97 (wet conditions); 1986/87, 1989/90, 1997/98 (dry conditions): a) June – October and b) November – May.

Deviations from the long term mean of annual precipitation versus annual deviations of discharge were plotted in order to assess the catchment's ability to buffer climate variations, both in terms of precipitation and evaporation (Figures 20 and 21). The effects of varying precipitation on discharge are presented as the annual percentage change from the long term mean of input versus output. Results show that precipitation and discharge varied disproportionately. For example, the 1995/96 record for the Harp basins shows an increase of 20% in precipitation and an increase of 38 – 40% in discharge. This implies that in years, such as 1995/96, when conditions are wet and storage capacities are filled a greater proportion of precipitation can be delivered as runoff. On the other hand, in 1997/98 when there is little precipitation input (-29 %) more of the incoming precipitation is stored within the basin resulting in a decrease of discharge of -45 %. It is evident throughout the results that HP 6 exhibits the greatest deviations during wet years but the smallest during dry years. This implies that catchments with little storage due to shallow tills, such as HP 6, produce relatively more discharge in response to any additional precipitation input. In comparison, catchments with deeper tills, hence greater storage potential, such as HP 4 retain more water and generally result in comparatively smaller deviations. During dry years, catchments with little storage will also produce relatively more runoff than catchments with high storage because saturation of soils is reached faster, resulting in the proportionally higher discharge value as the amount of surface runoff increases. In addition, differences in runoff during dry and wet years are influenced by evapotranspiration. Generally, potential evapotranspiration sets the upper limit for water losses within a basin. Basins with shallower tills and little storage potential experience a faster depletion of water hold in till/soils. The

evaporative demand, however still exists resulting in a moisture shortage in the basin contributing to the greater proportional deviation in discharge.

The influence of temperature can be observed during the years 1981/82 and 1983/84. Both years record a 5% decrease in annual precipitation, which in 1981/82 results in positive discharge values ranging from 2 to 27 %. In 1983/84 a decrease of 5 % in precipitation results in negative discharge values ranging from – 2 to – 14 % (Figure 20 – bottom). The year 1981/82 was cooler compared to 1983/84 (Figure 20: top) and both years were preceded by relatively wet years, suggesting that variation in temperature and variations in evapotranspiration rates caused the different response patterns.

Similar results can be observed in PC 1 and PC 1-08 (Figure 21). Less than average precipitation affects discharge to a greater extent in PC 1 (1987/88, 1993/94). Precipitation inputs are buffered within the PC 1 basin during wetter conditions but diverge to a greater extent during dry conditions for reasons previously discussed.

A few general conclusions can be drawn from these results. Catchment's attributes such as drainage density, storage potential, and gradient determine how quickly water will be expelled from a basin. Shallow tills have a greater effect on the hydrological response than drainage density as described in the example of HP 4 and HP 5. Catchments such as HP 6, with a high drainage density and shallow tills, have flashy peaks, indicated by the fast rise and fall of the hydrograph; thus, basins with shallow soils are more sensitive to climate variability, including dynamics of evapotranspiration in such that a higher demand during the summer results in a faster streamflow recession. In addition, the ability to buffer climate variations decreases if

the current storage approaches the limits of a catchment's storage capacity for both wet and drought conditions.
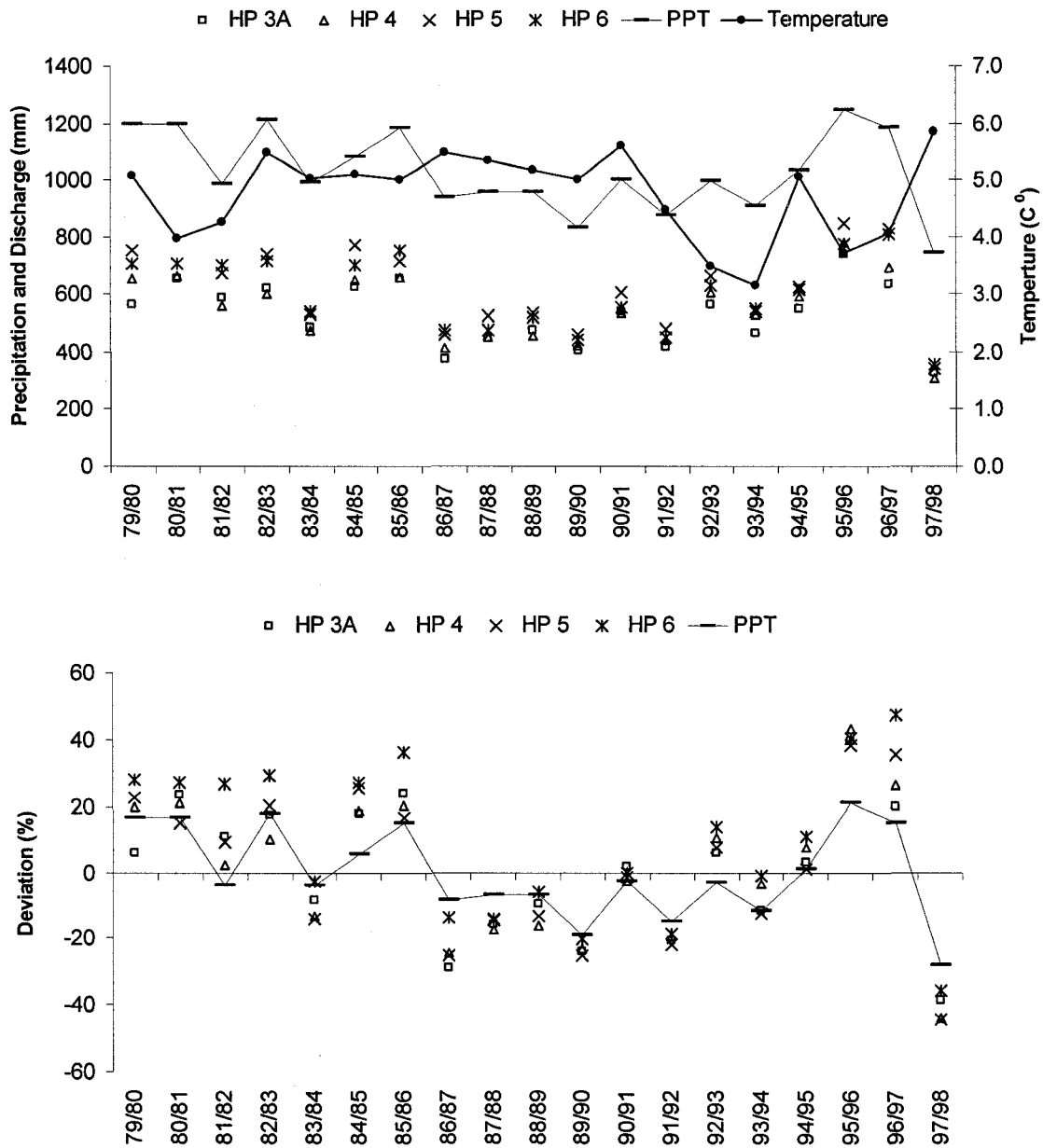
Figure 20: Annual temperature (C°), precipitation (mm) and discharge (mm) (top) and deviations (%) from the long term mean (bottom) in HP 3A, 4, 5 and 6 from 1987/88-1994/95.
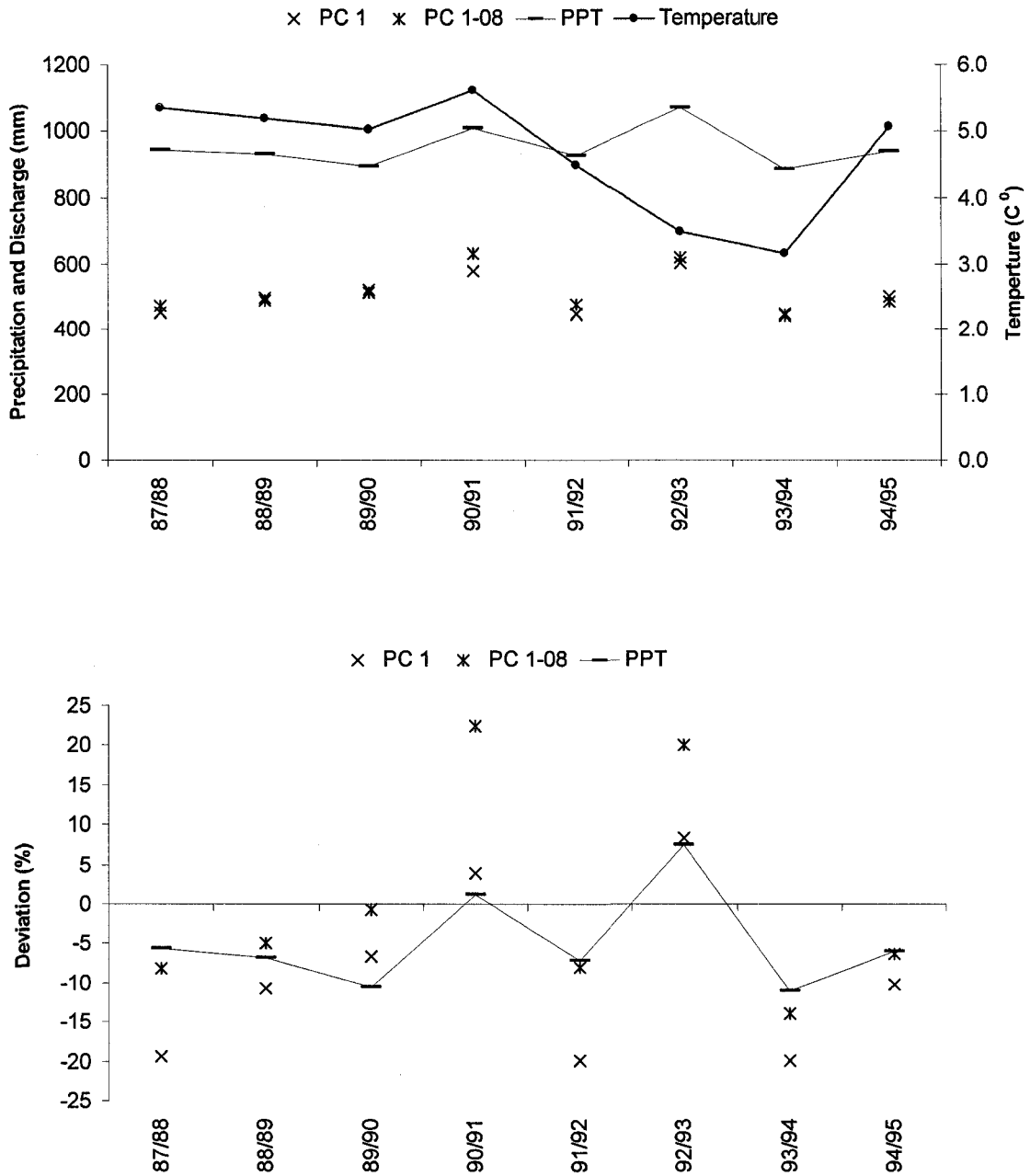
Figure 21: Annual temperature (C°), precipitation (mm) and discharge (mm) (top) and deviations (%) from the long term mean (bottom) in PC 1 and PC 1-08 from 1987/88-1994/95.

3.2.1 Storm event distribution

Rainfall storm event distribution was explored to identify temporal and spatial variations in precipitation inputs among basins and to assess the influence on antecedent storage. A subset of nine years, which differ in climate conditions, was examined based on the deviation from the long term mean record (Section 3.1.5). These years are: 1988/89, 1990/91 and 1993/94 (average); 1992/93, 1995/96 and 1996/97 (wet); 1986/87, 1989/90 and 1997/98 (dry).

The analysis is based on 338 storm events for the Harp Lake basins and 299 for the Plastic Lake basins. In summer, storms in Harp basins (HP) and Plastic basins (PC) accounted for 36 % and 33 %, in fall for 36 % and 37 %, and in spring for 27 % and 29 %, respectively, of all storm events that occurred (Figure 22).

To estimate intra-season variability of rainfall magnitudes, events are split into storms that are greater and less than 25 mm (Figure 22).

Fall rainfall inputs seem important to the Harp and Plastic catchment's annual water balance since between 13.6 % to 16.4 % of all events exceed 25 mm. This is approximately twice the number recorded in the summer or spring periods. Storm events smaller than 25 mm show a somewhat equal distribution over the fall and spring seasons; however, they are increased during the summer period by approximately 10 % for the Harp basins and about 3 % for the Plastic basins. The relative importance is amplified by significantly reduced evapotranspiration rates during the fall and early spring periods.
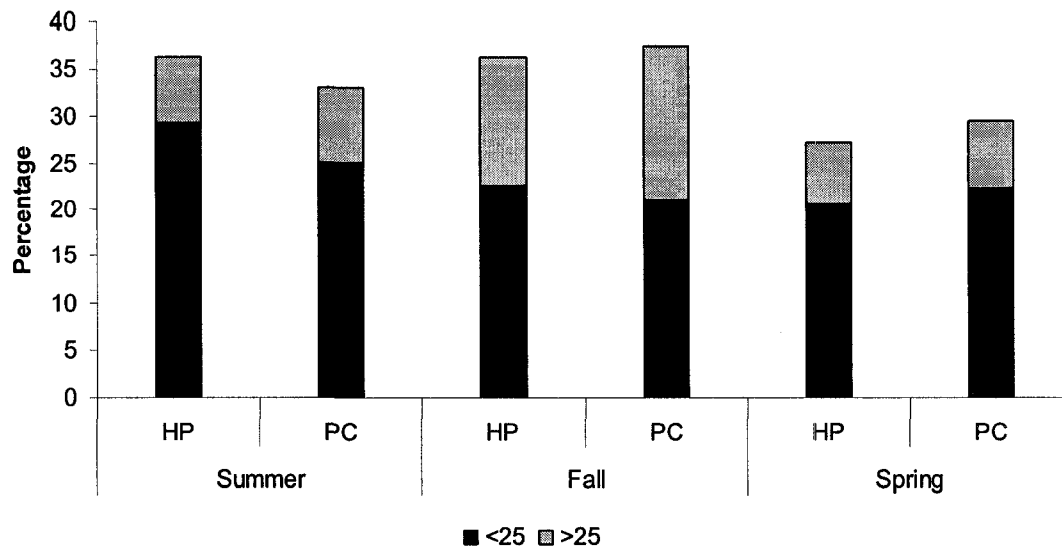
Figure 22: Seasonal distribution (%) of rain events greater than 25 mm and less than 25 mm.

The strong seasonal contrast of storm events indicates an important seasonal influence on streamflow responses and consequently must result in variations of antecedent storage within basins.

Figures 23a and b present regional estimates that characterize the seasonal variability of precipitation during dry, wet and average years.

a)

HARP

□ >25 mm ■ <25 mm

b)

Plastic

□ >25 mm ■ <25 mm
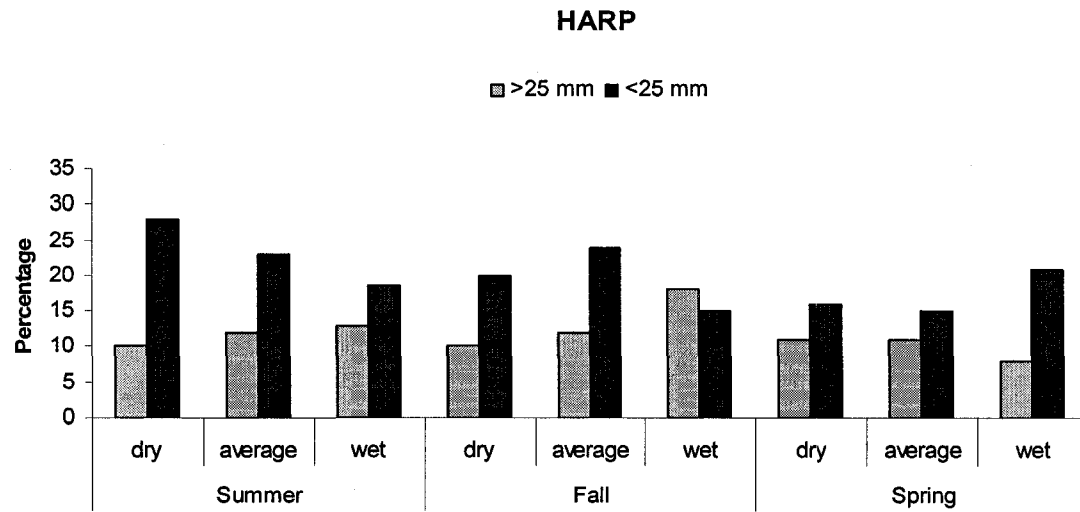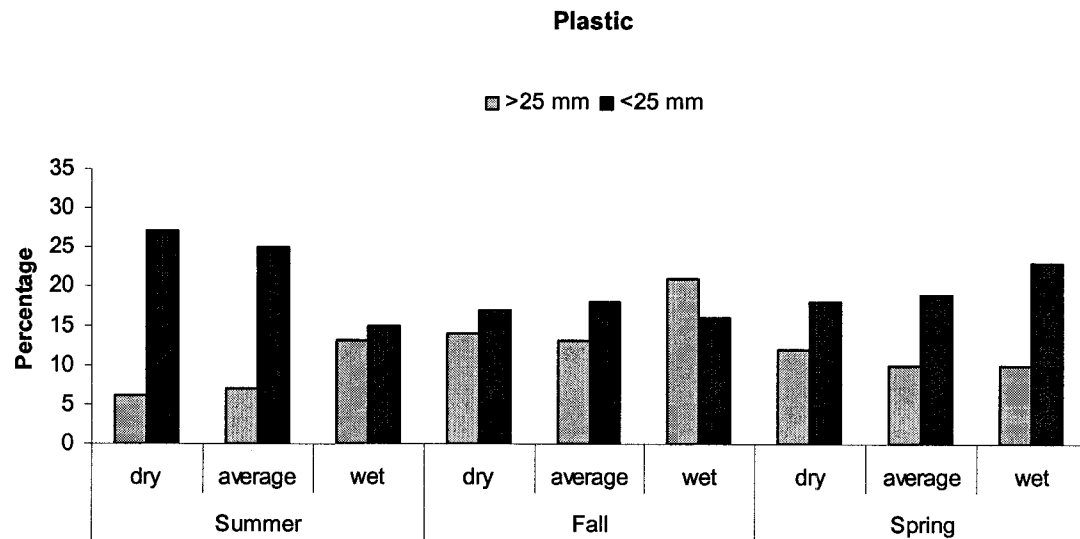
Figure 23a and b: Distribution of rainfall events (%) greater and smaller than 25 mm during average (1988/89, 1990/91, 1993/94); wet (1992/93, 1995/96, 1996/97) and (1986/87, 1989/90, 1997/98) dry conditions.

In summer, smaller events provide a significant proportion of rainfall inputs, especially during dry and average years. 20 % to 25 % of precipitation events are < 25 mm and approximately 5 to 10 % are > 25 mm. The proportion of summer precipitation during wet years that is < 25 mm is reduced to 10 % to 15 % while precipitation that is > 25 mm accounts for up to 20 % of total summer rainfall. In fall, smaller events are more frequent during dry and average years. Events > 25 mm exceed those < 25 mm by about 5 % in wet years in the Harp and Plastic catchments. In spring rainfall inputs greater than 25 mm drop approximately 5 % at Harp compared to the dry and average years. The results display the seasonal variability of rainfall inputs greater and lesser than 25 mm during climatically differing years, which in turn determines antecedent storage.
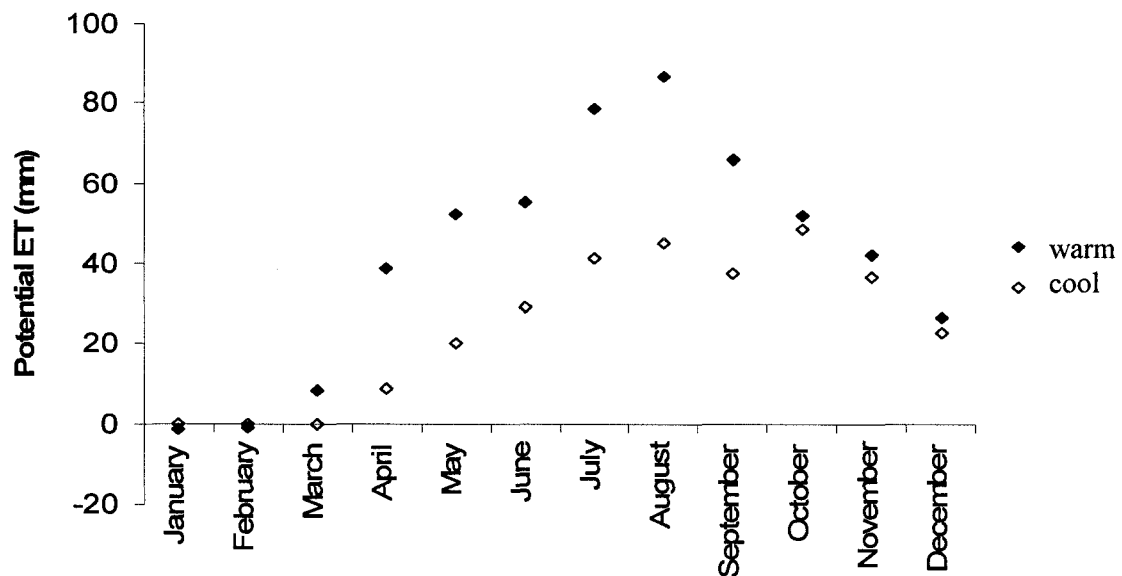
Figure 24: Potential evapotranspiration (mm) derived from four climatically differing years (1979/80, 1982/83 (cool) and 1986/87, 1991/92 (warm)).

The amount of water lost to evapotranspiration during cool and warm years was estimated for the Dorset area using the Penman-Monteith equation (Data from Buttle, 2007; personal communication). This study suggested that evapotranspiration during warm years accounts for approximately 50 % loss of all the water that enters the basin as precipitation, while during cooler years evapotranspiration drops to about 30 % (Figure 24).

Consequently, years with increased evapotranspiration would result in less water stored in a basin and reduced water available for runoff. Basins with little storage capacities due to thin soil/till cover could experience severe water limitations even if precipitation is high. Although deeper deposits of till retain more water, discharge response in these basins is also affected by increased evapotranspiration. Higher evapotranspiration can effectively remove water from the basin and groundwater depletion results in higher recharge demand, consequently runoff is smaller. However, basins with deeper till, such as HP 4 and HP 4-21 are more likely to meet the potential evapotranspiration (PET) requirements, hence equal actual evapotranspiration (AET) in the Muskoka-Haliburton region. This is because storage capacities in these basins are higher and provision of water is more balanced. Basins with shallow deposits of till dry up faster, and consequently are unable to supply enough water to meet the PET demand. Once the vegetation is unable to draw water from the soil/till, then the actual becomes less than the potential evaporation in thinner tilled basins.

Reduction in evapotranspiration would result in increased amounts of water remaining within the basin resulting in more water available for runoff, which is especially important for basins with shallow till.

3.2.2 *Influence of antecedent moisture conditions on streamflow response*

In order to evaluate the influence of antecedent moisture conditions to similar rainfall inputs on streamflow production and to quantify the link between climate signals and basin response during the spring, summer and fall seasons, a range of precipitation inputs of varying magnitude related to differing antecedent moisture conditions are examined. Antecedent moisture conditions (AMC) as defined previously (Section 3.1.3) and the runoff coefficient (RC), defined as the ratio of direct runoff to precipitation (Q/R), are indices of basin response to rainfall events. The observed annual pattern of streamflow responses is governed by several factors, such as topography, the temporal variation of rainfall inputs, duration and intensities, snowmelt, and underlying antecedent moisture. Plotting runoff versus precipitation is often used to derive the runoff coefficient. This approach assumes that the relationship of precipitation and runoff is linear, which means that an increase in precipitation results in a proportional increase in runoff. However, runoff coefficients vary widely with equal precipitation inputs suggesting a non-linear relationship between precipitation and runoff. A major control on the non-linearity is caused by antecedent moisture conditions within a basin. The role of antecedent moisture conditions on runoff coefficients will vary between basins because larger basins with deeper soils, gentle slopes, low drainage density or contain wetlands have more water storage potential, and precipitation inputs and evapotranspiration dynamics will affect streamflow differently compared to basins with steeper slopes, shallower soils, and high drainage density. Consequently, each basin has the potential to portray a unique signature of hydrological responses. For this reason the

influence of antecedent wetness on runoff coefficients of the study basins is examined in this section by using regression lines as an estimate of the runoff coefficients.

Figures 25a-d present the relationship between antecedent moisture conditions (AMC) and the runoff coefficient (RC) for the main Harp basins.

Initial antecedent moisture conditions prior to each storm event are organized into 40 moisture classes ranging from 0.5 % to 20 % and one class > 20% where corresponding RCs of each summer, fall and spring storm event are sorted into these classes according to the initial moisture condition at the start of the event. Runoff coefficients having a value higher than 1 are not included in the analysis as they result from spring melt and do not present actual runoff produced by rainfall at that time.
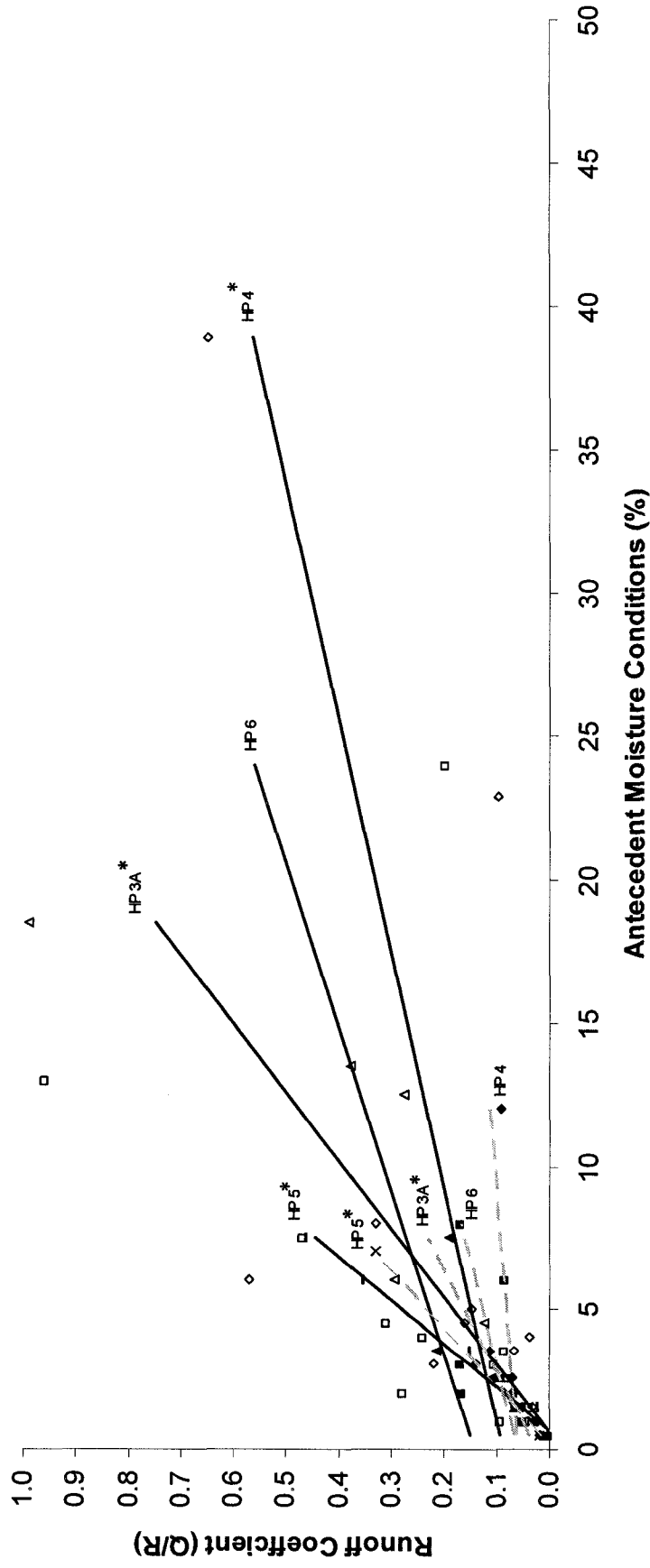
Figure 25a: Runoff coefficients versus antecedent moisture (%) regressions for rainfall sizes 0 - 5 mm and 5 - 10 mm for the catchments Harp 3A, 4, 5 and 6.

Asterisk indicates significant relationship (see Table 5 for more detail).
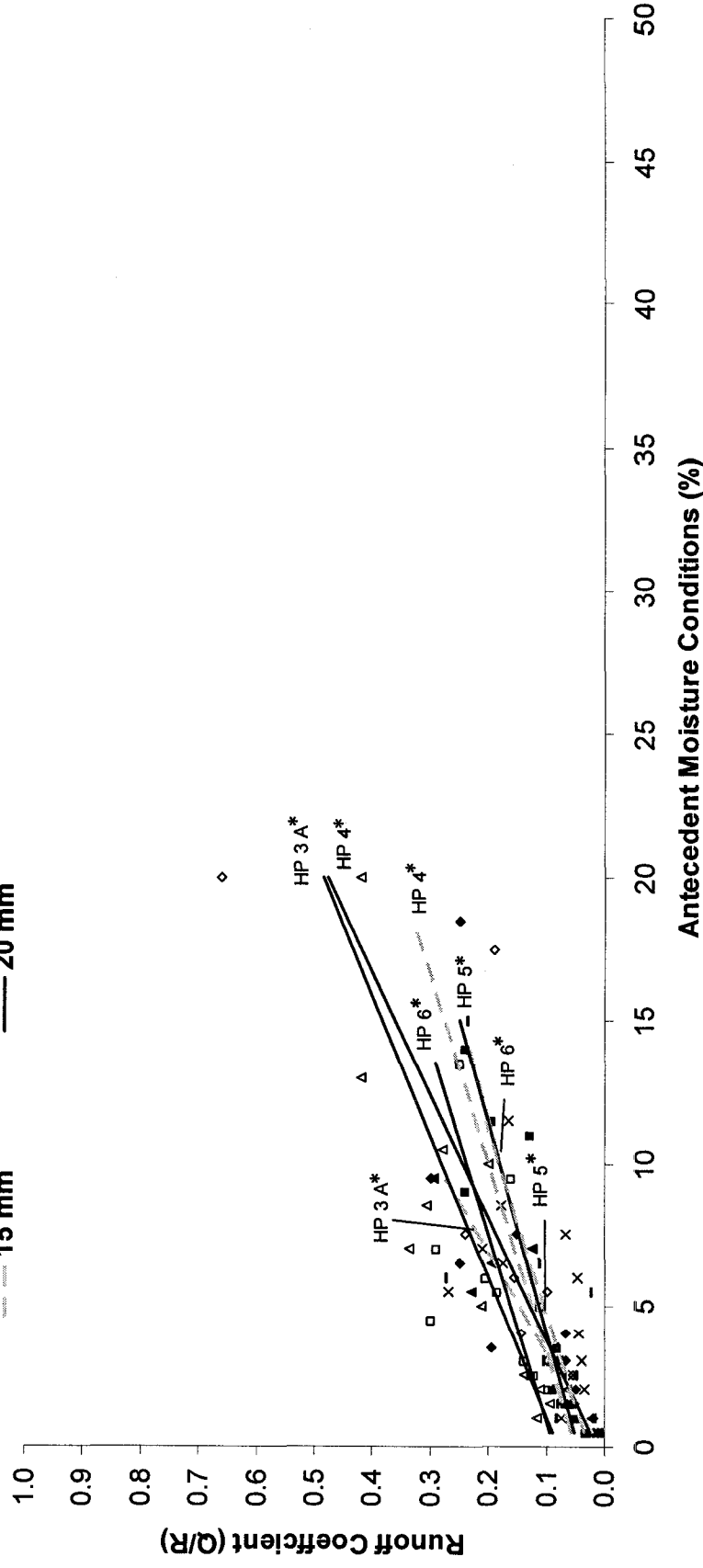
RC versus AMC

Figure 25b: Runoff coefficients versus antecedent moisture (%) regressions for rainfall sizes 10 - 15 mm and 15 - 20 for the catchments Harp 3A, 4, 5 and 6.

Asterisk indicates significant relationship (see Table 5 for more detail).
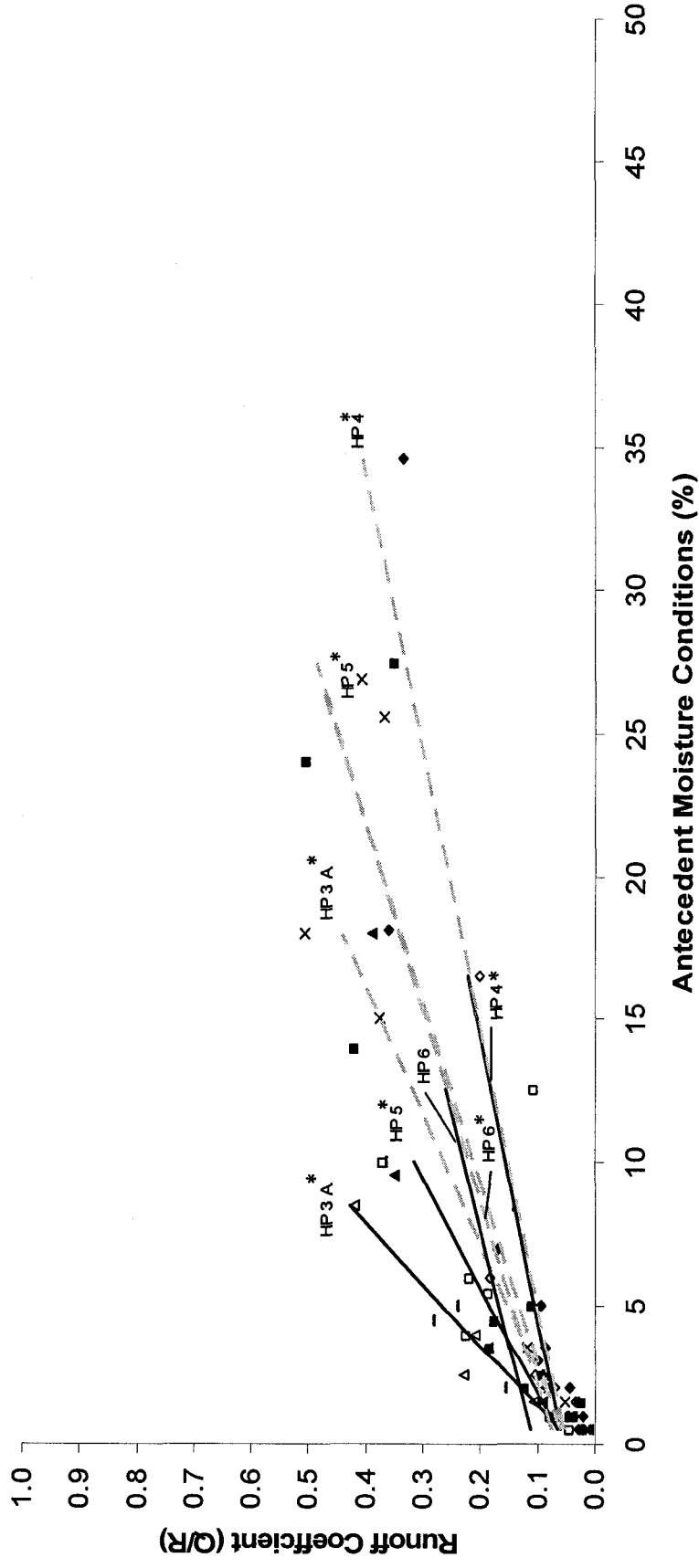
RC versus AMC

Figure 25c: Runoff coefficients versus antecedent moisture (%) regressions for rainfall sizes 20 - 25 mm and 25 - 30 mm for the catchments Harp 3A, 4, 5 and 6.

Asterisk indicates significant relationship (see Table 5 for more detail).

RC versus AMC
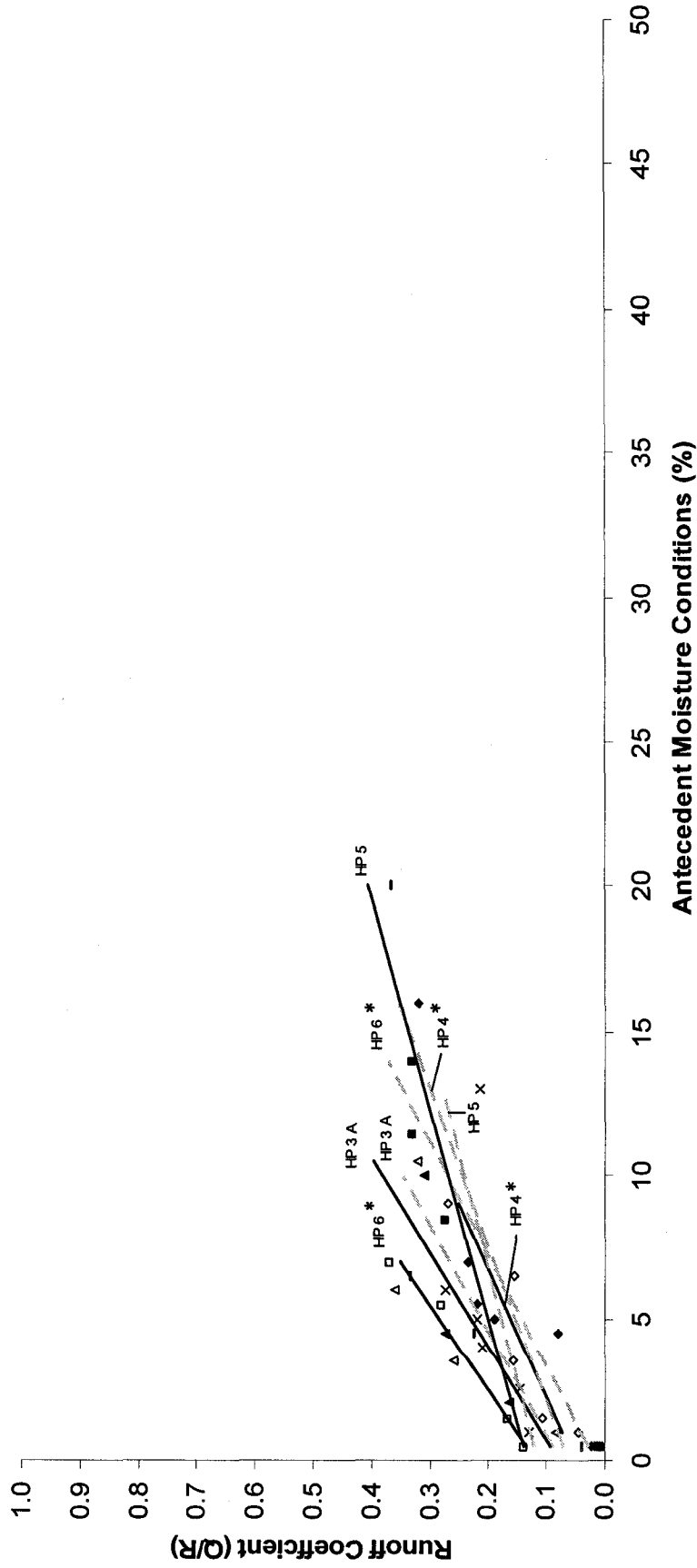
Figure 25d: Runoff coefficients versus antecedent moisture (%) regressions for rainfall sizes 30 - 35 mm and 35 - 40 mm for the catchments Harp 3A, 4, 5 and 6.

Asterisk indicates significant relationship (see Table 5 for more detail).

Table 5: Regression equations for RC on varying antecedent wetness conditions under differing rainfall input sizes.

PPT size	N	HP 3A	HP 4	HP 5	HP 6
05 mm	22	$y = 0.0273x + 0.025$ $R^2 = 0.67*$	$y = 0.0045x + 0.0592$ $R^2 = 0.16$	$y = 0.0486x - 0.0115$ $R^2 = 0.99*$	$y = 0.0133x + 0.0595$ $R^2 = 0.32$
10 mm	23	$y = 0.0418x - 0.0266$ $R^2 = 0.81*$	$y = 0.0122x + 0.0882$ $R^2 = 0.41*$	$y = 0.0652x - 0.0435$ $R^2 = 0.97*$	$y = 0.0174x + 0.1409$ $R^2 = 0.24$
15 mm	31	$y = 0.0283x + 0.0062$ $R^2 = 0.84*$	$y = 0.0151x + 0.0496$ $R^2 = 0.59*$	$y = 0.0156x + 0.0267$ $R^2 = 0.39*$	$y = 0.013x + 0.0515$ $R^2 = 0.76*$
20 mm	19	$y = 0.0204x + 0.0782$ $R^2 = 0.79*$	$y = 0.0233x + 0.0122$ $R^2 = 0.72*$	$y = 0.0137x + 0.0441$ $R^2 = 0.46*$	$y = 0.0152x + 0.086$ $R^2 = 0.42*$
25 mm	18	$y = 0.0222x + 0.0409$ $R^2 = 0.89*$	$y = 0.0103x + 0.05$ $R^2 = 0.80*$	$y = 0.0159x + 0.0532$ $R^2 = 0.83*$	$y = 0.0153x + 0.0668$ $R^2 = 0.78*$
30 mm	13	$y = 0.0462x + 0.0369$ $R^2 = 0.92*$	$y = 0.0101x + 0.0552$ $R^2 = 0.70*$	$y = 0.0262x + 0.0534$ $R^2 = 0.60*$	$y = 0.0123x + 0.1071$ $R^2 = 0.24$
35 mm	9	$y = 0.0272x + 0.0756$ $R^2 = 0.74$	$y = 0.0183x + 0.0608$ $R^2 = 0.76*$	$y = 0.0126x + 0.1143$ $R^2 = 0.39$	$y = 0.0255x + 0.0148$ $R^2 = 0.94*$
40 mm	5	$y = 0.0304x + 0.0788$ $R^2 = 0.70$	$y = 0.0223x + 0.0511$ $R^2 = 0.85*$	$y = 0.0137x + 0.1329$ $R^2 = 0.62$	$y = 0.0336x + 0.1173$ $R^2 = 0.97*$

- significant at $p < 0.05$

Table 6: Runoff coefficients calculated for 5% antecedent wetness.

PPT size	Harp 3A	Harp 4	Harp 5	Harp 6
05 mm	0.16	0.08	0.23	0.13
10 mm	0.18	0.15	0.28	0.23
15 mm	0.15	0.13	0.10	0.12
20 mm	0.18	0.13	0.11	0.16
25 mm	0.15	0.10	0.13	0.14
30 mm	0.27	0.11	0.18	0.17
35 mm	0.21	0.15	0.18	0.14
40 mm	0.23	0.16	0.20	0.29

Regression equations from Table 5.

The hydrological response of each basin to rain influx is highly correlated with the antecedent moisture status. With increasing antecedent wetness the resulting water yield after a storm event rises in response to decreased water table depth, increased hydrologic gradient and hydrological connectivity. Figures 25a-d reveal unique hydrologic responses for each catchment to a range of precipitation inputs shown as runoff coefficients (Q/R) averaged for the years 1986/87 (dry), 1990/91 (average), 1995/96 (wet), 1996/97 (wet) and 1997/98 (dry), which represent climatic differing years of average, wet and dry conditions described earlier (Section 3.1.5). These years have been chosen to represent the greatest variety of typical climatic conditions; however, the response to, for example, 5 mm of rain on a basin with 5 % antecedent moisture should hypothetically be similar for each event. Variations, however, are caused by higher evapotranspiration rates during summer and fall. Results show that the higher the antecedent wetness prior to an event the greater the response seen in increased runoff coefficients (Figures 25a-d).

A comparison of stream flow responses for 5 % initial wetness across basins reveals that runoff for rainfall inputs from 1 mm to 5 mm and 6 mm to 10 mm generates greater runoff coefficients than compared to rainfall inputs of 15 mm, 20 mm and 25 mm. This effect seems to be true for all catchments. Possible reasons for this pattern may be based on the fact that in summer and early fall evapotranspiration rates are higher, storage capacity is greater and much of the water is consumed by plant uptake or is evaporated due to higher temperatures, causing the drop in runoff coefficients even though input sizes are higher. In addition, 5 mm and 10 mm events occur more often than storm sizes higher in magnitude and thus are likely to fall on

pre-wetted conditions. In these cases streamflow may have decreased but moisture conditions are still wetter than during times of prolonged dry spells where higher precipitation events cause only small runoff ratios. Overall the results indicate that runoff increases with higher precipitation inputs, as represented by the higher runoff coefficients (Figures 25a-d). Examining the runoff coefficients for rainfall inputs from 1 mm to 5 mm and 6 mm to 10 mm results show that the Harp 5 basin produces highest responses followed by Harp 3A, Harp 6 and Harp 4 for precipitation inputs of up to 5 mm in size and RCs from Harp 5 are also highest for inputs with magnitudes between 6 mm and 10 mm. This might be caused by low topographical gradients in this basin leading to a groundwater table closer to the surface. Consequently, storage capacity is low resulting in a greater amount of surface runoff contributing to streamflow. Catchment Harp 4, compared to Harp 3A, 5 and 6, shows the lowest runoff coefficients throughout results, which could be caused by the beaver pond that covers parts of the basin and thicker soil-till cover (Table 1, Chapter 2), which both provide a higher storage potential for water. Effects of evapotranspiration contribute to water loss depending on how much water is stored in the rooting zone and how much is transpired by plants as discussed previously (Section 3.2.1). As a result rainfall contributes to groundwater storage causing smaller RCs within this basin.

Precipitation events between 15 mm and 40 mm progressively increase RCs for all basins; however RCs appear to increase most rapidly for Harp 3A and 6. Runoff coefficients of both basins are high with increased precipitation on relatively high antecedent wetness suggesting that large areas contribute to streamflow during higher rainfall inputs (Figure 25d). Harp 6 has fairly steep slopes, shallow soils and a

high drainage density, which allow soils to saturate and drain quickly, accounting for the elevated runoff coefficients. Increased precipitation also causes runoff coefficients to rise in Harp 4 and 5; however, RCs of Harp 4 comparatively remain lowest in most cases indicating that relatively more of the precipitation is stored within soils due to a greater storage potential resulting from deeper tills that cover this basin. Harp 5 is comprised of many smaller wetlands, shallow soils and has a low drainage density (Table 1, Chapter 2). Compared to the other basins runoff coefficients of Harp 5 increase more rapidly for small precipitation inputs (Figure 25a), suggesting that more water is held in surface storage or retained in soils due to poor drainage. Smaller precipitation inputs are therefore sufficient to raise the water table close to the surface, thereby expanding the area of saturation resulting in an increase of the amount of surface overland flow.

3.3 Discussion

In general, the variability of streamflow within the DESC basins is largely governed by the seasonal cycle of precipitation, temperature and basin properties. Depending on the basin's physical characteristics and the meteorological condition at a particular time, streamflow response differs among basins with respect to antecedent moisture conditions. It is evident that runoff generated from a specific event reflects the synthesis of a basin's geological composition, topography, changes in seasonal rainfall patterns and antecedent moisture conditions. The results above show that streamflow responses during dry and wet conditions vary considerably for

some basins, such as Harp 3A, 5 and 6; however, they are less variable for Harp 4 as suggested by the lower range of RCs in this basin (Table 6). The temporal variability in streamflow response may be controlled by the tendency of the basin's hydrological linkage between upslope and valley to become disconnected as summer rainfall inputs are insufficient to sustain flow (Devito et al., 1996; Buttle et al., 2004). Different hillslope processes may operate during different times. Basins with steeper slopes and a higher distribution of shallower soil cover, such as Harp 6, will deliver proportionally more runoff compared to basins that cannot develop a hillslope response during dry conditions, such as Harp 3A (Hinton, 1998). In Harp 3A antecedent wetness is not sufficient to allow for water transport from upland areas to the stream valley if conditions are dry. During wet conditions, hillslope and stream valley stay hydrologically connected (Buttle et al., 2004).

Basins that have low drainage density, shallow soils, contain wetlands and have gentler slopes, such as Harp 5, retain more water suggesting that even with little precipitation input, saturation of soils can occur faster resulting in greater runoff production. Harp 4 has the greatest storage potential due to deeper till cover. The hydrological response of this basin is more stable as represented by a) regression slopes that are less steep and b) runoff ratios that are less variable. As soils gradually wet up with subsequent storms or longer duration precipitation events, greater areas of the basin reach saturation, and both overland and subsurface flow contribute to streamflow. It is important to realize that the hydrological response in a catchment is governed by more than one process and that streamflow outputs are coupled with climate variability and catchment characteristics; however, given the long term

structural stability of these basins prevailing antecedent moisture is one of the major

controls governing streamflow response.

Chapter 4

The effect of soil thickness on runoff production inferred from four differing forested catchments of the Precambrian Shield, south-central Ontario, Canada

4 Introduction

A basin's topography is a dominant control on the wetness of a certain location within a basin and depends on the rate of rainfall input, antecedent soil moisture and the ability of the soil to conduct water downhill. Canadian Shield basins often exhibit variable depths of till cover. Soil properties, such as depth and texture (e.g. well drained versus poorly drained soils), and their distribution within a basin influence runoff variability. Studies (Devito, 1994, 1995; Devito and Hill, 1997, 1998; Devito et al., 1999; Hinton et al., 1994) conducted in this region of south central Ontario highlight the fact that differing till thickness influences runoff processes within the basin. A major control governing the water movement on a hillslope valley scale is the state of hydrological connectivity within the soil. Combined hydrometric and hydrochemical methods show that, typically in a dry state, the hydraulic conductivity is low and the movement of water slow or non-existent. Re-wetting of the soil takes time until saturation is reached to conduct water. During a saturated state the hydraulic gradient is elevated and hydraulic conductivities increase (Stieglitz et al., 2003; Buttle et al., 2004). Only few studies examine the contributions of flow during high antecedent moisture deficits (Pionke et

al., 1993; Bazemore et al., 1994). However, the understanding of how different landscape elements such as upland, slope and valley hydrologically connect remain poorly understood. Therefore, knowledge and applicability gleaned from one basin is not necessarily transferable to another. This may be due to the large spatial heterogeneity of physiographic structure even in small basins. In addition, soil water contributions from developing perched water tables, which are likely to be spatially and temporally variable and dependent on preferential flow pathways, complicate the conceptualization of streamflow generation processes at a hillslope - valley scale.

The objective of this study is to examine the influence of soil thickness on runoff patterns of four physiographically differing basins under a range of antecedent conditions. In this section hydrometric data for the years of 1988/89 to 1991/92 were utilized.

4.1 Study Sites
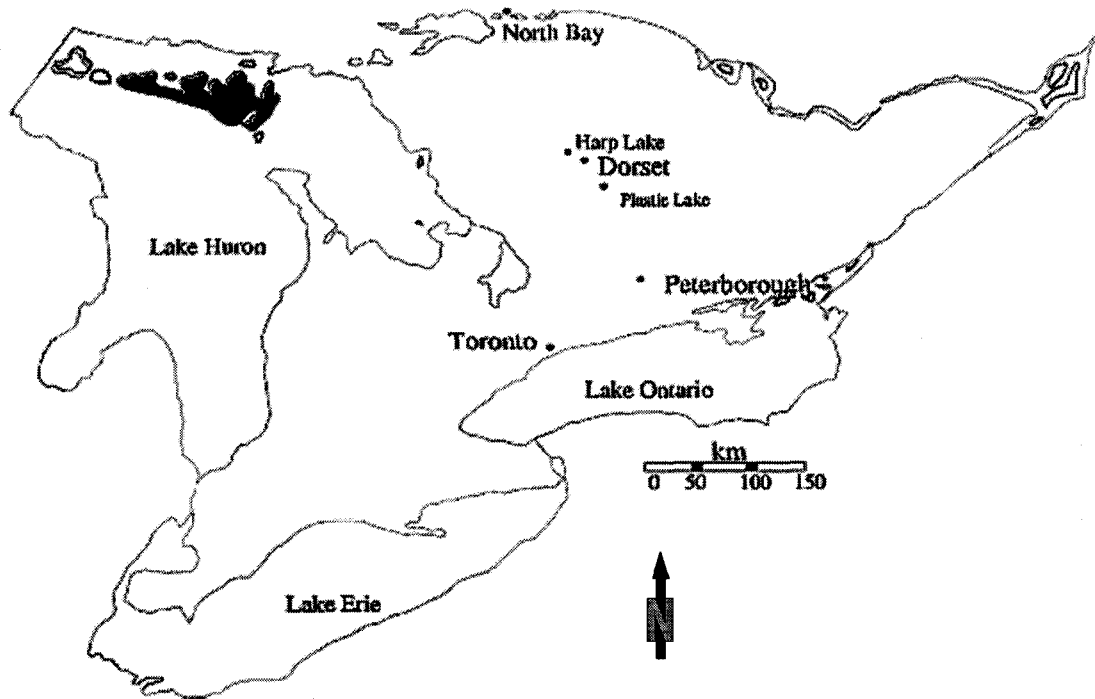
Figure 26: Location of the study sites in Muskoka-Haliburton, Ontario, Canada. (Modified after Watmough and Dillon, 2003).

The Plastic Lake watershed (45°11'N 78°50'W) is located in Haliburton County, south-central Ontario, Canada and covers about 32 ha on the Precambrian Shield (Figure 26). The entire lake is fed by one major stream Plastic 1 (PC 1), and six ephemeral streams. PC 1 is the largest catchment (23.3 ha) in the watershed (Figure 27). This site has been monitored since 1985 by the Ministry of Environment as part of the Acid Precipitation In Ontario Study (APIOS). The forest at PC 1 is primarily coniferous, dominated by white pine (*Pinus strobus*, 43 % of total basal

area) and eastern hemlock (*Tsuga canadensis*, 19 % of total basal area) in the upland

part of the catchment, and by white cedar (*Thuja occidentalis*) and black spruce

(*Picea mariana*) in the swamp regions (Watmough and Dillon, 2001). PC's

watershed is underlain by impermeable Precambrian granitic gneiss bedrock.
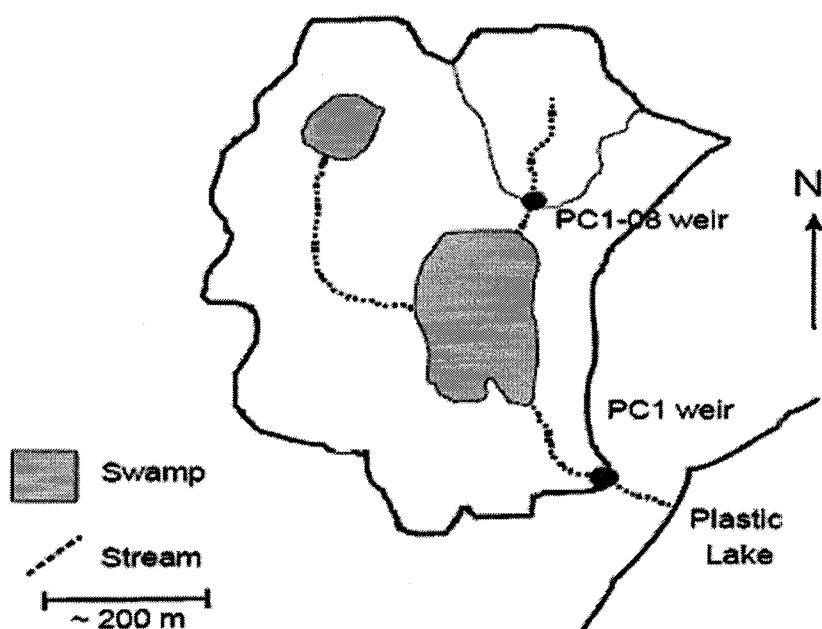
Figure 27: Map of basins PC 1 and PC 1-08, Haliburton County, Ontario, Canada.

A large wetland (2.2 ha) is located approximately 50 m above the basin's

outflow draining more than 85 % of runoff from the PC 1 basin before discharging

into the lake (Eimers et al., 2003). The mean annual precipitation for four years

(1988/89 to 1991/92) was 937 mm and the mean runoff was 510 mm per year. On

average the stream ceases to flow on 77 days during summer and early fall. The range of non-flow days varies from 49 to 92 days during the four year data record; the year with the most days of stream cessation was in 1988/89 (Figure 28).

The Plastic 1-08 basin (PC 1-08; 3.45 ha; Figure 27) is located to the northeast of PC 1's wetland and is drained by a short (< 250 m) ephemeral stream before discharging into the swamp. Overall PC 1-08 is covered with < 0.5 m glacial till deposits and bedrock outcrops cover about 10 % of the basin. Data for this basin were collected by the Dorset Environmental Science Centre at Plastic Lake meteorological station. The annual precipitation for the four year study period of PC 1-08 averages 937 mm and the runoff averages 525 mm during that time. The PC 1-08 stream is ephemeral and the days where streamflow ceases during summer and early fall ranges from 111 in 1988/89 to 53 days in 1991/92 (Figure 28), averaging 86 days a year. The vegetation is largely mixed forest, with deciduous forests dominating where the soil is thicker and conifers dominating where the soils are thin.

Data for the Harp Lake catchment were also collected by the Dorset Environmental Science Centre at Harp Lake meteorological station and span from 1977 until 1998 for the Harp 3A (HP 3A) basin and from 1988 until 1992 for the Harp 4-21 (HP 4-21) basin. The Harp Lake watershed (45°23' N 79°07'W) is divided into seven basins (Figure 29) and is fed by six inflows. The basins are covered with till deposits of varying thickness and when compared to the Plastic Lake basins are much thicker (> 2 m). The HP 3A basin is 21.7 ha and the overburden is composed of approximately 97 % glacial sediments, rarely exceeding 1.5 m thickness (Hinton et al., 1998). The mean annual precipitation for this basin is 918 mm (1988/89 – 1991/92) and mean annual runoff is 458 mm (Table 7).

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Table 7: Four year average of precipitation and discharge.

Basin	Mean PPT (mm)	Standard deviation (mm)	Mean Q (mm)	Standard Deviation (mm)	N (years)
HP 3A	918	+/-76	458	+/-62	4
HP 4-21	918	+/-76	409	+/-145	4
PC 1	937	+/-49	510	+/-55	4
PC 1-08	937	+/-49	525	+/-71	4

The HP 4-21 basin is 3.7 ha, has a basin area comparable to PC 1-08 and till

depth ranges from 0 m at the southeast corner of the catchment up to 15 m along

certain slopes (Hinton et al., 1993). A wetland is not present in HP 4-21; however, an

extended riparian zone can be found at the upper portion of HP 4-21 basin, which

varies in size depending on antecedent hydrological conditions (Hinton, 1998). Data

for this study extend from 1988/89 (June 1 to May 31) to 1991/92. The four year

average of precipitation is 918 mm and average runoff is 409 mm. Soils are underlain

by Precambrian metamorphic silicate bedrock, similar to the bedrock found in the PC

watershed. The vegetation is comprised of mixed deciduous-coniferous forest

dominated by sugar maple (*Acer saccharum*), yellow birch (*Betula alleghaniensis*),

poplar (*Populus spp.*), balsam fir (*Abies balsamea*) and hemlock (*Tsuga canadensis*)

(Hinton et al., 1997).
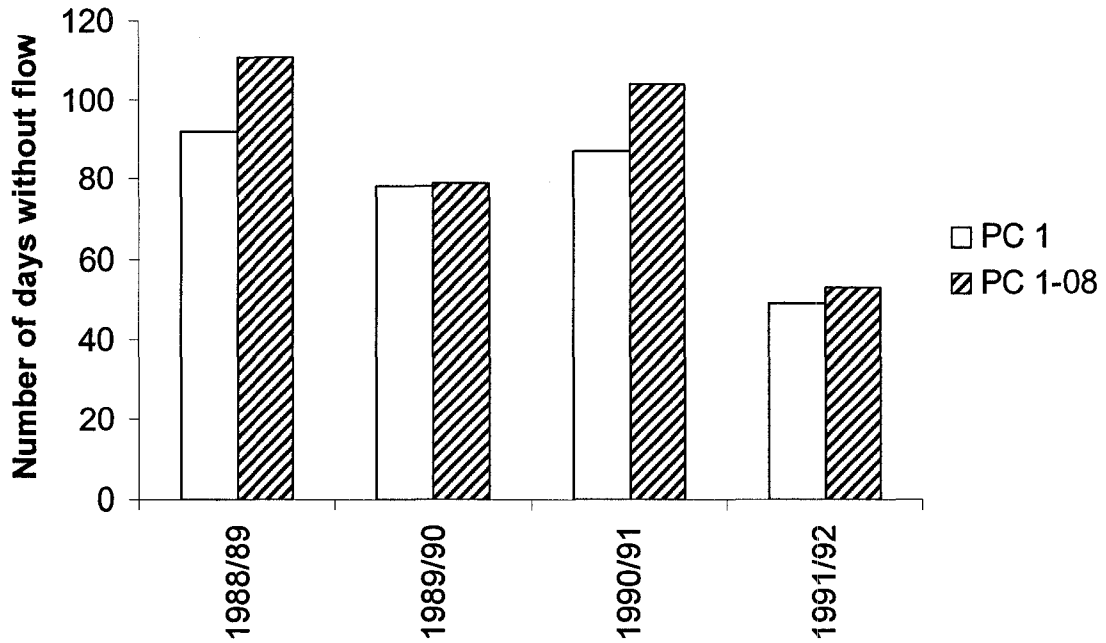
Figure 28: Days with zero flow during summer (June – August) and early fall (September) for the basin PC 1, PC 1-08.
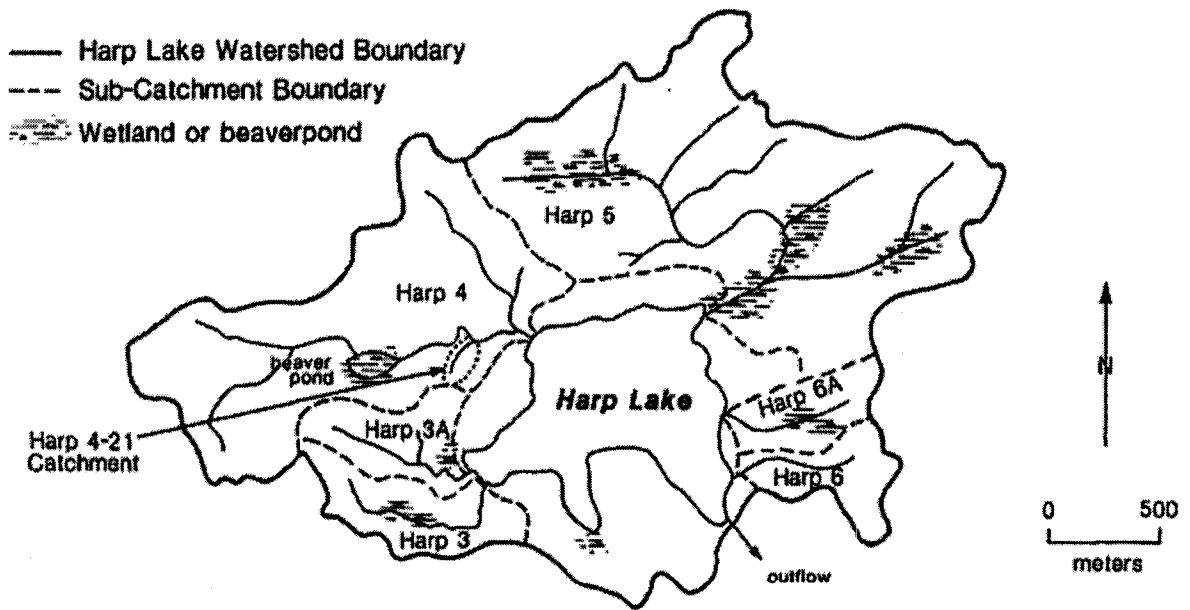
Figure 29: Harp Lake watershed with basins. Wetland areas within the basins are shaded (from Schiff et al., 1997).

4.2 Methods

4.2.1 Streamflow and meteorological data

Data records for precipitation (mm) and streamflow (L/s) were obtained from

the Ontario Ministry of Environment and span from 1977 to 1998. However, in order

to have consistent averages for comparisons of baseflow and precipitation only data

from 1988 until 1992 were utilized because one of the catchments, HP 4-21, has only

records for those years. Discharge data for all catchments were continuously

monitored at a 90° V-notch weir enclosed in a heated structure to maintain ice free

conditions using a Leopold and Stevens A-71 float operated water level recorder.

Using established stage-discharge relationships for each stream, stage measurements

were converted to discharge (Scheider et al., 1983).

The climate prevailing within the study area is northern temperate. The mean

monthly temperatures range between –5 and –10 °C during the coldest winter months

(December – February) and between 22–25 °C during summer (July and August).

In order separate baseflow from stormflow a web-based analyzing tool

WHAT (Web-Based Hydrograph Analysis Tool system,

http://pasture.ecn.purdue.edu/~what) was used, which is described in detail in

Chapter 3.

Estimates of soil moisture conditions are given by an antecedent moisture

index (AMC) and are used to define antecedent wetness conditions for the catchments

using spring melt hydrographs averaged for each basin's individual data record as

standard value for the basin's wetness. The AMC is initialized at the beginning of

each hydrological year on June 1. For this computation it is assumed that during the

spring melt season the storage capacity of soils is equal or close to 0 %, saturation in turn is assumed to be 100 %, which is the base to calculate daily antecedent wetness for each year. From there, daily streamflow is calculated as a fraction of the mean annual springflow and defined as antecedent moisture (Section 3.1.3).

Runoff coefficients are used to assess variation in runoff production throughout the year. The runoff coefficient is derived as: runoff coefficient = Q_d/R, where Q_d is the direct runoff caused by an event, and Q_d results from Q_t-Q_b where Q_t is the total runoff and Q_b is the baseflow at the time of the event. R is the precipitation attributed to the storm event in question.

Comparisons and assessments of precipitation among the different sites were conducted by using F and ANOVA tests to evaluate precipitation inputs systematically. The data record for each basin is divided into hydrological years starting June 1 and ending May 31. To determine that sample sets for precipitation for the different basins are homogeneous, each sample can be described by its mean and variance. F and one-way ANOVA tests are performed for the years from 1986/87 to 1997/98 to evaluate whether precipitation depths from year to year are statistically equal. If the sample sets are not significantly different from each other, it can be assumed that differences in the physical make up of the basin account for variable streamflow response. Both analyses are performed to test for statistically significant differences among those means and variances. The hypotheses for the F-test are:

H_O: there is no difference between the two variances
H_A: larger variance s^2_1 is significantly different than the smaller variance s^2_2.

The test results of Table A1 and A2 show that in both cases the null hypotheses H_0 is accepted (Appendix 1). It therefore can be assumed that differences in runoff of the four compared basins are caused by unique catchment properties.

4.3 Results

4.3.1 Hydrological variability

In order to assess the timing of high and low hydrological responses on a monthly scale, mean monthly precipitation input and baseflow output in percent (%) is presented in Figure 30 for the PC 1 and PC 1-08 basins and for the HP 3A and HP 4-21 basin in Figure 31. Mean monthly runoff coefficients, Q/R, are illustrated in Figure 32 and antecedent moisture (%) in Figure 33. Antecedent moisture prior to a storm was calculated as a three day average of the moisture index described earlier (Section 4.2.1) for each storm that occurred during that month. The derived values were then averaged to obtain a monthly value.
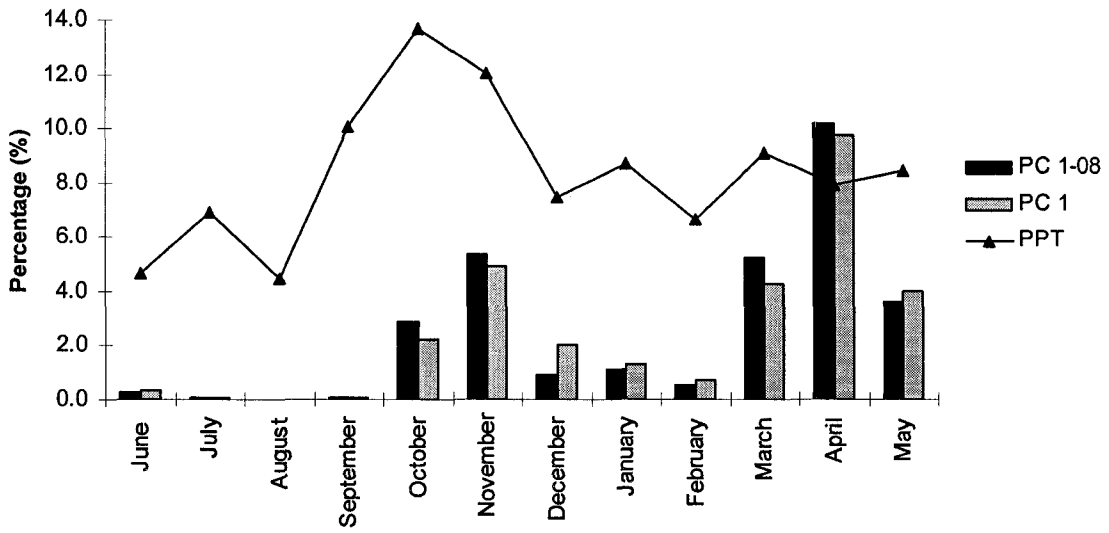
Figure 30: Mean monthly base flow given as percentage of annual precipitation for the basins PC 1 and PC 1-08.
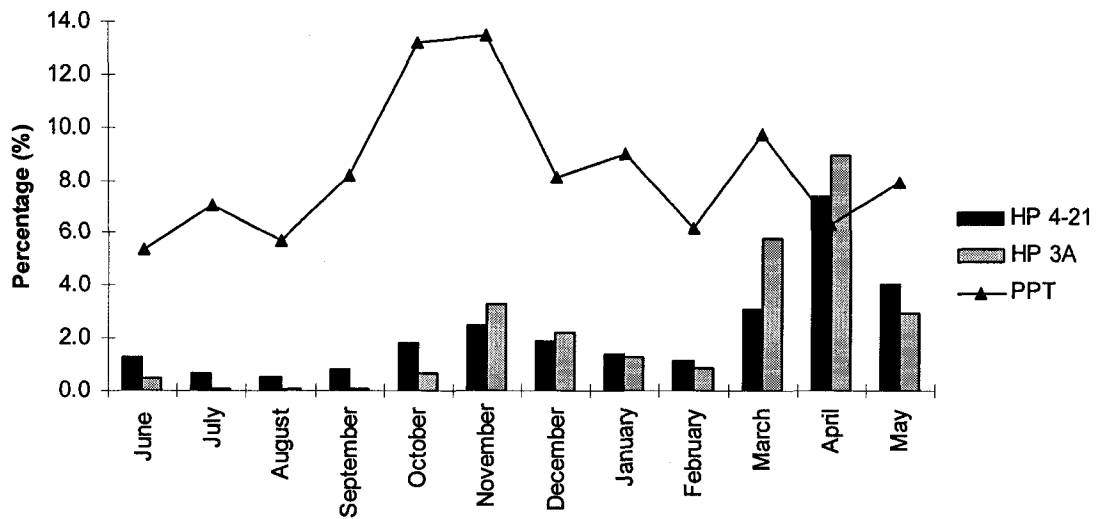
Figure 31: Mean monthly base flow given as percentage of annual precipitation for the basins HP 4-21 and HP 3A.
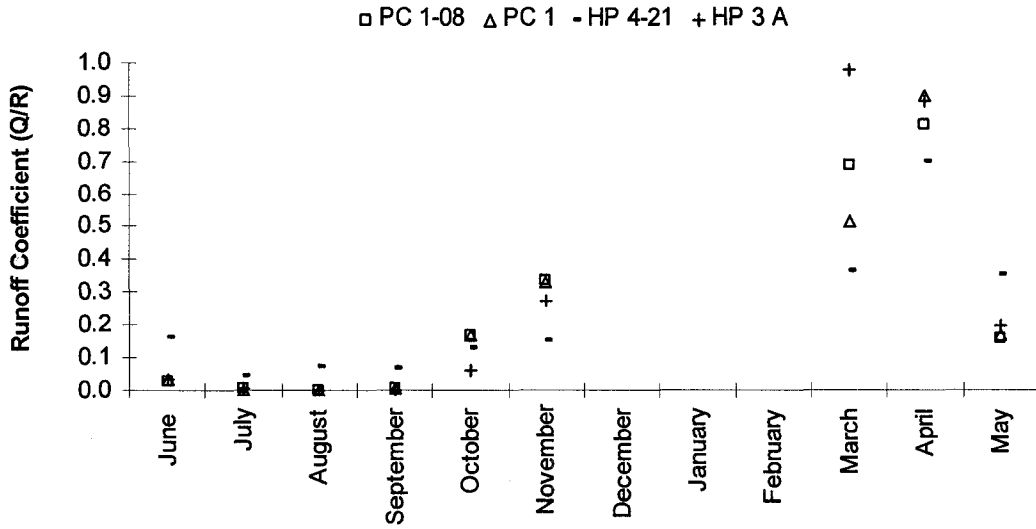
Figure 32: Mean monthly runoff coefficients for the basins PC 1, PC 1-08, HP 4-21 and HP 3A.
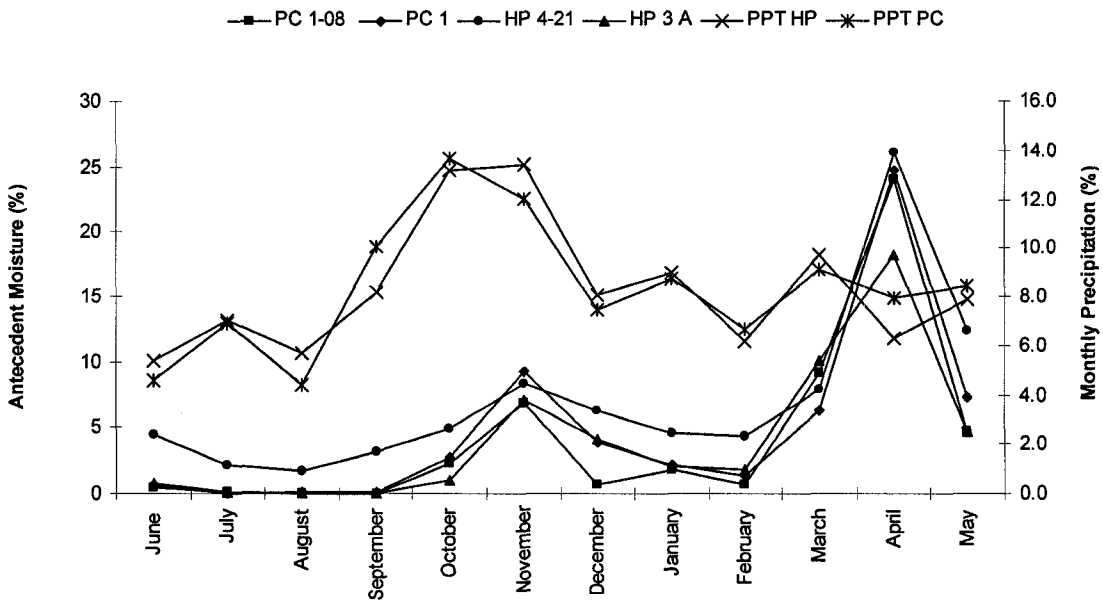
Figure 33: Proportion of mean monthly precipitation in percentage and average monthly antecedent moisture conditions prior to a storm event for HP 4-21, HP 3A, PC 1 and PC 1-08.

The baseflow response of the four different basins (Figure 30 and 31) throughout the year indicates a clear temporal pattern, which switches between dry and wet conditions. Though all basins show an overall similar pattern with peaks in October, November and spring due to overall seasonal changes, such as precipitation input or snowmelt, differences in magnitudes of baseflow can be observed. This is attributable to basin specific characteristics. For example, all basins indicate high baseflow conditions during November due to decreased evapotranspiration rates and increased precipitation in fall; however, proportions range from 2.5 % for HP4-21 to 5.3 % for PC 1-08 for that month. In April, all basins show the highest baseflow during the course of a year due to influences of spring melt waters but differ individually, equating to 7.3 % (HP 4-21), 8.9 % (HP 3A), 9.8 % (PC 1) and 10.2 % (PC 1-08) of the mean annual precipitation. While PC 1 and PC 1-08 exhibit no baseflow in August, and baseflow in HP 3A is close to nil, HP 4-21 sustains baseflow throughout the year. A comparison between HP 4-21 and HP 3A reveals that the proportion of baseflow of HP 4-21 exceeds the proportion of baseflow of HP 3A for most of the year except during late fall, March and April (Figure 31). This is consistent with findings from Hinton (1998), who conducted a study about the role of glacial till on groundwater levels in these basins. This study showed that thicker tills in HP 4-21 result in a deeper groundwater level in upslope areas of the basin, which gradually release water to sustain flow from these areas throughout the summer. Absent or minor till coverage in the upslope area of HP 3A does not allow for precipitation to be stored in these areas; thus, flow is not sustained during dry periods resulting in small baseflow values.

The dynamics of baseflow for the Plastic catchments are somewhat different as the PC 1-08 drains into PC 1. PC 1-08's baseflow exceeds that of PC 1 for most of the year, except during winter and May, which is probably due to the wetland proportion within PC 1 providing a greater storage capacity for water. Figure 33 shows that on average antecedent moisture conditions throughout the year are highest for the HP 4-21 basin. Given the thick glacial deposits covering this basin more water can be stored within the soil column resulting in more consistent moisture conditions. During the course of a year antecedent moisture of the PC 1 catchment exceeds PC 1-08 basin indicating that the ability of the PC 1 basin to store and release water is more consistent due to its wetland proportion compared to the PC 1-08 catchment, which only is covered with thin till layers.

In PC 1, highest runoff coefficients are observed in spring and lowest during late summer and the beginning of fall (Figure 32), which is as expected consistent with patterns of baseflow and antecedent moisture. HP 4-21 shows less variable runoff coefficients compared to the other basins and generates higher runoff during dry periods. In November, March and April; however, runoff coefficients are higher for PC 1 and PC 1-08, when conditions are wet. The increased runoff production during that time could be related to re-established hydrological hillslope-valley connections, which are interrupted during dry periods but reconnected when large rainfall events restore the soil water content and allow for water transfer from upslope to streams and wetlands (Stiegliz et al., 2003; Buttle et al., 1999, 2002, 2004). Moreover, it takes much less water to refill the storage capacity in thin tills; consequently when spring melt starts, basins with thinner till experience a higher

response. This is evident in response patterns observed in HP 3A, where runoff coefficients in spring and fall exceed those of HP 4-21 (Figure 32).

To emphasize the role of antecedent moisture conditions, Figures 34 to 49 illustrate precipitation and runoff coefficients on an event scale basis and antecedent moisture conditions for individual years. Compared to the four year average (Table 7), 1988/89 was a fairly dry year for all basins and was especially dry for HP 4-21 with only 217 mm annual discharge. 1991/92 was a dry year for all catchments but HP 4-21; 1990/91 was a wet year for all catchments and 1989/90 depicts a year with average discharge conditions (Table 8).

Table 8: Annual precipitation and discharge for HP 4-21, HP 3A, PC 1 and PC 1-08.

	Harp PPT (mm)	HP 4-21 Q (mm)	HP 3A Q (mm)	Plastic PPT (mm)	PC 1 Q (mm)	PC 1-08 Q (mm)
1988/89	959	217	476	927	497	488
1989/90	834	402	401	891	520	511
1990/91	1002	568	538	1007	579	629
1991/92	875	447	418	924	446	473
Mean	918	409	458	937	510	525
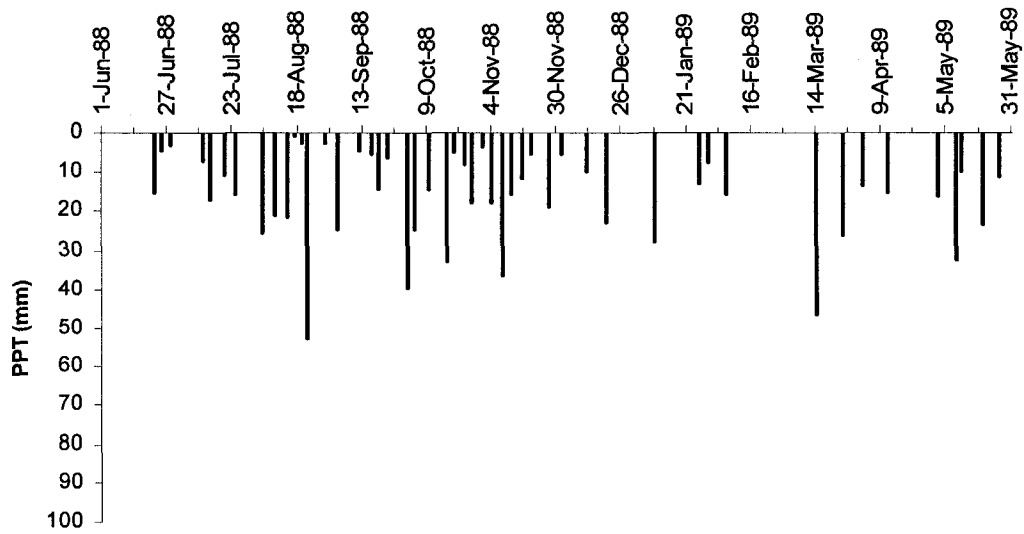
Figure 34: Harp catchments precipitation 1988/89.
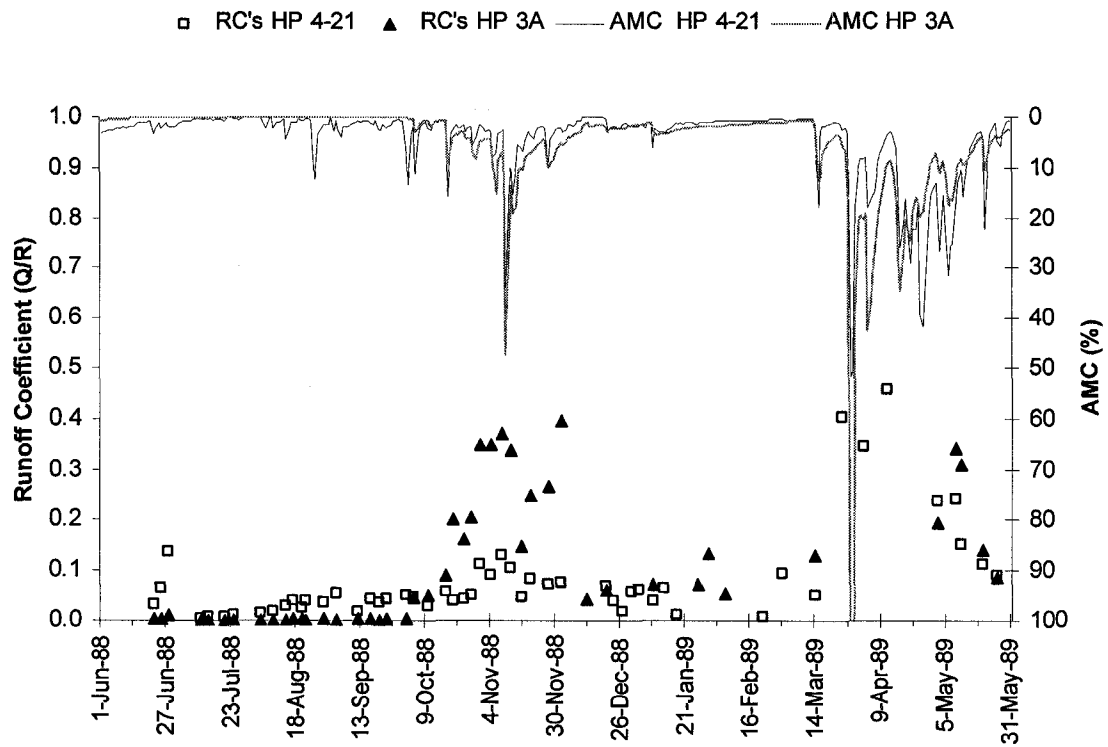
Figure 35: Time series of antecedent moisture vs. runoff coefficients 1988/89; Harp 3A and Harp 4-21.
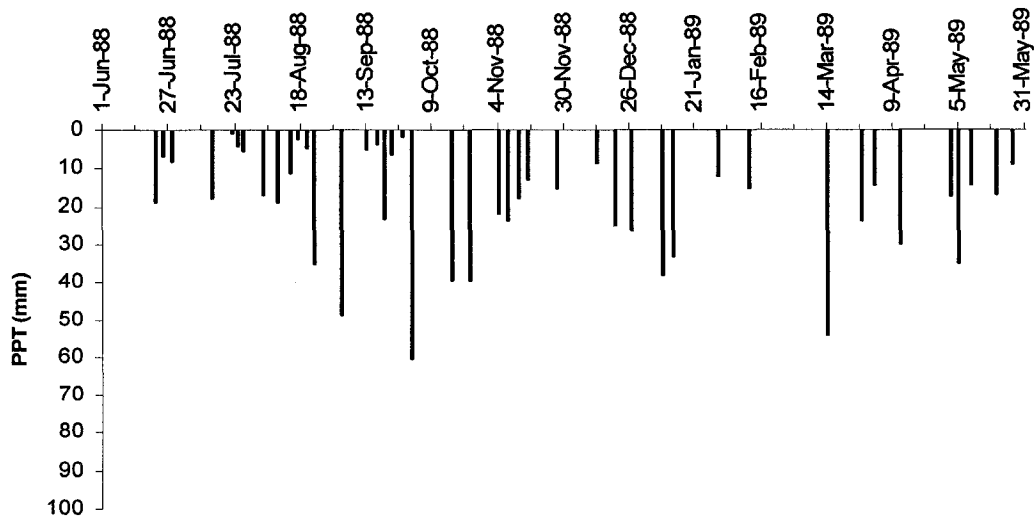
Figure 36: Plastic catchments precipitation 1988/89.
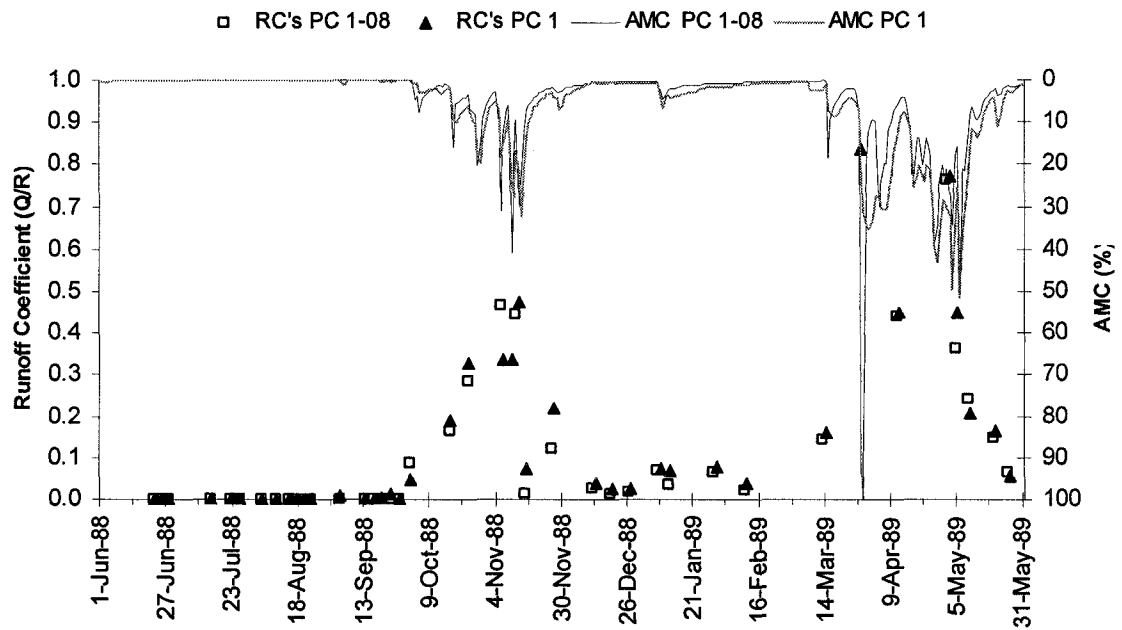
Figure 37: Time series of antecedent moisture vs. runoff coefficients 1988/89; Plastic 1 and Plastic 1-08.
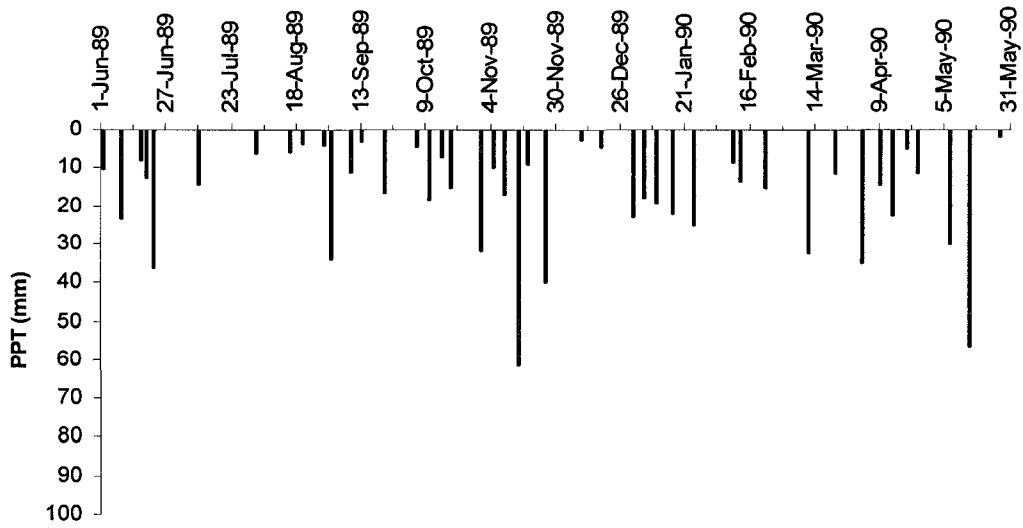
Figure 38: Harp catchments precipitation 1989/90.
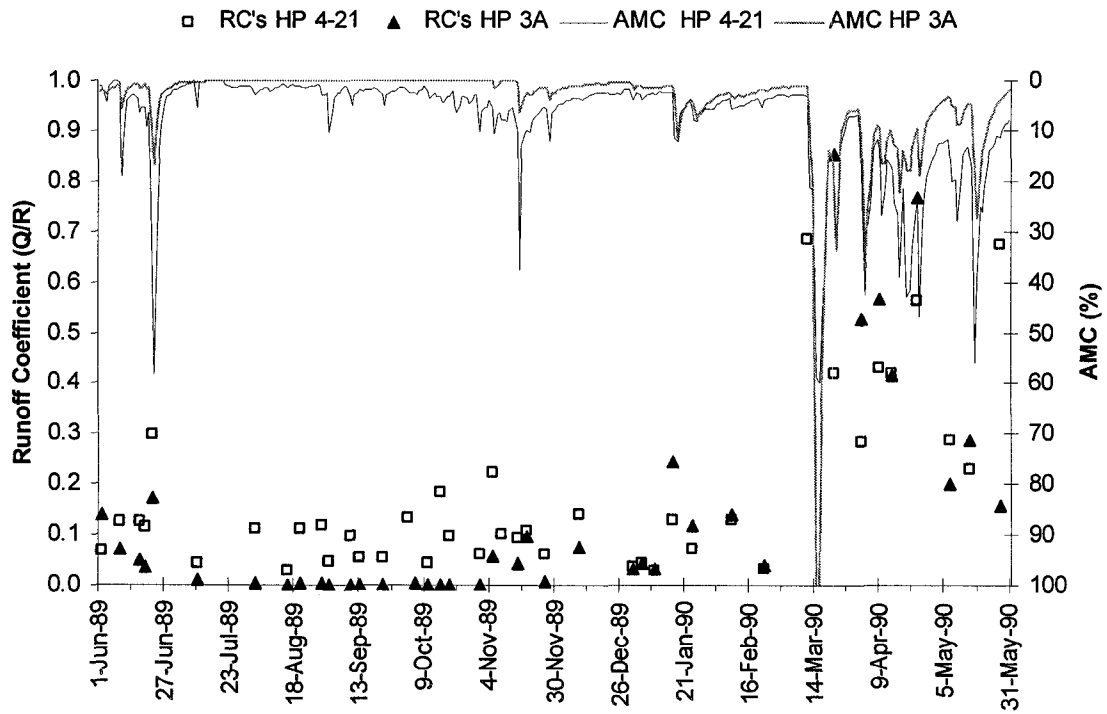
Figure 39: Time series of antecedent moisture vs. runoff coefficients 1989/90; Harp 3A and Harp 4-21.
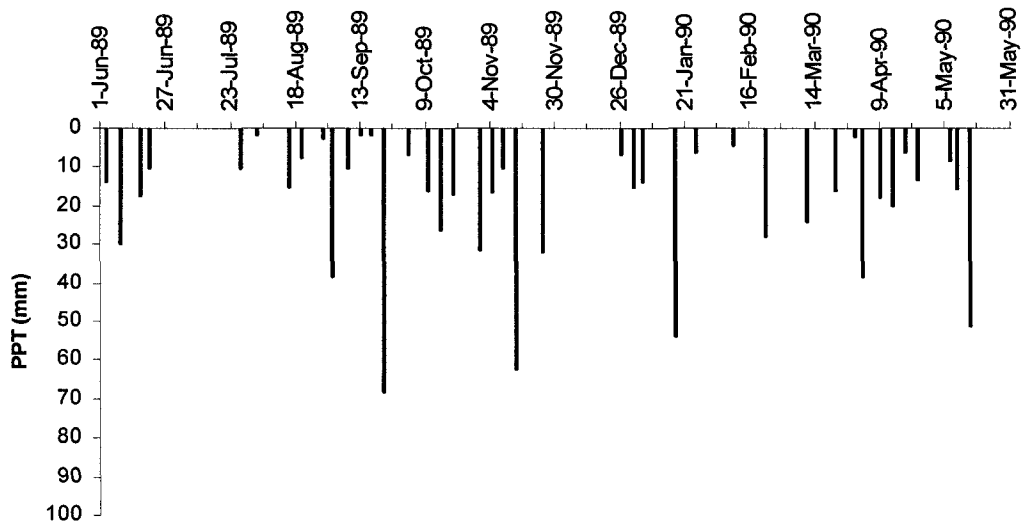
Figure 40: Plastic catchments precipitation 1989/90.
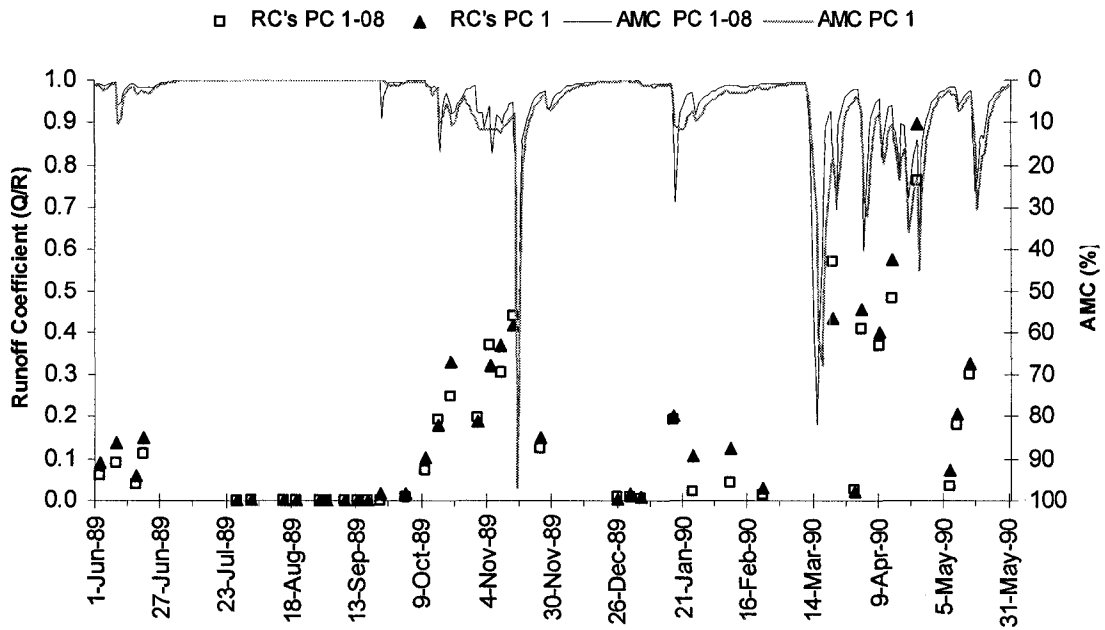
Figure 41: Time series of antecedent moisture vs. runoff coefficients 1989/90; Plastic 1 and Plastic 1-08.

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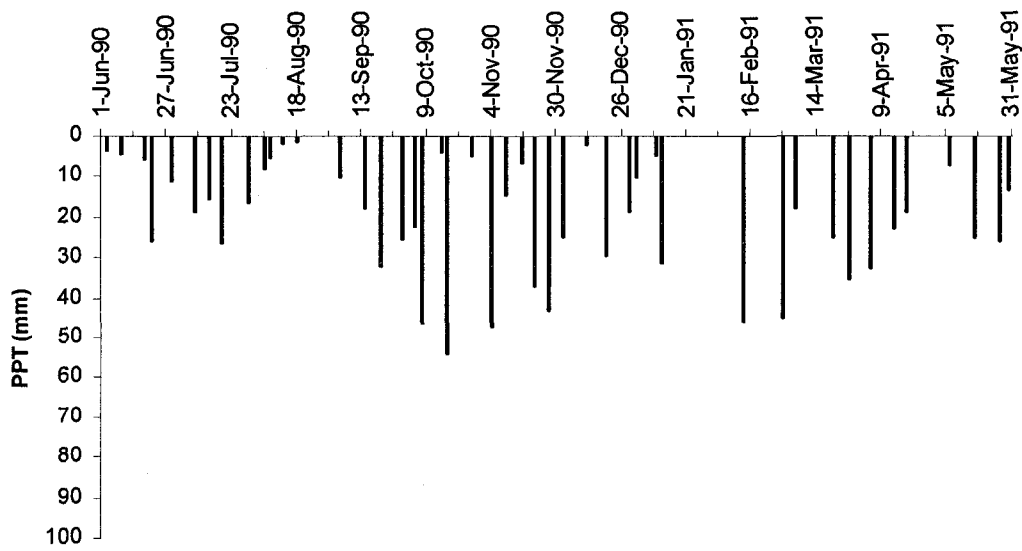
Figure 42: Harp catchments precipitation 1990/91.
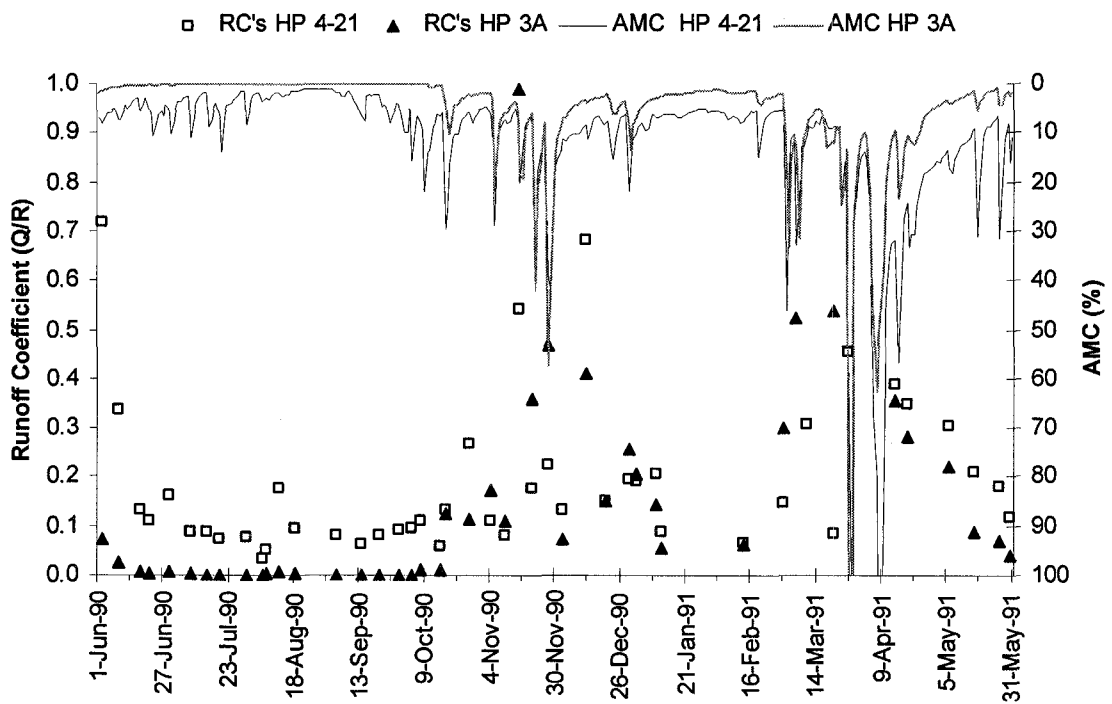
Figure 43: Time series of antecedent moisture vs. runoff coefficients 1990/91; Harp 3A and Harp 4-21.
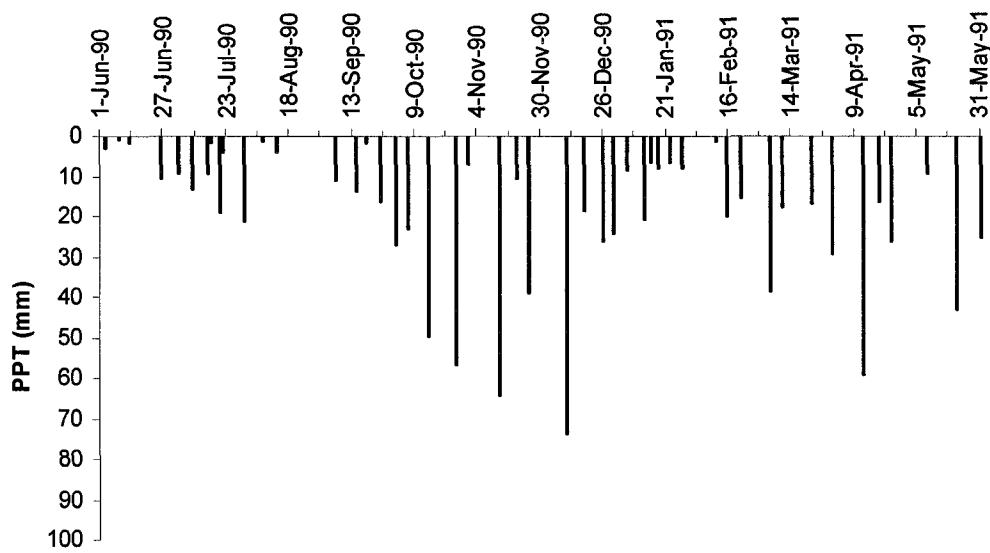
Figure 44: Plastic catchments precipitation 1990/91.
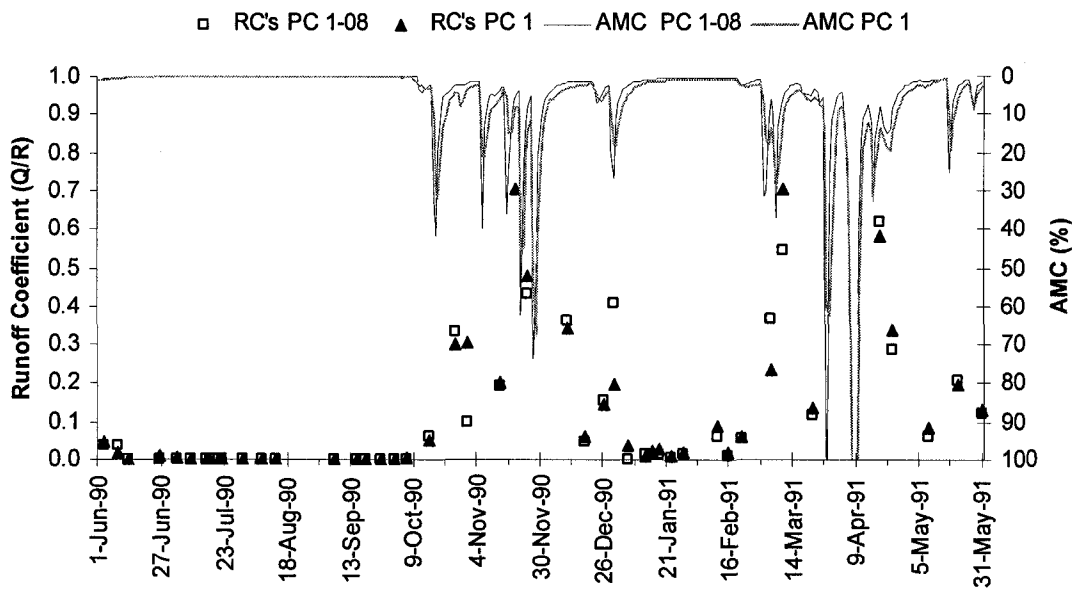
Figure 45: Time series of antecedent moisture vs. runoff coefficients 1990/91; Plastic 1 and Plastic 1-08.

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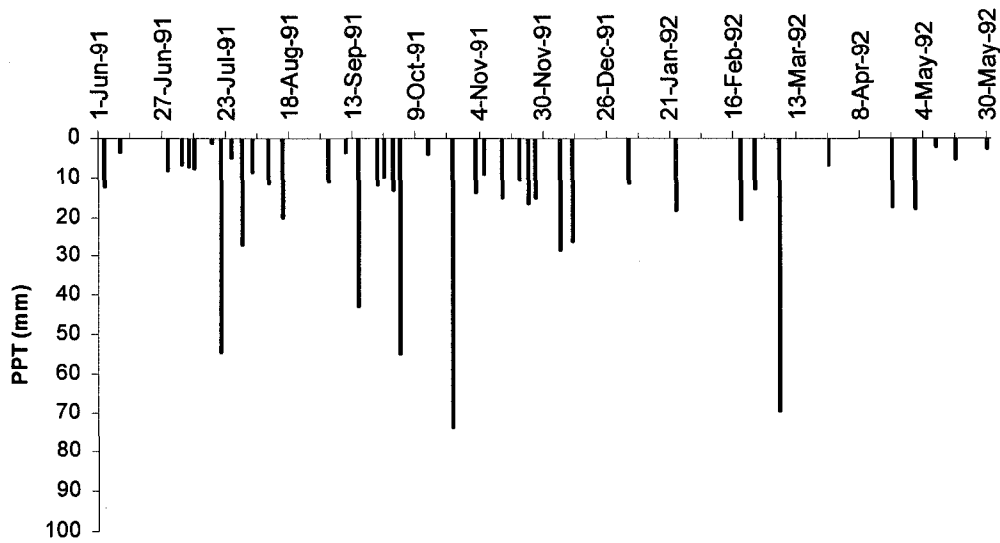
Figure 46: Harp catchments precipitation 1991/92.
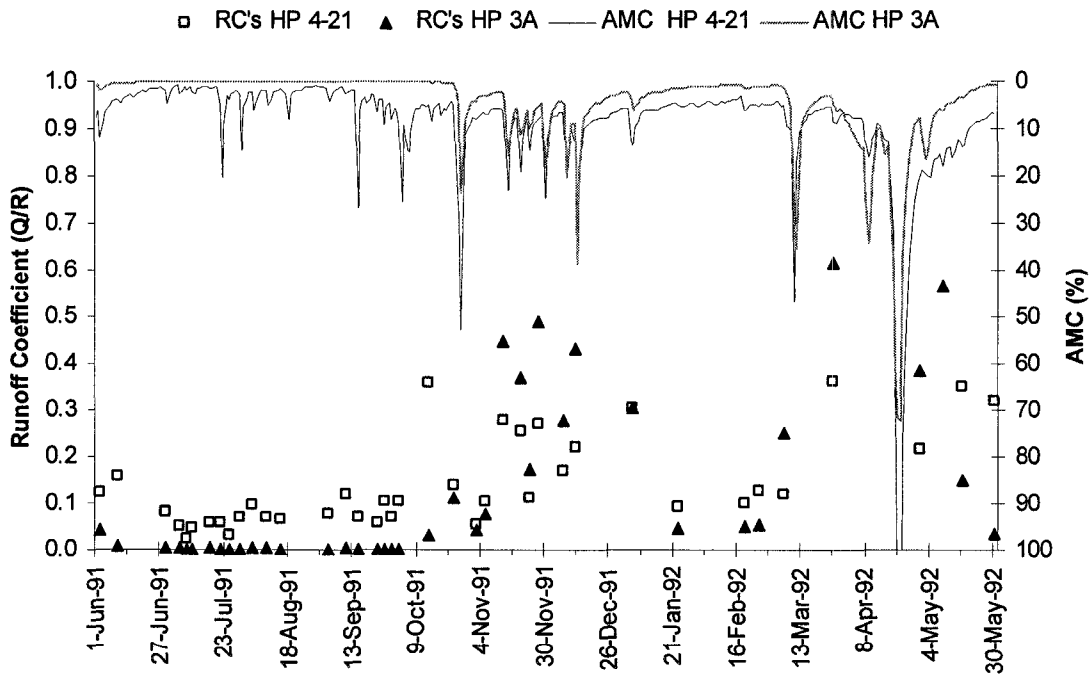
Figure 47: Time series of antecedent moisture vs. runoff coefficients 1991/92; Harp 3A and Harp 4-21.
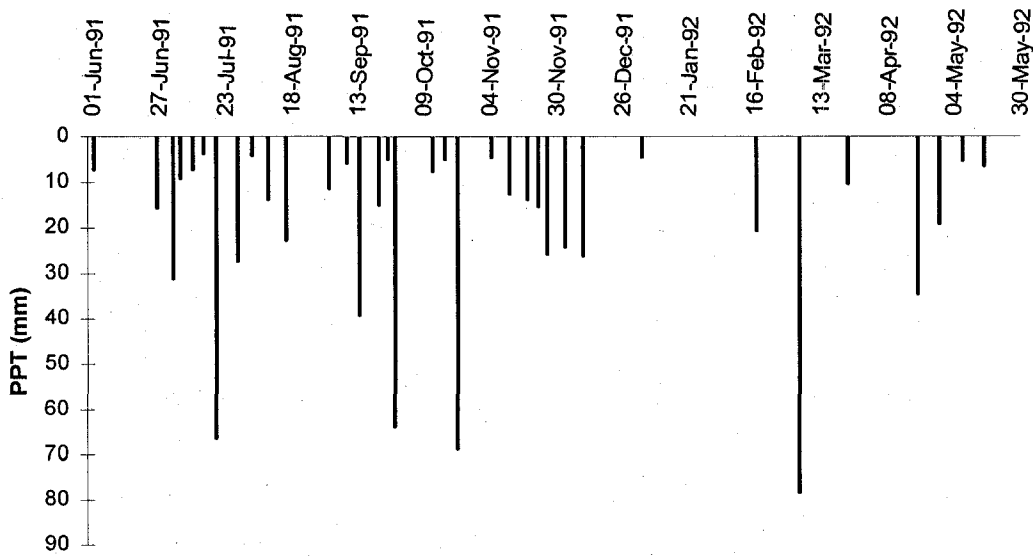
Figure 48: Plastic catchments precipitation 1991/92.
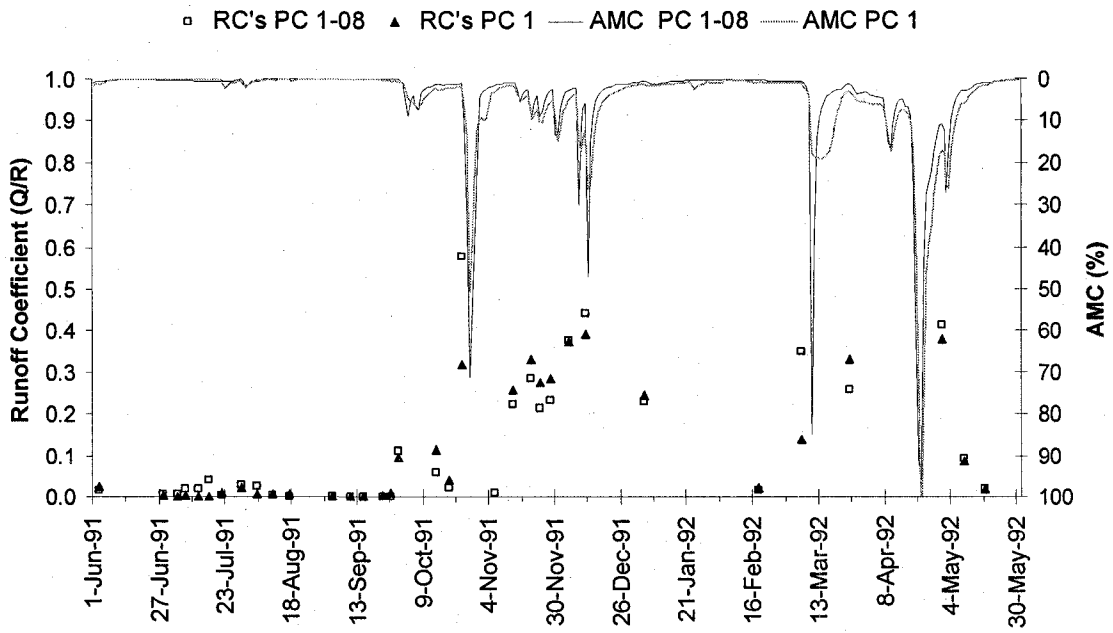
Figure 49: Time series of antecedent moisture vs. runoff coefficients 1991/92; Plastic 1 and Plastic 1-08.

4.4 Discussion

Runoff production varies from one season to the next in each basin and is governed by the basin's ability to store and release water, which in turn is controlled by the physical make up of each basin. During spring, when conditions are humid, and precipitation exceeds evapotranspiration, water tables are high and hydrological connectivity within a basin is widespread. During the drying phase, from spring to summer, spatial patterns of soil moisture change. Water tables are low and the transport of water, percolating into the now unsaturated zone, is predominantly vertical. Evapotranspiration is high and under these conditions it may be possible that dry soil pockets develop, where soil characteristics change, resulting in the disruption of hydrological connectivity between hillslope and valley. A recent study conducted by McNamara et al. (in press) identified five soil moisture conditions that occur during a year. The authors conclude that hydrological connectivity between hillslope and stream is driven by changes in the water balance between rain, snow, snowmelt and evapotranspiration. Low rates of water input to the soil after the dry state allow dry soil regions to persist at the soil–bedrock interface, which act as barriers to lateral flow.

Some catchments, however, are less prone to drying out and are persistently wetter than others, such as the HP 4-21 basin (Figures 35, 39, 43 and 47). HP 4-21, with the deepest till cover of the four catchments, sustains baseflow year-round resulting in the least variable hydrological response during the study period. In comparison, although the drainage area of the PC 1-08 catchment is of similar size, runoff cannot be generated during the summer suggesting insufficient water content

within soils, reflective of the thin till veneer covering this basin (Figure 37 and 45). However, Buttle et al., (2004) conducted a study to examine the coupling of slopes and riparian zones within the PC 1-08 basin and reported that bedrock depression storage controlled runoff delivery from slopes by storing water within these cavities. Stormflow could only be generated if these depression were filled, thus coupling the upslope area with the valley.

Similarly, HP 3A with shallow soils upslope does not produce any runoff during the dry summer month of 1989/90 and 1991/92 (Figure 35 and 47). After the onset of fall storm events, and seasonally reduced evapotranspiration, tills wet-up, allowing previously decoupled areas within the catchment to hydrologically reconnect, as is indicated by the sudden increase of runoff coefficients (Figure 35 and 43).

Runoff of the PC 1-08 basin immediately after the onset of fall storm events exceeds PC 1 runoff (Figure 37, 45 and 49). This is probably an effect of the proportion of wetland within the PC 1 basin. During the preceding summer the water table of the wetland decreases, creating storage; thus, less water contributes to stormflow. Once the storage capacity of the wetland is reached, more PC 1 runoff is generated resulting in higher runoff coefficients, which at this time exceed those of PC 1-08 (Figures 37, 41 and 45). As wetland storage becomes available again, PC 1 runoff declines lagging behind contributions of the PC 1-08 basin. This alternating behavior of streamflow response on a short term basis between the two catchments PC 1-08 and PC 1 cannot be observed for the HP 3A and HP 4-21 basins. For most of both years, runoff production of the HP 4-21 basin exceeds that of HP 3A. However, near mid – October when antecedent moisture increases, HP 3A generates higher

stormflow compared to the HP 4-21 basin. HP 4-21, due to its deeper tills, has a greater storage potential than HP 3A resulting in smaller runoff coefficients (Figure 35).

To summarize, runoff events during summer tend to occur as a result of short-duration, high-intensity storms over dry soils and deep water tables causing low stormflow, suggested by the low runoff coefficients of, for example, HP 4-21. Rainfall that occurs over PC 1-08 is not sufficient to cause runoff due to bedrock depressions acting as storage reservoirs and need to be filled first in order to produce runoff (Buttle et al., 2004). PC 1 does not generate runoff for parts of the year due to its wetland proportion, which acts as a reservoir. If saturation of the wetland is satisfied and the source area is expanded, contributions to stormflow exceed runoff generation of PC 1-08. However, as soon as wetland storage is available again PC 1-08 surpasses the runoff production of PC 1.

The HP 4-21 basin, which has sufficient baseflow fed by groundwater sources, generates runoff even during summer drought periods. Sufficient soil water content exists in the deeper soil layers of HP 4-21 allowing for perennial water transport from upslope to the stream. HP 3A does not sustain baseflow during summer due to thin mid and upslope soils (< 1m) that dry out during summer, which is consistent with findings from Hinton et al. (1998). Hillslopes and valleys are hydrologically disconnected from each other and water from the upper reaches will only contribute to streamflow if the mid-slopes areas are wet enough to support water flow. Runoff events during late fall and spring are generated by larger rainfalls on wetter soils. The water table is shallower and streamflow increases quickly after rainfall due to increased hydraulic conductivity and greater hydraulic gradients.

While HP 3A shows a steeper response indicated by high runoff coefficients, HP 4-21 runoff contributions do not rise to the same extent due to greater storage potential. Due to the thicker tills within the HP 4-21 the water table is deeper compared to HP 3A. Thus, hydraulic conductivity is lower resulting in comparatively lower immediate runoff coefficients during fall as some of the rainfall input will be retained and released only slowly throughout the year.

Chapter 5

Temporal solute export patterns from two forested basins of the Canadian Shield, south-central Ontario, Canada

5 Introduction

Stream storm water chemistry during and after an event is generally composed of solutes that have been discharged into the stream channel via different flow pathways which prevail within the basin at the time of and following the storm event (Bonell, 1993). Within the surficial geological structure of a basin a finite set of variables, including water table fluctuations, soil moisture conditions, evapotranspiration and precipitation input, govern the process of streamflow generation. Depending on rainfall intensity, soil depth variability, underlying bedrock topography and antecedent moisture conditions, these flow pathways vary temporally and spatially due to a variety of physical mechanisms governing the delivery of water to the stream through time (Elsenbeer et al., 1994; Ross et al., 1994; Brammer and McDonnell, 1995). The temporal and spatial changes of physical mechanisms operating in a catchment obscure the understanding of hydrological processes among different landscape elements despite the extensive study of streamflow generation processes. Many studies have focused on hydrograph separation techniques to evaluate storm runoff components via mixing models of pre-event and event water (Mulholland et al., 1990; Jenkins et al., 1994; Hinton et al., 1998). Numerous studies have dealt with nutrient transport in agricultural and forested basins (Hornberger et al. 1994; Hinton

et al., 1997; Creed and Band, 1998; Schiff et al., 1997, 2002; Macrae et al., 2003) and some on modification of nutrient transport by wetlands (Devito et al., 1997, 1999; Hinton et al., 1993, 1998; Schiff et al., 1998, 2002). Other studies examine the linkage between landscape elements and hydrological processes to elucidate the amounts and timing of materials exported from a system (Schiff et al. 1990, 1997; Trudgill et al., 1981). The overall conclusion of these studies is that the most important influence on solute and/or water flux is the water stored within the unsaturated zone of the soil column. Soil moisture in turn is closely linked to antecedent wetness, and combined with the amount of precipitation input, governs water flow pathways, which vary with storm intensity and duration. In order to apply tracers to evaluate hydrological processes, it is essential that the tracer employed is able to accurately identify the source area.

The chemical signature of a flowpath's water is a function of the hydrological residence time and the chemical reactions along it (Ball and Trudgill, 1997). Water traveling rapidly through a catchment will have shorter contact time with soil, whereas water moving slowly has more possibility to undergo chemical transformation through processes such as adsorption, oxidation, reduction, dissolution and cation exchange (Buttle, 1998; Whitehead et al., 1986). In order to employ chemical tracers successfully to infer hydrological processes, it is necessary that the catchment is a major source of some constituent, such as dissolved silica and base cations, whereas the atmospheric input is a source of other components, such as sulfate, which then undergo biogeochemical transformations while passing through the catchment. Discharge entering the stream represents the changing mix of these waters. For example, at baseflow conditions water is more alkaline and has higher

silica and base cation concentrations, calcium (Ca^{2+}), sodium (Na^+), potassium (K^+) and magnesium (Mg^{2+}), resulting from till/bedrock weathering reactions.

Given that basins of the Muskoka-Haliburton region are underlain by granitic gneiss bedrock and are covered with similar vegetation, largely composed of mixed forest, differences in basin export are tied to the ability of the catchment to either store, release and/or cycle different chemical constituents, which is associated strongly with flow pathways and residence times of water in soil/till and the relationships among hillslope groundwater drainage within the basin in question.

The objective of this chapter is to examine and quantify temporal patterns of chemical concentrations in streamwater and to assess the impact of extreme basin responses on solute export of two similar sized forested catchments, with differing physical make-up during climatically contrasting years.

5.1 Methods

5.1.1 Study sites

Both basins, Harp 4-21 (HP 4-21) and Plastic 1-08 (PC 1-08) are located in the Muskoka-Haliburton Region, in south central Ontario (45°13'N, 78°56'W) (Figure 50). The climate is classified as humid continental with long cool summers (Köppen class Dfb, Eimers and Dillon, 2002). During the time of data record from June 1988 to May 1992 the annual average precipitation at HP 4-21 was 918 mm and average runoff was 409 mm. The average annual precipitation of PC 1-08 was 947 mm and the mean annual runoff was 499 mm during the data record from June 1987

to May 1995. For this region the average temperatures ranged from 18.4° C in July to -10.5° C in January, with a mean annual temperature of 4.7° C (Chapter 2). PC 1-08 is covered with < 0.5 m glacial till deposits and bedrock outcrops cover about 10 % of the basin, which is drained by a short (< 250 m) ephemeral stream that discharges into a swamp. The shallowness of these surficial deposits, combined with the effective impermeability of the bedrock, suggests that only local groundwater aquifers develop in PC 1-08 (Devito et al., 1999).

Harp 4-21 is 3.7 ha and thus has a basin area comparable to PC 1-08. However, till deposits of HP 4-21 are deeper and generally have a thickness of up to 15 m throughout the basin. Only a small part at the southeast corner of the catchment (< 10 %) has no deposits (Hinton et al., 1993). Both catchments are underlain by impermeable Precambrian granitic gneiss bedrock. The vegetation is largely composed of mixed forest, with deciduous forests dominating where the soil is thicker and conifers dominating where the soils are thin (Dillon et al., 1991). In general, well-drained soils have deciduous or mixed forests, whereas poorly drained soils have mixed or coniferous forest (Dillon et al., 1991).
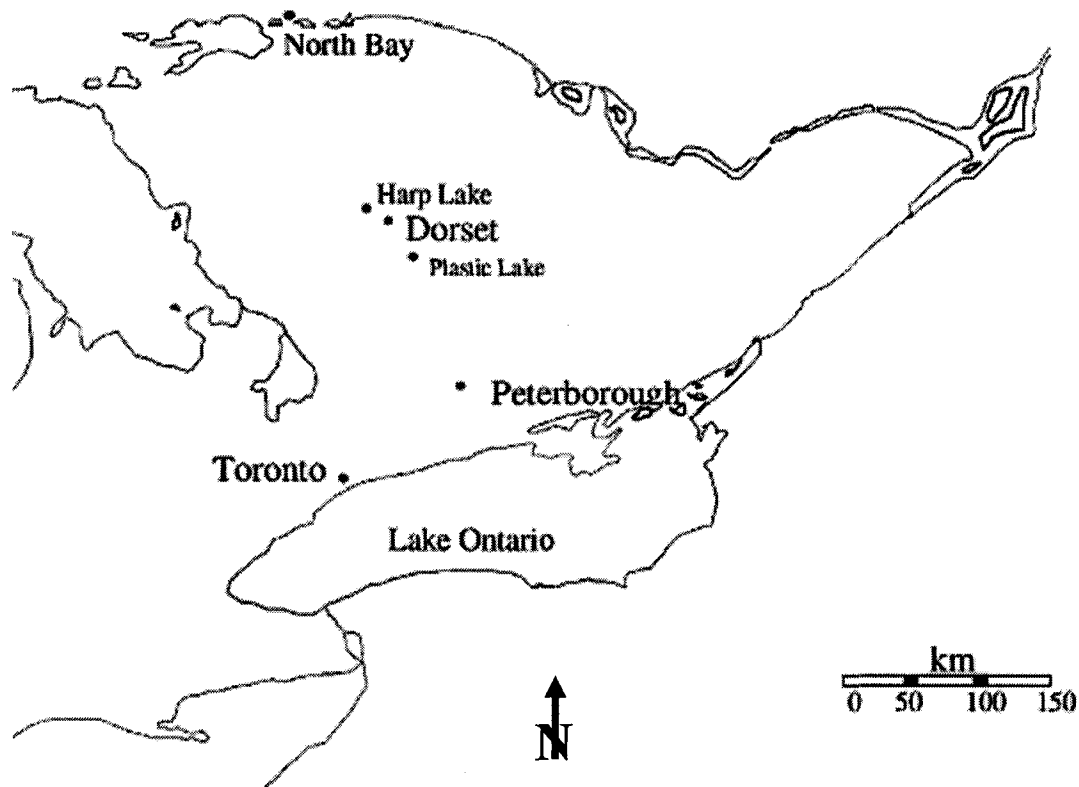
Figure 50: Location of study basins within the Muskoka-Haliburton County, south central Ontario, Canada.

5.1.2 Data collection and analysis

Data for the PC 1-08 and HP 4-21 basins were collected from the Dorset Environmental Science Centre located within a ~30 km radius of Plastic Lake and Harp Lake meteorological station, respectively. Precipitation and streamflow data spans from 1987 until 1995 for the PC 1-08 catchment but only from 1988 until 1992 for the HP 4-21 basin. Stream water samples were generally collected weekly or biweekly over the period from 1987 - 1995. However, during periods of high flow,

especially during spring melt, sampling was more frequent; on some occasions daily. Since the data record for HP 4-21 is present only for 1988/90 – 1991/92, stream flow and stream chemistry data were compared for these hydrological years (June 1 to May 31) in order to examine temporal variations of chemical export. All samples were filtered in the field (80 μm Nitex mesh) into pre-rinsed bottles, and transported to the laboratory in temperature-controlled containers for chemical analysis (Eimers et al., 2003). Water samples were analyzed for SO_4^{2-} and Cl^- by ion chromatography, for Ca^{2+} by atomic absorption spectrophotometry, while SiO_2 was analyzed by colourimetry (OME 1983). Stream water samples for PC 1-08 are not available during the summer months (June until August) as streamflow ceases during this period.

In this study a combination of observed and predicted values is used to fill missing chemical data. For some periods of time during the four year data set, for both Harp and Plastic catchments, it was necessary to interpolate chemical data to fill in missing stream water concentrations. After May 1992 water samples were collected only biweekly in PC 1-08; therefore interpolation of missing data seems inappropriate for this analysis. In order to calculate missing solute concentrations, discharge (independent variable) was used to calculate chemical values (dependent variable). The interpolated solute is then calculated utilizing the measured discharge and linear equation between solute and stream discharge. The standard error of estimate was then used to provide information on the error of the predicated solutes employing the built-in equation for standard error prediction in Excel. Table 9 to 12 summarize the results:

Table 9: PC 1-08: Standard error of estimate for predicted solutes in mg/l:

	Calcium	Chloride	Silica	Sulfate	Alkalinity
1988/89	0.02	0.03	0.03	0.16	0.08
1989/90	0.02	0.02	0.04	0.08	0.09
1990/91	0.03	0.04	0.03	0.09	0.05
1991/92	0.04	0.01	0.02	0.06	0.05

Table 10: PC 1-08: Best-fit equations; observed vs. predicted values:

Calcium	$y = 0.93x + 0.12$	$R^2 = 0.96$
Chloride	$y = 0.97x + 0.02$	$R^2 = 0.98$
Silica	$y = 0.99x + 0.04$	$R^2 = 0.98$
Sulphate	$y = 0.96x + 0.38$	$R^2 = 0.96$
Alkalinity	$y = 0.94x + 0.09$	$R^2 = 0.94$

Table 11: HP 4-21: Standard error of estimate for predicted solutes in mg/l:

	Calcium	Chloride	Silica	Sulfate	Alkalinity
1988/89	0.08	0.61	0.38	0.19	1.27
1989/90	0.06	0.02	0.16	0.19	0.32
1990/91	0.05	0.02	0.14	0.17	0.54
1991/92	0.08	0.03	0.12	0.12	0.50

Table 12: HP 4-21: Best-fit equations; observed vs. predicted values:

Calcium	$y = 0.99x + 0.03$	$R^2 = 0.99$
Chloride	$y = 0.95x + 0.02$	$R^2 = 0.96$
Silica	$y = 0.99x + 0.05$	$R^2 = 0.99$
Sulphate	$y = 0.95x + 0.42$	$R^2 = 0.95$
Alkalinity	$y = 0.98x + 0.20$	$R^2 = 0.99$

The resulting standard errors for the varying solutes indicate that typical data values differ from their predicted values in HP 4-21 on average by about 0.07 mg/l for calcium, 0.17 mg/l for chloride, 0.20 mg/l for silica, 0.17 mg/l for sulfate and 0.66 mg/l for alkalinity and in PC 1-08 by about 0.03 mg/l for calcium, chloride and silica,

0.10 mg/l for sulfate and 0.07 mg/l for alkalinity suggesting that the independent variable, which in this case is discharge, can be used to predict solute concentrations with an overall average precision of 0.25 mg/l in HP 4-21 and 0.05 mg/l in PC 1-08.

To understand fully the relationship between dissolved load and antecedent moisture conditions, and to describe the interplay between hydrochemistry and differing climatic conditions, temporal variations in solute concentration of stream water are examined with respect to hydrological flow patterns under varying moisture conditions. The hydrological year was divided into four seasons: summer (June, July, and August); fall (September, October and November); winter (December, January and February); and spring (March, April and May) to infer seasonal patterns in solute export from the basins.

To compare temporal and spatial variations of mass export during wet and dry periods, four solutes, chloride (Cl^-), dissolved silica (SiO_2), calcium (Ca^{2+}) and sulfate (SO_4^{2-}) were selected. Silicate minerals are subject to the complex chemical reactions of weathering. Weathering rates of silica are very slow and continuous dissolution of silica minerals takes place. SiO_2, therefore, is a useful geochemical tracer because of its prevalence in stream water from weathering of the granitic bedrock, its near-zero concentration in precipitation (Likens et al., 1979; Scanlon et al., 2001), and its differing concentrations in groundwater and soil water. Chloride (Cl^-) also has often been used to identify flow paths, water residence times and solute sources (Pearce et al., 1986; Sklash et al., 1986; Peters and Ratcliffe, 1998) because generally it is not adsorbed onto surfaces or does not play a role in soil forming processes (Johnston, 1987; Hauhs, 1987; Williamson et al., 1987). Within the two study basins

atmospheric deposition is the main input source of chloride. The increase of Cl^- in Birkenes streamwater in Norway (Christophersen et al., 1990), for example, is partly a result of evaporative concentration of soil solutions during the preceding drier summer months and partly due to seasonally elevated Cl^- concentrations in precipitation inputs. Sulfate has been reported to increase after prolonged droughts during summers attributed to S-mineralization processes in a basin (Eimers et al., 2004, Christophersen et al., 1982). Calcium is an important nutrient for forest growth and has been reported to decrease over the past four to five decades in the northeastern portion of the United States (Johnson et al., 1994) due to acid deposition (Adams, 1999; Likens et al., 1998) and precipitation inputs and was selected to evaluate differences in availability between the two basins.

5.2 Results

5.2.1 Hydrology

Mean annual discharges are 499 mm for the PC 1-08 basin and 409 mm for the HP 4-21 basin (Table 1, Chapter 2). Annual deviations from the long term mean of streamflow, given in percentage, show that stream discharge in PC 1-08 is lowest during 1991/92, which is therefore considered the driest year. The hydrological year 1990/91 was wettest for both basins (Figure 51 and 52). The driest conditions in HP 4-21 occurred in 1988/89 (Figure 52).

5.2.2 Stream chemical analysis

Annual water discharge and mass export varied greatly during the study period. From year to year, solute export follows patterns of discharge in both catchments. For example, wet years, such as 1990/91, yielded overall the highest export for all solutes in both catchments, whereas dry years, such as 1988/89 in HP 4-21, generated considerably lower solute mass. In HP 4-21, water discharge ranged from 217 mm in 1988/89 to 569 mm in 1990/91 (Figure 53). Calcium export ranged from 7.57 kg ha^{-1} to 19.67 kg ha^{-1}, chloride from 0.87 kg ha^{-1} to 2.37 kg ha^{-1}, silica from 12.03 kg ha^{-1} to 31.84 kg ha^{-1}, sulfate from 19.75 kg ha^{-1} to 49.52 kg ha^{-1} and alkalinity from 18.31 kg ha^{-1} to 49.38 kg ha^{-1}, respectively (Figure 54).

In PC 1-08, during this study period, annual discharge was lowest in 1991/92 with 473 mm and highest in 1990/91 with 629 mm (Figure 55). Correspondingly, solute export was lowest during the drier year in 1991/92 and highest in 1990/91. Calcium export ranged from 7.85 kg ha^{-1} to 10.6 kg ha^{-1}, chloride from 2.16 kg ha^{-1} to 3.18 kg ha^{-1}, silica from 12.51 kg ha^{-1} to 16.38 kg ha^{-1}, sulfate from 39.48 kg ha^{-1} to 55.98 kg ha^{-1} and alkalinity from 5.80 kg ha^{-1} to 7.17 kg ha^{-1}, respectively (Figure 56).
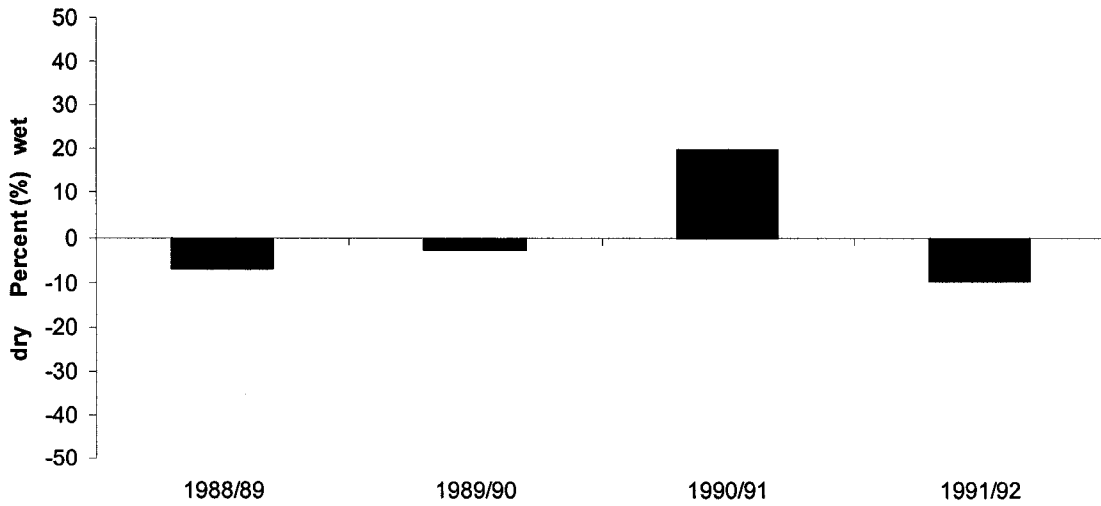
Figure 51: Histogram of annual deviations of Plastic 1-08 (PC 1-08) from a four year average of stream discharge record (1988/89-1991/92).
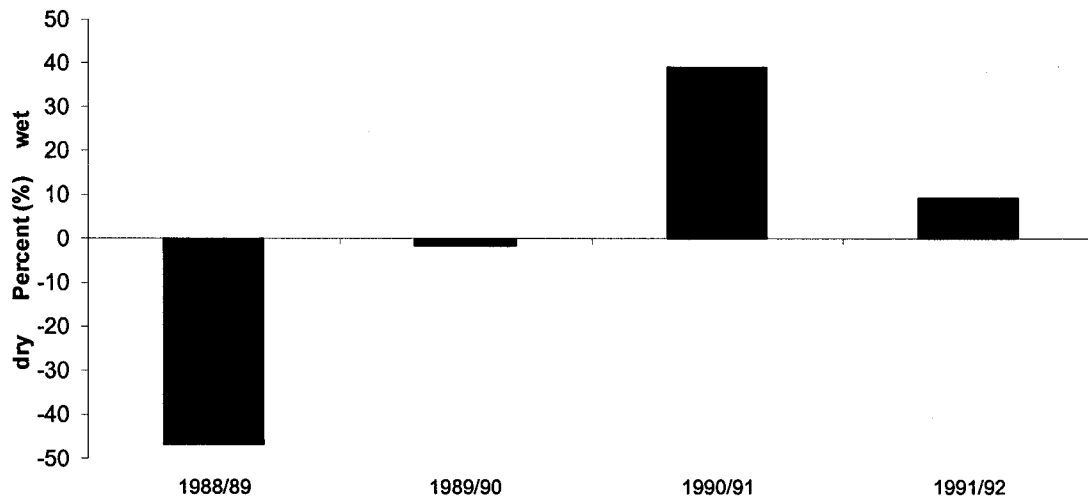
Figure 52: Histogram of annual deviations of Harp 4-21 (HP 4-21) from the four year average of stream discharge record (1988/89-1991/92).
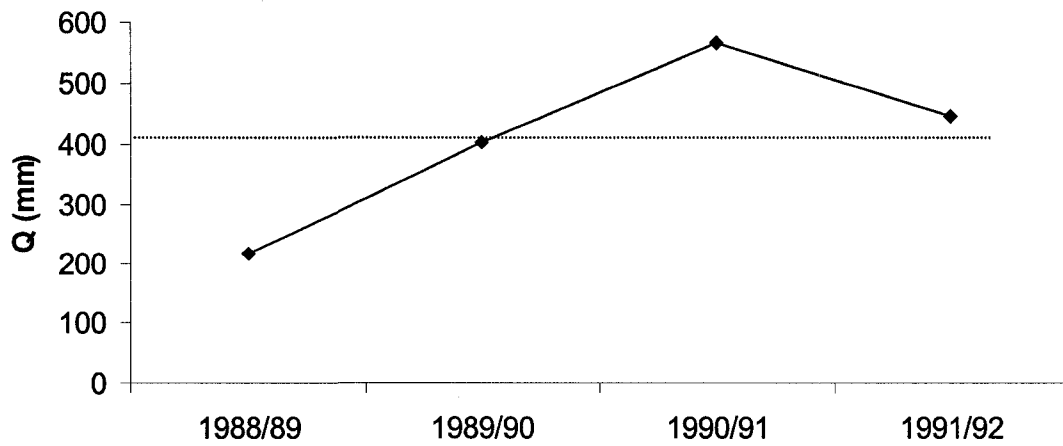
Figure 53: Annual discharge of HP 4-21 from 1988/89 until 1991/92. Dashed line marks average discharge.
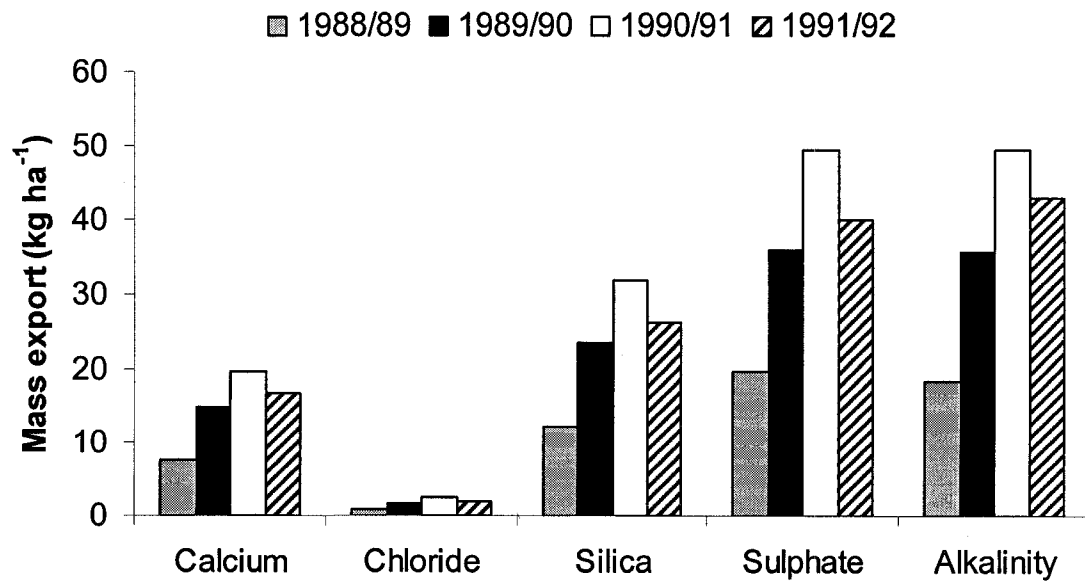
Figure 54: Mass export in kg/ha for calcium, chloride, silica, sulfate and alkalinity, HP 4-21 basin.

Figure 55: Annual discharge of PC 1-08 from 1988/89 until 1991/92. Dashed line marks average discharge.
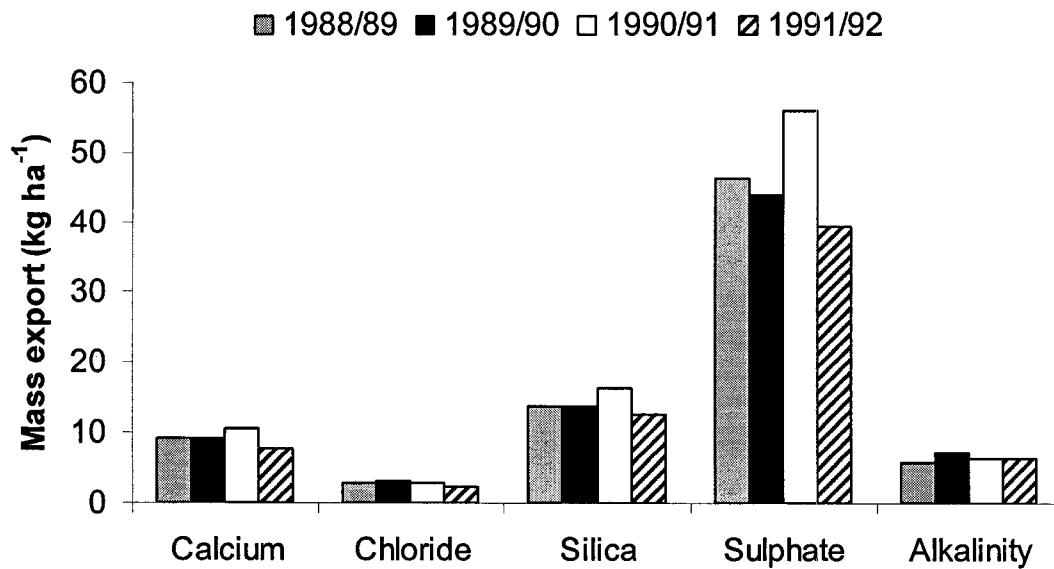
Figure 56: Mass export in kg/ha for calcium, chloride, silica, sulfate and alkalinity; PC 1-08.

The differences in export are related to variations in flow pathways routing through the basins. Streamwater during drier years constitutes a greater fraction of deeper groundwater that originates in the lower till layers, while a greater proportion of runoff during wetter years is likely to originate in the upper soil layers due to increased water tables. Alkalinity, dissolved silica and base cations, such as Ca^{2+}, generally have increased concentrations in water that has longer contact with weatherable material, thus streamwater that has higher concentrations of these solutes is comprised of a larger portion of groundwater. On the other hand, streamwater that has low concentrations of these solutes is comprised of waters that follow shallow or near-surface pathways.

Table 13: Ratios of mass solute (g) to discharge (mm) for basin HP 4-21.

HP 4-21	Calcium	Chloride	Silica	Sulfate	Alkalinity
1988/89	35:1	4:1	55:1	91:1	84:1
1989/90	37:1	4:1	58:1	89:1	89:1
1990/91	35:1	4:1	56:1	87:1	87:1
1991/92	38:1	4:1	58:1	90:1	96:1

Table 14: Ratios of mass solute (g) to discharge (mm) for basin PC 1-08.

PC 1-08	Calcium	Chloride	Silica	Sulfate	Alkalinity
1988/89	19:1	6:1	28:1	95:1	12:1
1989/90	18:1	6:1	27:1	86:1	14:1
1990/91	17:1	5:1	26:1	89:1	10:1
1991/92	17:1	5:1	26:1	83:1	14:1

Mass exports of solutes differ between the two basins. Tables 13 and 14

illustrate the ratio of mass solute (g) to discharge (mm). Calcium and silica ratios are

approximately twice as high in the deeper tilled Harp 4-21 basin, whereas sulfate has

more or less the same ratio in both catchments. Alkalinity is approximately eight

times higher in HP 4-21 compared to PC 1-08.
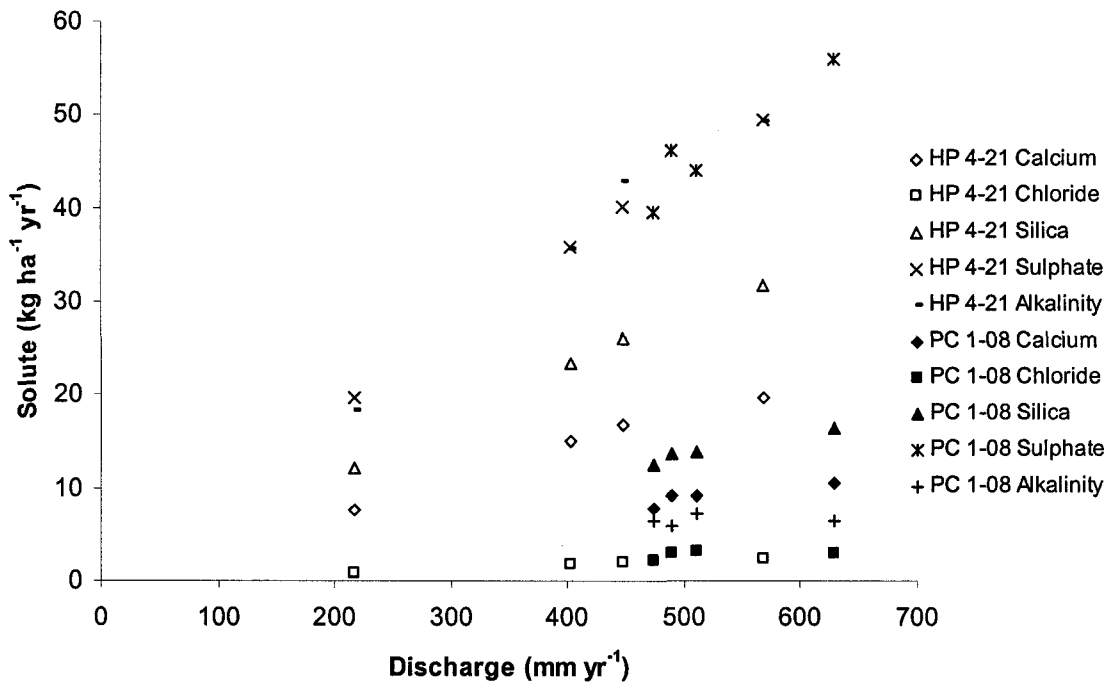
Figure 57: Differences of annual calcium, chloride, silica, sulfate export and alkalinity in (kg ha^{-1}) between PC 1-08 and HP 4-21.

Cl$^-$ is considered to be non-reactive as it passes from rain to the groundwater

resulting in similar export rates in the two basins despite the differing soil depth.

However, the higher ratio in PC 1-08 suggests that this basin is more prone to effects

of evapotranspiration. Ca^{2+} and SiO$_2$ are weathering derived, thus export of these

solutes are twice as high in HP 4-21 compared to PC 1-08. Alkalinity differs greatly

between the basins: water draining from the PC 1-08 basin has lower concentrations compared to HP 4-21 suggesting that soils of PC 1-08 have less buffer capacity to the deposition of hydrogen associated with the acid anions, such as SO_4^{2-} (Figure 57).

5.2.3   Temporal patterns

Cumulative graphs of annual mass export for five different solutes were generated to describe differences in mass export between HP 4-21 and PC 1-08. The abrupt increases in the slope of the lines, illustrating events with elevated export rates, suggest that in HP 4-21 major solute export occurs around mid-November likely because of elevated groundwater tables due to increased precipitation and decreased evaporation and with the onset of spring melt in March (Figure 58 and 59). Significant export in PC 1-08 occurs during the melt season in March and April, in mid-November during the average and wet years, and in 1991/92, the dry year, at the end of October (Figure 60 and 61). Compared to HP 4-21, the temporal distribution of mass export in PC 1-08 is less gradual, and occurs in distinctive events as indicated by the abrupt increases of the slope of the lines over a short time period. For example, in just two months, from October to November, approximately 30 % of solutes are exported. In comparison, HP 4-21 exports about 30 % of solutes in six months.

The steep increases in the slope of the lines in both catchments are followed by periods of steadier gradual rises indicating reduced discharge and lower mass loads. During the summer months, prior to the major solute exports, when the source of flow is mainly old groundwater with longer residence time, the cumulative line is characterized by a slight, but steady increase of solutes.

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5.2.4 Quantitative analysis

Quantitative assessment regarding the relationship between discharge ranges and mass load is provided in Figures 62 through 65 for the HP 4-21 basin and Figures 66 through 69 for PC 1-08. These graphs illustrate cumulative solute export during runoff events for the four consecutive years. Clearly, periods of high discharges are responsible for the majority of solute export in both catchments.

In HP 4-21 during the dry year (1988/89), 20% of the time, event discharge exceeded 0.8 l/sec and delivered 62 % of calcium, 64 % of chloride, 65 % of silica and 68 % of sulfate of annual export to the stream. In 1990/91, during the wet year, 20 % of the time, event discharge exceeded 2.5 l/sec and delivered 46 % of calcium, 55 % of chloride, 33 % of silica and 49 % of sulfate of annual export (Figure 64, Table 15) to the stream suggesting that export predominantly occurs during periods of high discharge but quantitatively varies between dry and wet years.

In drier years, runoff volume is small; however, mass export is comparatively high. During wet years higher discharge volumes per event result in lower solute mass loads per event suggesting a shift of mass export from spring melt driven export to proportionally higher mass export during high discharge events in fall.

Table 15: HP 4-21; percentage of annual solutes export in relation to storm discharge that is exceeded 20 % of the time during the course of a year (Figures 62 - 65).

	Calcium	Chloride (%)	Silica (%)	Sulfate (%)
1988/89 (dry)	62	64	65	68
1989/90 (average)	55	63	48	58
1990/91 (wet)	46	55	33	49
1991/92 (average)	52	56	34	56
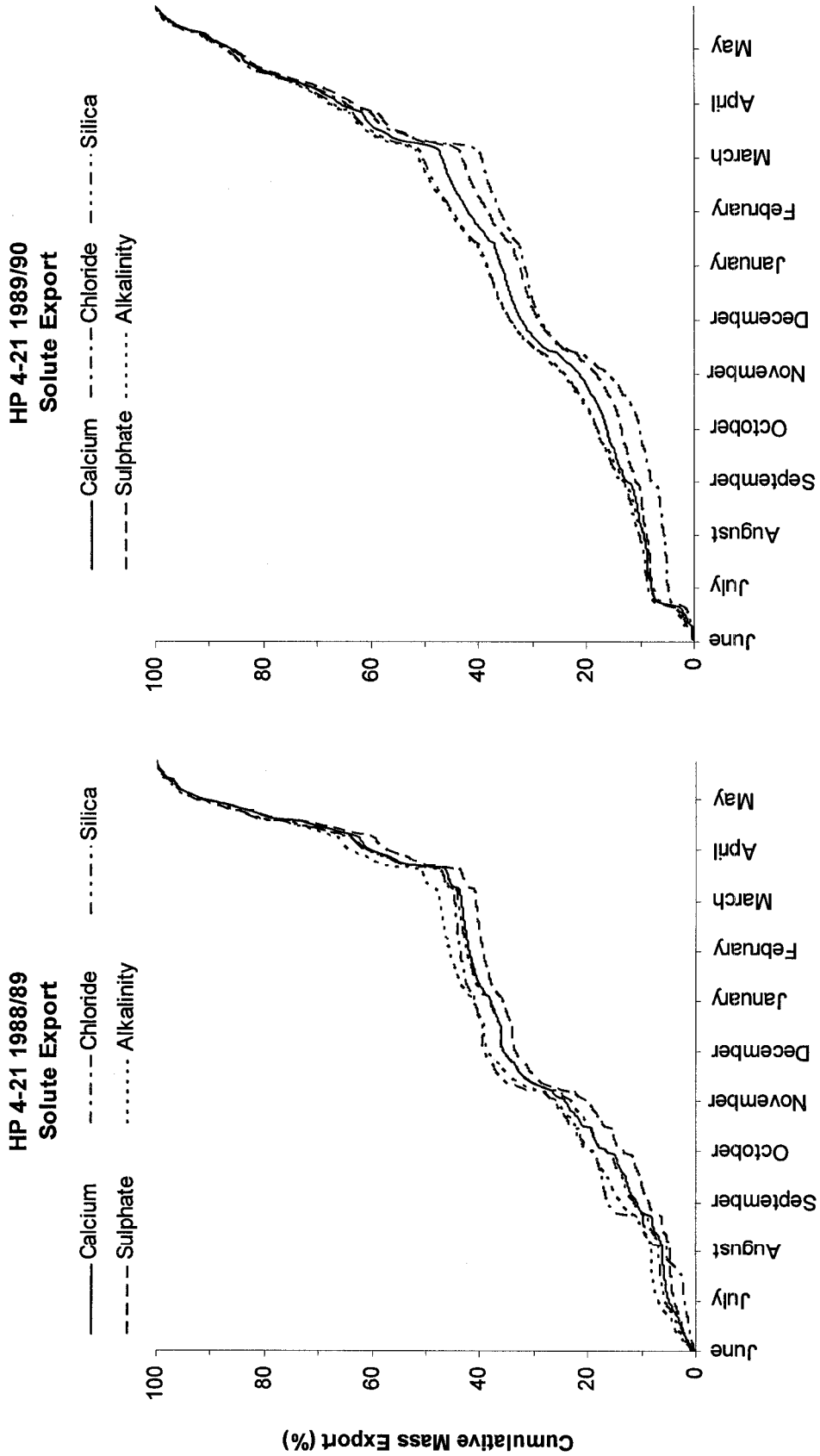
Figure 58a and b: Cumulative percentage of mass export for the years (a) 1988/89 and (b) 1989/90.

Figure 59a and b: Cumulative percentage of mass export for the years (a) 1990/91 and (b) 1991/92.

PC 1-08 1989/90
Solute Export

——— Calcium   – – –Chloride   –··–··Silica

– – – Sulphate   ········· Alkalinity

PC 1-08 1988/89
Solute Export

——— Calcium   – – –Chloride   –··–··Silica

– – – Sulphate   ········· Alkalinity
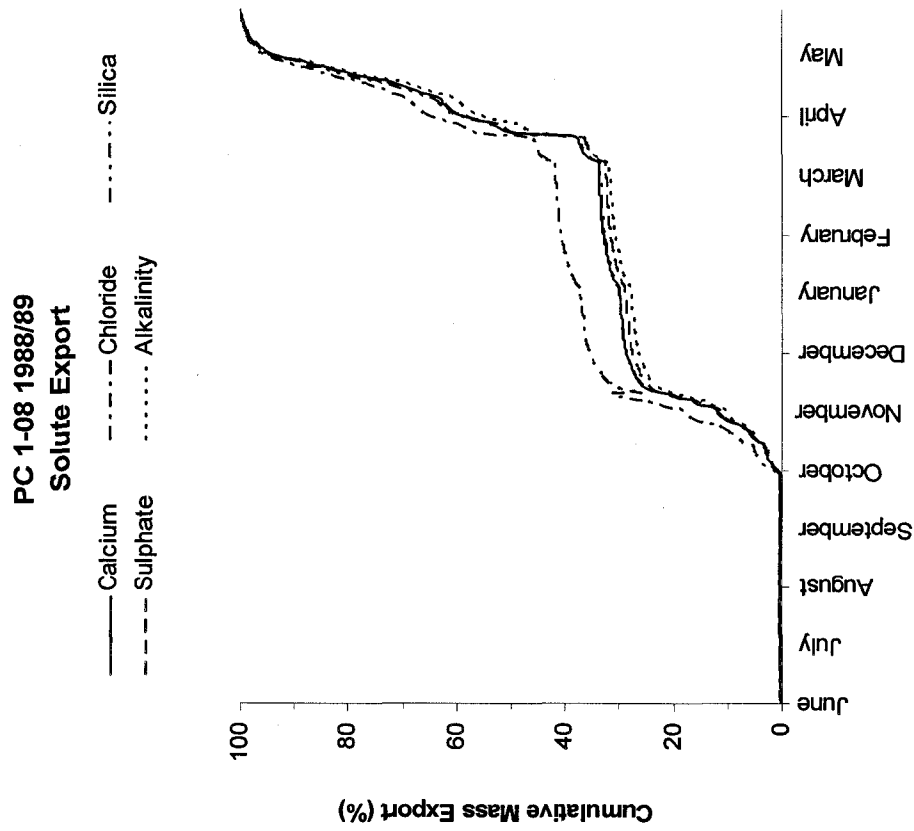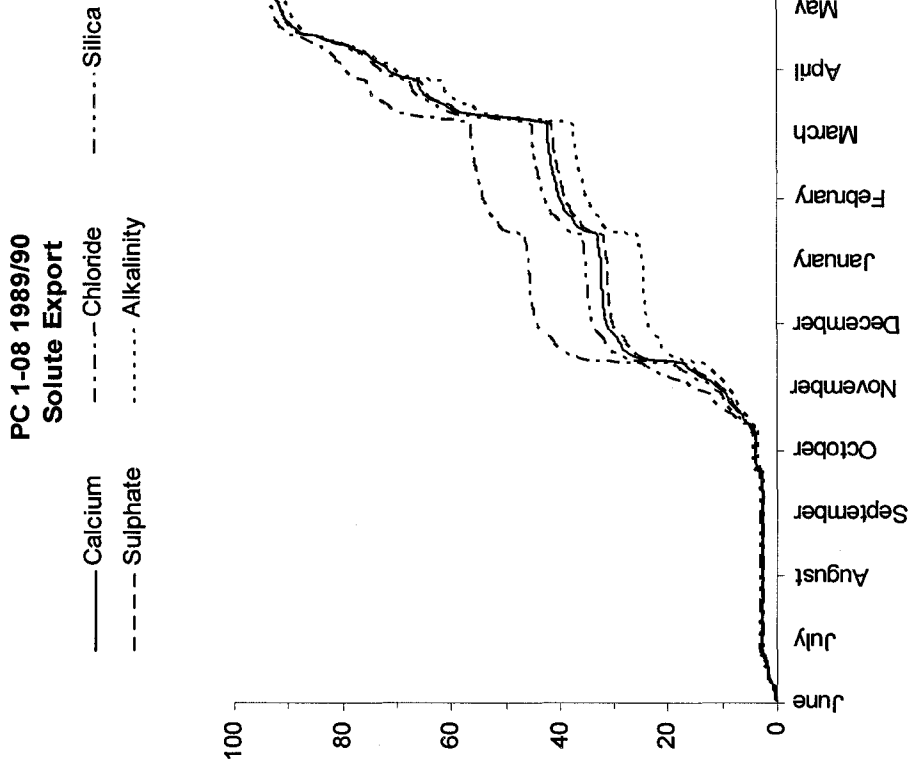
Figure 60a and b: Cumulative percentage of mass export for the years (a) 1988/89 and (b) 1989/90; PC 1-08.

PC 1-08 1991/92
Solute Export

——— Calcium   — - — -Chloride   — - - —··Silica
— — — -Sulphate   ········· Alkalinity

PC 1-08 1990/91
Solute Export

——— Calcium   — - — -Chloride   — - - —··Silica
— — — -Sulphate   ········· Alkalinity
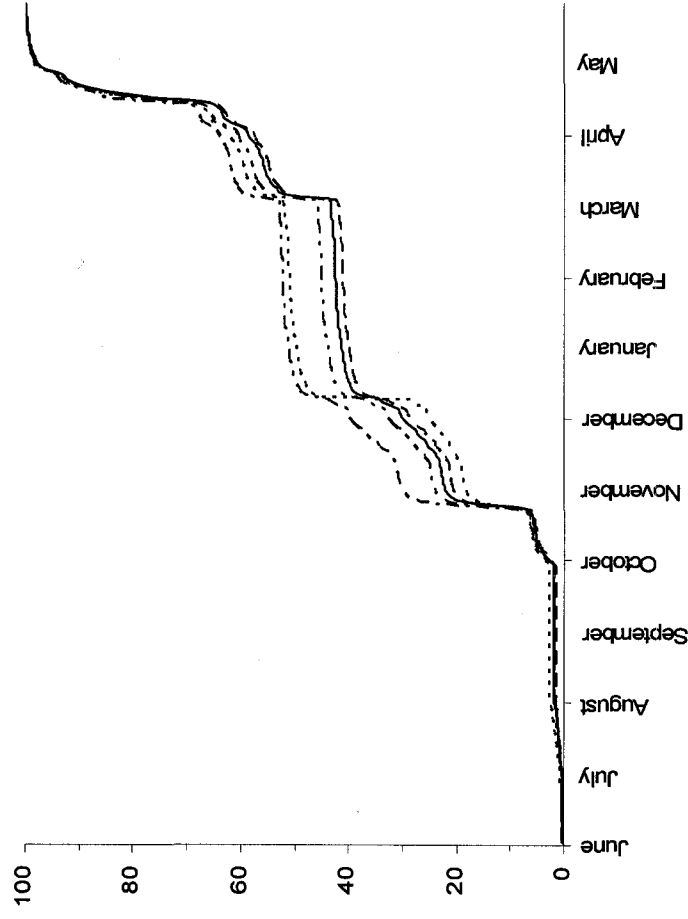
Figure 61a and b: Cumulative percentage of mass export for the years (a) 1990/91 and (b) 1991/92.

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HP 4-21 1988/89

——— Storm events — — Calcium — · · Chloride - · · · Silica ———Sulphate
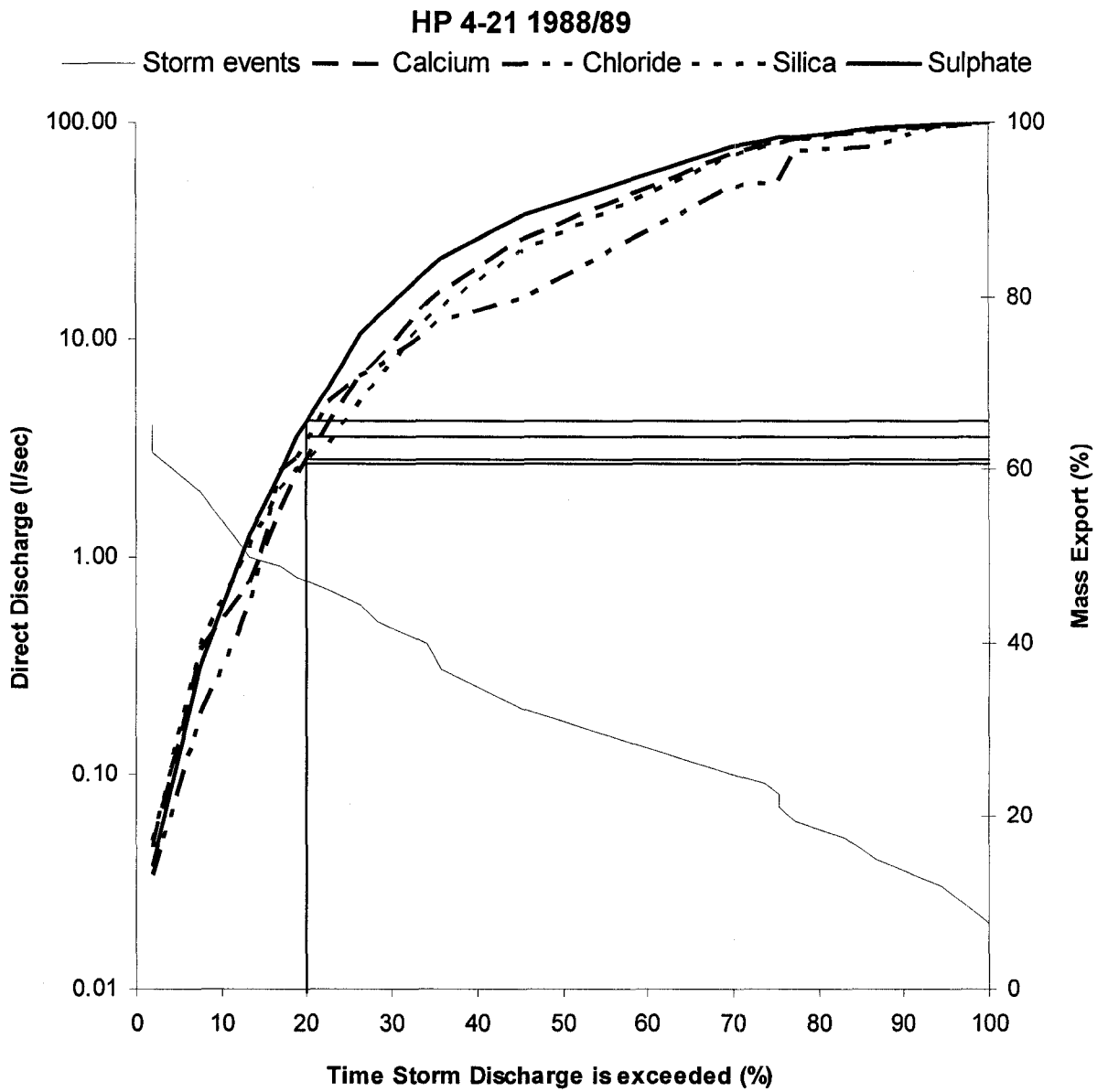
Figure 62: Cumulative mass export in relation to storm discharge occurrence; HP 4-21 1988/89.
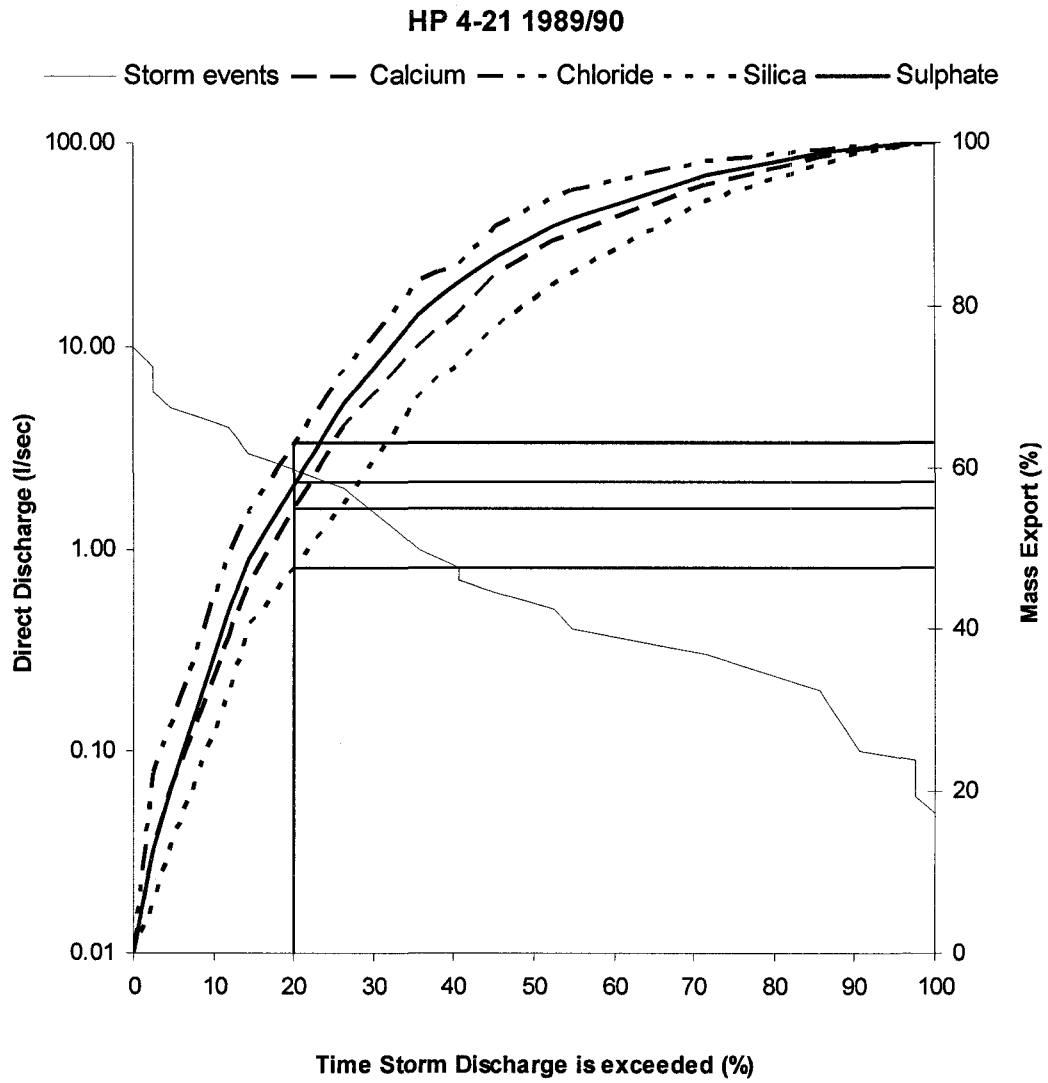
HP 4-21 1989/90

Figure 63: Cumulative mass export in relation to storm discharge occurrence; HP 4-21, 1989/90.
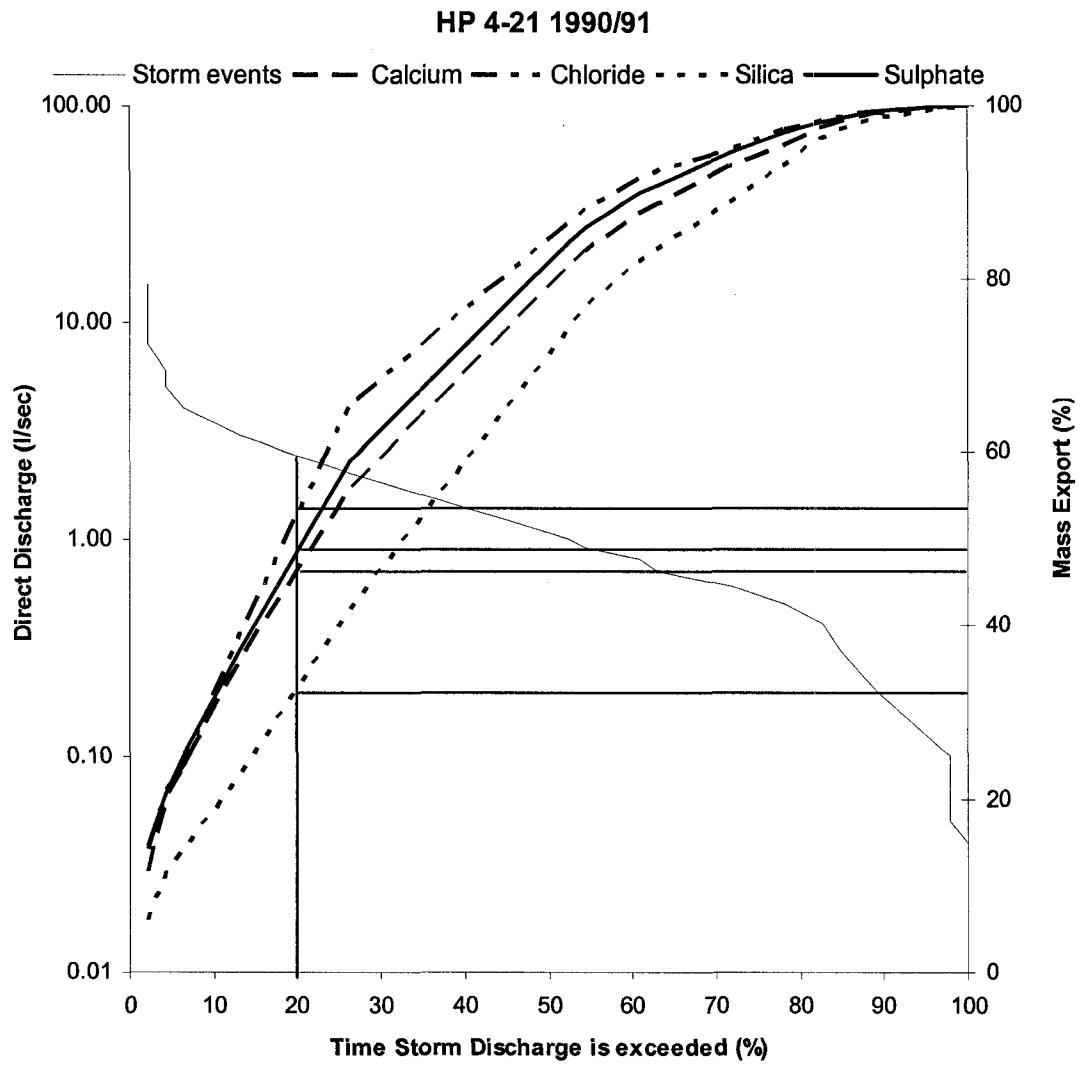
Figure 64: Cumulative mass export in relation to storm discharge occurrence; HP 4-21, 1990/91.
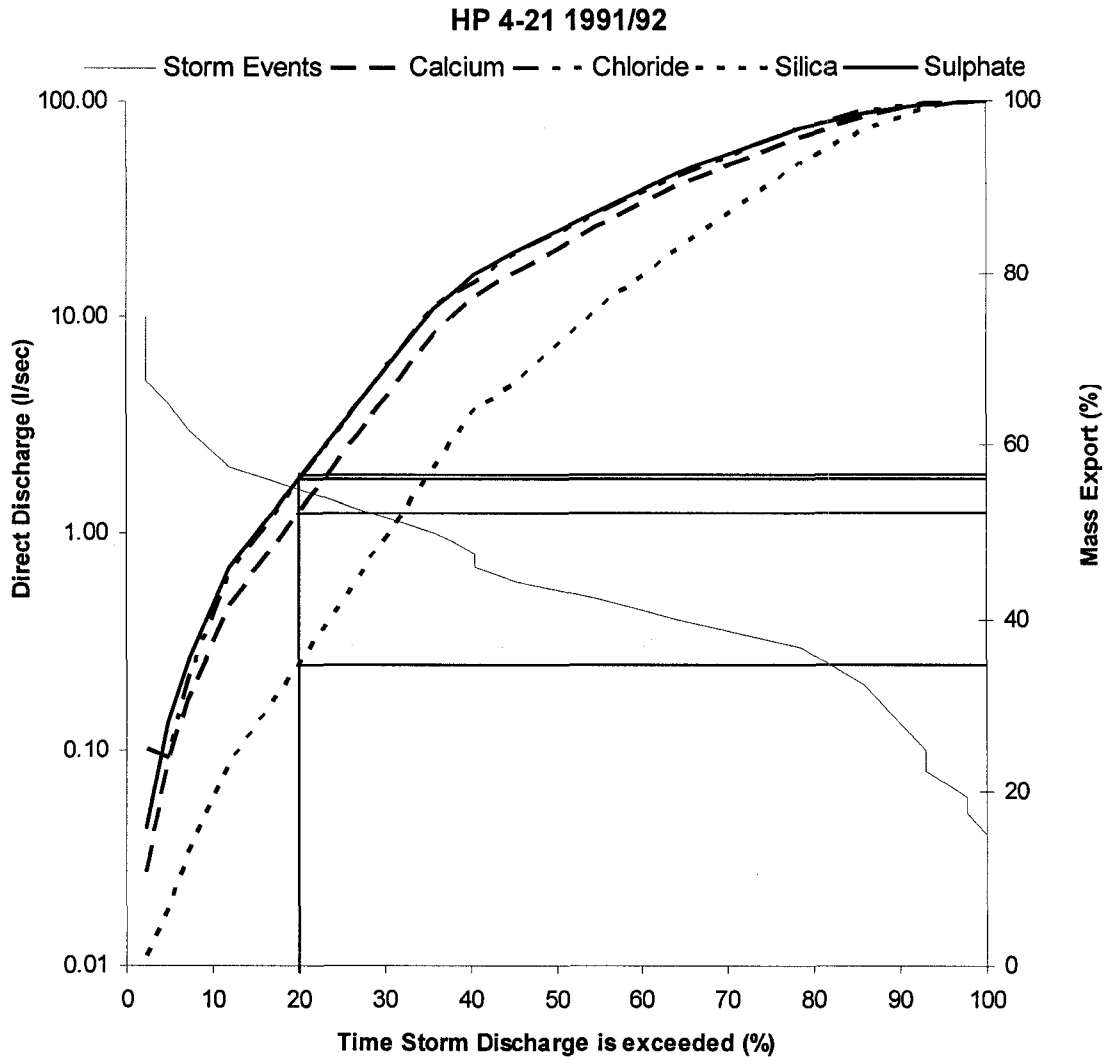
Figure 65: Cumulative mass export in relation to storm discharge occurrence; HP 4-21, 1991/92.

PC 1-08 1988/89

——— Storm event — — Calcium — - - Chloride - - - - Silica ———Sulphate
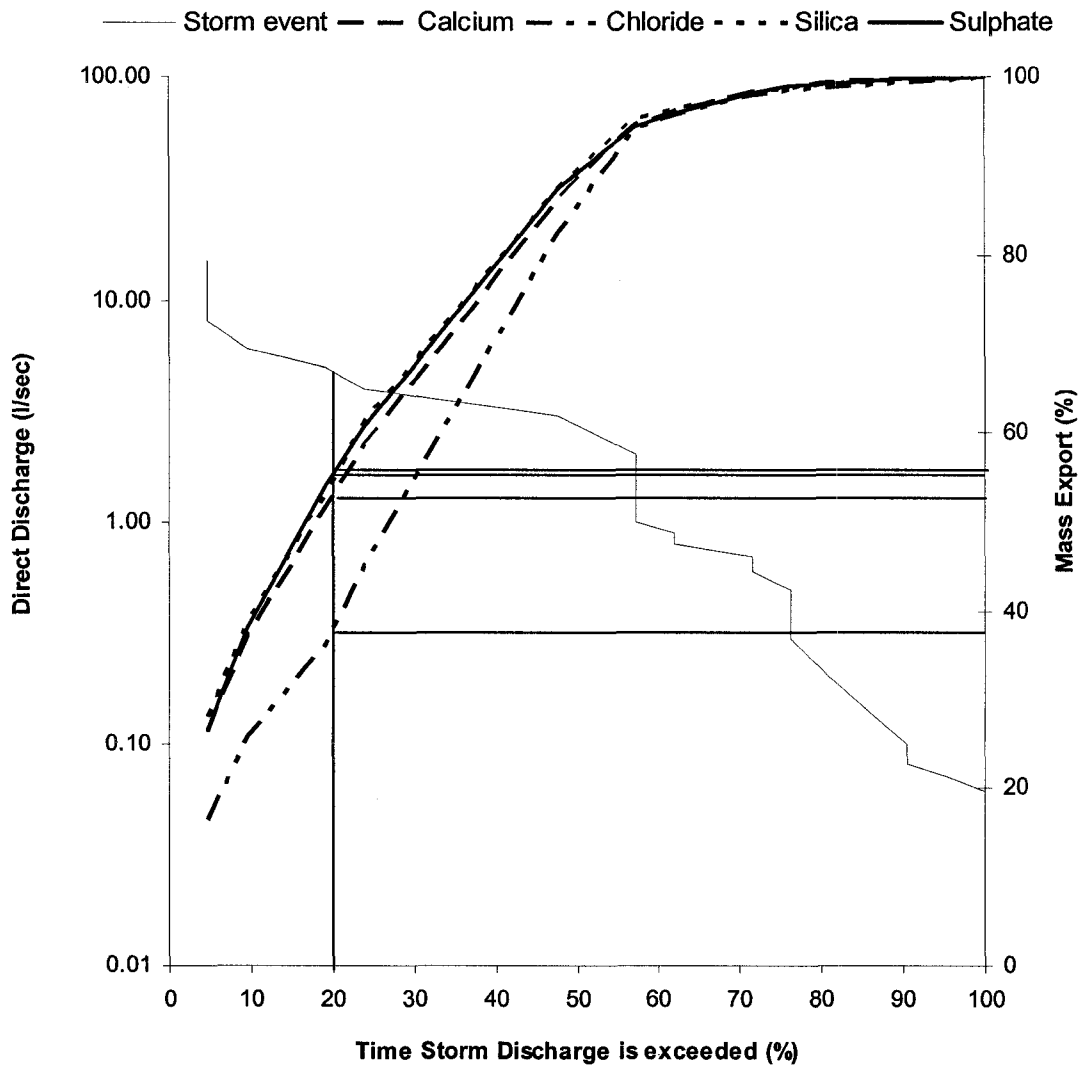
Figure 66: Cumulative mass export in relation to storm discharge occurrence; PC 1-08, 1988/89.

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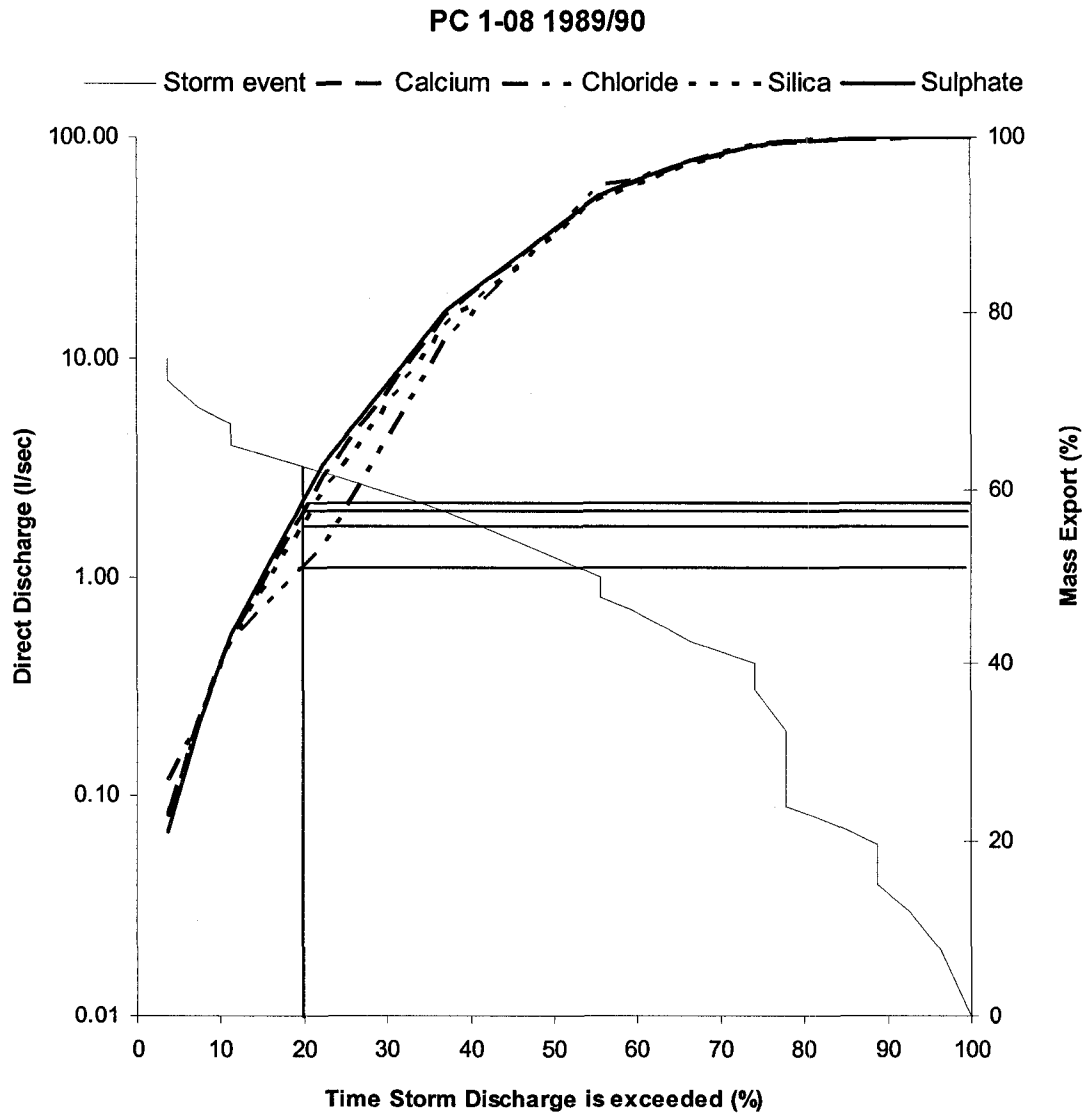
Figure 67: Cumulative mass export in relation to storm discharge occurrence; PC 1-08, 1989/90.
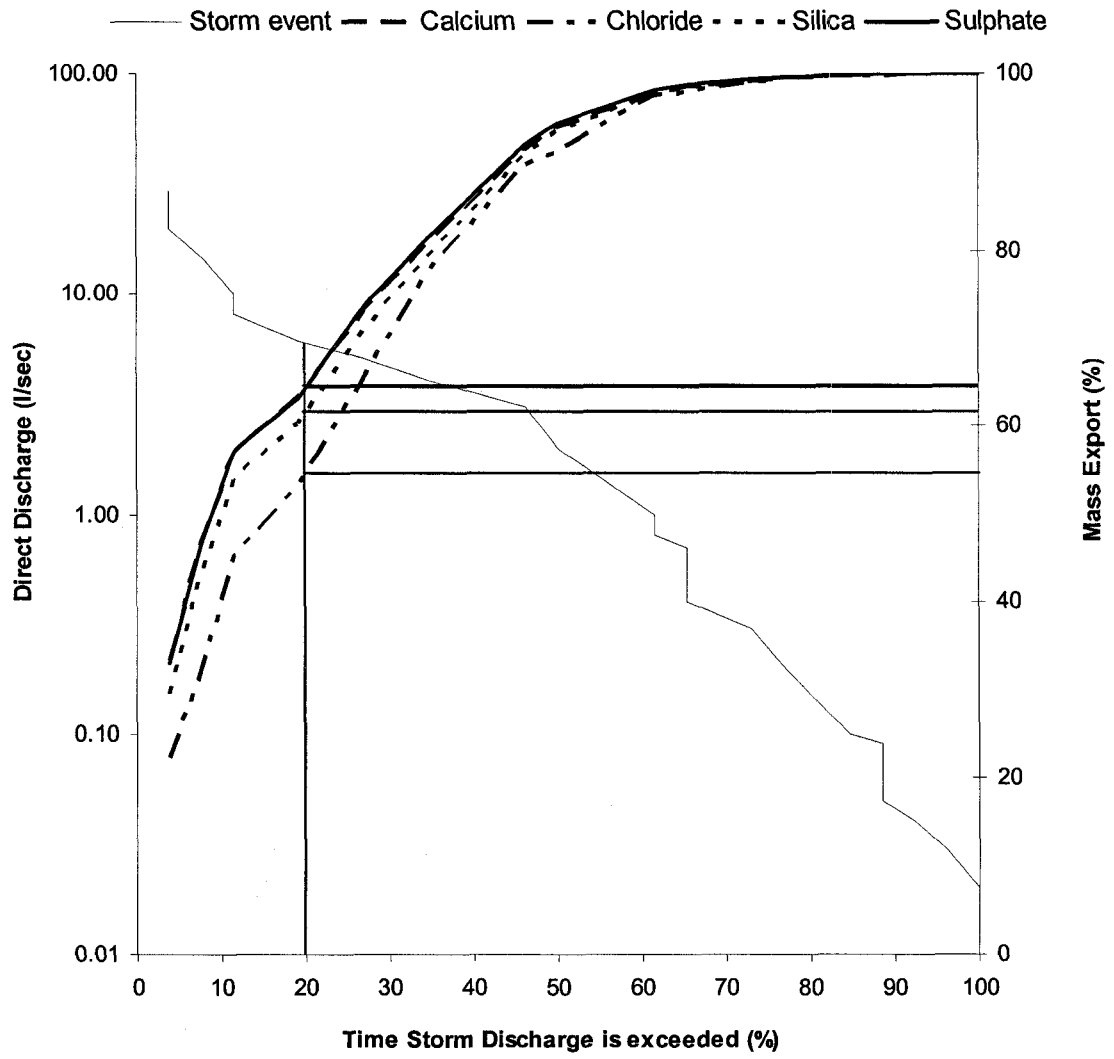
Figure 68: Cumulative mass export in relation to storm discharge occurrence, PC 1-08, 1990/91.

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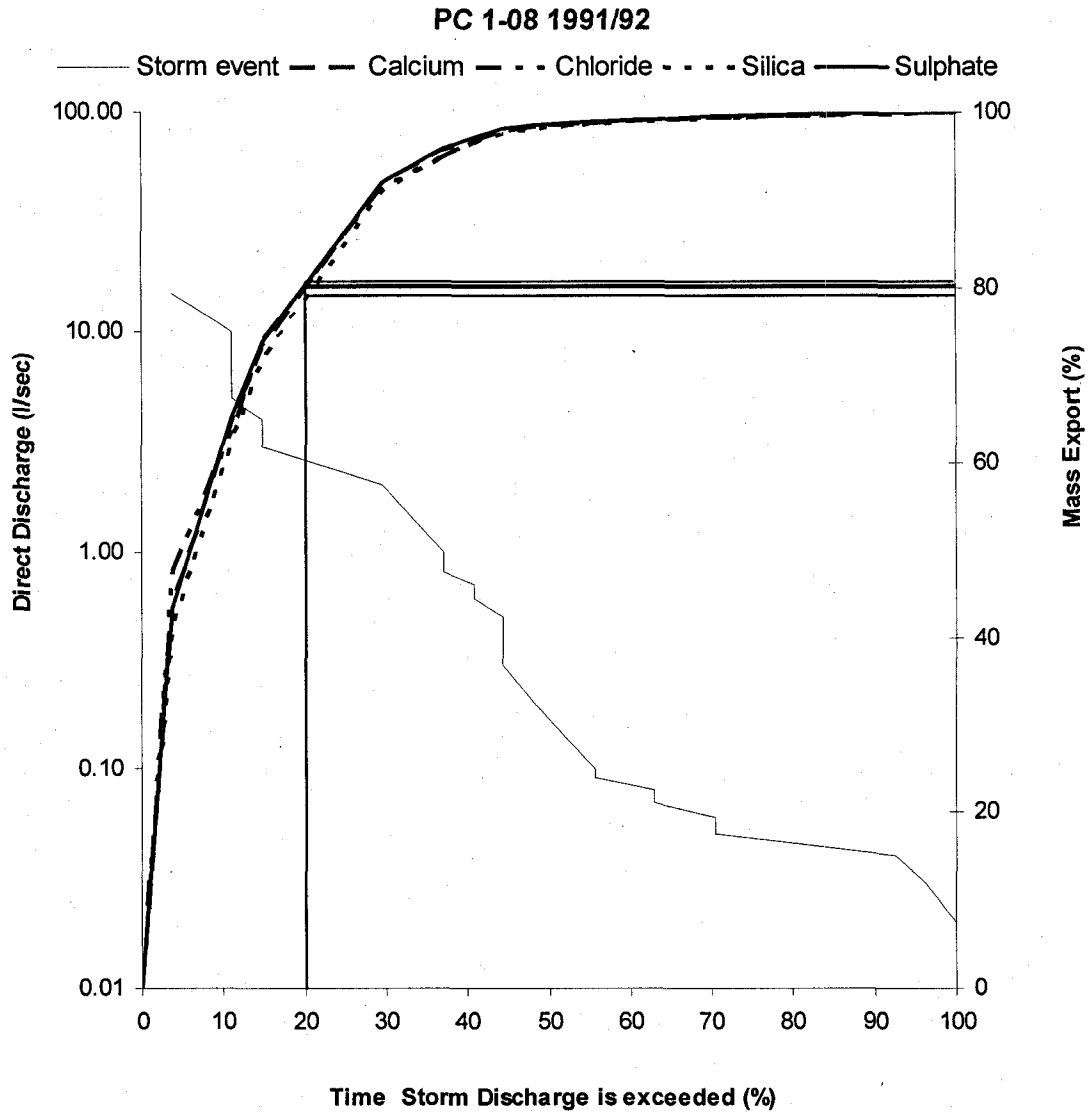
PC 1-08 1991/92

Figure 69: Cumulative mass export in relation to storm discharge occurrence; PC 1-08, 1991/92.

Table 16: PC 1-08; percentage of annual solutes export in relation to storm discharge that is exceeded for 20 % of the time during the course of a year (Figures 66 - 69).

	Calcium (%)	Chloride (%)	Silica (%)	Sulfate (%)
1988/89 (< average)	55	37	56	56
1989/90 (average)	58	52	57	59
1990/91 (wet)	64	52	61	63
1991/92 (dry)	81	81	79	81

The relationship of event discharge and mass export in PC 1-08 shows a similar pattern during the dry year. 20% of the time, event discharge exceeded 3.0 l/sec and delivered approximately 80 % of the annual solute export to the stream (Figure 69, Table 16). In PC 1-08, the quantitative relationship between solute export and storm flow intensifies with discharge that exceeds 20 % of the time in wet years. Event discharge, in 1990/91, that exceeded 20 % of the time and produced more than 5.0 l/sec runoff, accounted for about 60 % of annual calcium, silica, sulfate, and approximately 50 % of chloride export (Figure 68) suggesting that spring melt is the most significant hydrological event in this basin.

5.3 Discussion

In both catchments three hydrochemical seasons can be distinguished: (a) baseflow season, where storm chemistry is largely dictated by groundwater solutes; (b) stormflow season, where stream water chemistry is likely to be comprised of water reacting with vadose zone entering the stream via interflow and shallow water flow pathways; and (c) springflow season, where stream chemistry is largely influenced by

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melting snow (Figures 58 to 61). Further, periods of storm flow can be classified into flushing or diluting episodes. Mass export of solutes is greatest in both catchments during spring season as indicated by the steep slopes of the cumulative percentage graphs. Spring melt quickly connects stream, riparian, and upland regions and stream water chemistry is likely to be controlled by snow water inputs across the basin causing high export rates.

At the beginning of the storm flow season, effects of solute flushing indicated by the abrupt steep increase of slopes of the lines can be observed. The elevated exports during this time may be attributed to high intensity rainfalls resulting in solute flushing effect (Creed and Band, 1998, 1996) after the dry period during summer. Increased runoff effectively leaches solute-rich water of lower and upper soil layers resulting in a pulse/dilution pattern of solutes in stream water. This is consistent with results from Biron et al. (1999), who found that sulfate concentrations in soil lysimeters at a small, forested catchment near Montreal, Quebec were significantly higher during early season events in a dry year compared to a wetter year. They attributed high sulfate concentrations to accumulation of soil solutes during preceding dry periods. With the onset of fall rain, previously dry soils re-wet and flush for the first time after an extended dry period over several months causing high chemical loads in stream water. Similar patterns of higher solute concentrations after dry antecedent conditions have been reported by Dillon et al. (1997); Watmough and Dillon (2003) and Eimers and Dillon (2002), however they are related to increased sulfate release from organic surface soils in catchments without wetlands. As the season progresses, evapotranspiration decreases and soils are thoroughly re-wetted by the end of

November, causing water tables to rise. In HP 4-21 storm flow is now dominated by diluting storms rather than flushing, which is reflected in the gradual increase of the slopes of the lines (Figures 58 and 59). Subsequent storms drain soil horizons that have already been flushed resulting in lower export rates. Although both catchments show an overall similar pattern of mass export, with an abrupt increase of mass export after summer, PC 1-08 has more pronounced changes compared to HP 4-21 due to thinner soils, which are rapidly saturated and generate more runoff per unit precipitation (Figures 60 and 61).

Temporal patterns of solute export are also evident on a storm scale basis. The quantitative relationship of highest storm discharges and solute export varies between dry and wet years and between basins (Figures 62 and 69). During dry years runoff peaks that exceed 20 % of the time have comparatively lower water volume; however, a higher percentage of solutes is delivered to the stream in both basins. This may be related to the absence of midwinter melt or rain-on-snow events, where ions remain stored in the snowpack until they are released during spring melt. Snowpacks act as ionic and nutrient reservoir and hydrological and hydrochemical effect of rain-on-snow events is complex (Semkin et al., 2001, Maclean et al., 1995). The chemical load of rain-on-snow runoff in HP 4-21 has been reported to be influenced by the thermal and hydrophysical properties of the snowpack, which vary with time and the quantity and rate of release of water from the snowpack (Maclean et al., 1995). For the opposite reason, the lower export during wet years in HP 4-21 (Figure 64, Table 15) points to mid-winter melts and rain-on-snow events that released ions from the snowpack and

therefore contributions of spring melt runoff is deprived of solutes or more snowmelt water becomes groundwater.

Solute export in PC 1-08 is higher during wet years than during average years (Figure 68, Table 16). Solute chemistry in PC 1-08 seems controlled by a fast saturation of soils resulting in higher mass exports because only little water can be stored due to the thin till cover in this basin. During the snowmelt period excess water moves through and over the soil/till cover in this basin and hence a larger proportion of the snowmelt water will contribute to flow causing a higher mass export in this basin.

Though the results demonstrate the importance of spring melt on annual mass export, a detailed examination is necessary to determine the processes involved that lead to the temporal differences in export patterns, which is beyond the scope of this study.

Chloride export of the HP 4-21 catchment is generally lower compared to PC 1-08. This is likely due to the deeper tills within the HP 4-21 basin allowing infiltrating water to percolate to deeper soil layers, preventing evapotranspiration processes to concentrate chloride in these layers. In contrast, thin till cover within the PC 1-08 basin result in a shallow groundwater table close to the soil surface allowing evapotranspiration processes to reduce water thereby increasing chloride concentrations. Moreover, the shallow water table causes saturation and flow formation occurs at the soil surface and more of the incoming precipitation translates to runoff, which results in proportionally higher chloride export in PC 1-08.

Generally calcium is released gradually into groundwater and soil water due to weathering processes but was found to have declined over the past two decades in the

Muskoka - Haliburton region (Watmough and Dillon, 2003). The same study observed strong year to year changes in soil solution chemistry including calcium, which was attributed to climatic variations. However, calcium loss was also related to extreme loadings of atmospheric sulfate deposition, which was found to significantly increase calcium leaching. In this study, the calcium ratio is more or less twice as much in the HP 4-21 catchment compared to that of PC 1-08, whereas sulfate ratios are roughly the same between the two catchments supporting evidence of similar atmospheric sulfate deposition. The differing availability of soil calcium may have consequences on the forest health in thinner tilled catchments such as the PC 1-08 basin. The already lower calcium pool within PC 1-08 may be depleted at a faster rate and as a result will limit forest growth due to insufficient amounts of calcium in soils.

Chapter 6

Conclusions and Contributions to Research

6 Conclusions

In this chapter, the main outcomes of the applied approach will be evaluated to determine to what extent they contribute to and improve the current understanding of runoff processes within small forested catchments in the Muskoka-Haliburton region, Ontario, Canada.

The primary objective of this thesis focuses on identifying how physical characteristics of Canadian Shield basins in central Ontario couple with climatic/hydrological antecedent moisture conditions and how temporal variations in discharge result in different solute export patterns. The results of this study also provide insight into the hydrological and hydrochemical relationships within some forested catchments on a broader scale.

One of the main research topics in the literature on streamflow generation processes within forested catchments has been to identify various runoff processes in forest landscapes under varying climatic conditions. Climate variations affect the prevailing hydrological regime in a region. In order to quantify climatic variability and to characterize the hydrological regime at the regional scale, eight small forested catchments were analyzed. Specifically the relationship between precipitation input and streamflow output, coefficient of variation and flow duration curves were assessed (Chapter 2). The purpose of this approach was to identify long and short term spatial

and temporal patterns across basins and to characterize the structure of the climatic and hydrological system in order to delineate baseline data for future comparisons.

Climatic input signals clearly affect the hydrological response of streams within the Muskoka – Haliburton region. In years with little precipitation and above average winter temperatures, storage of water drastically declines and causes dry conditions. Subsequently above average temperatures during the summer months cause streamflow to cease, especially in catchments with little storage capacity. Catchments with thicker till or a sufficiently large wetland exhibit less extreme variability in streamflow in response to changing precipitation inputs and rising temperatures.

Coefficients of variation for annual streamflow were examined. Basins, such as PT 1 and HP 6 with steeper slopes and high drainage density, which lack the presence of surface storage features have less variable annual responses. Basins, such as PC 1 and HP 3A, exhibit more variable annual runoff patterns, on a year to year basis, suggesting that different catchment characteristics greatly influence annual runoff patterns. Flow duration curves from daily discharge were generated to assess the overall range of discharge in the region on an annual and seasonal basis. Seasonal flow duration curves were used as a tool to determine changes of discharge caused by dry and wet periods. Results indicate that the range of discharge in each basin and season is fairly similar suggesting that all basin examined are located within a region that is hydrological homogenous. A slight difference was noted in the summer curve of the PC 1 basin compared to other basins. The difference in shape of the curve was related to the wetland proportion in PC 1, which has a storage effect on runoff causing the curve to be flatter in the mid ranges of discharge.

Standard departure statistics of annual streamflow, precipitation, and temperature for each site were performed in order to compare and contrast climate variables between and within basins. Significant regressions show that discharge of the study basins is more affected by changes in precipitation than in temperature (Figures 11 and 12).

Autocorrelation analysis was performed for monthly precipitation and streamflow in order to understand the variability of the data and to identify if there are any regular or irregular pattern, and if so, to describe and understand the physical causes that lead to the pattern. A clear seasonal pattern in the time series of streamflow in each basin could be identified, which supports the previously made statement that basins located in the Muskoka-Haliburton region show good regional coherence of streamflow patterns.

For this reason, hydrological response pattern were related to basin properties. If sufficiently accurate linkages between basin attributes and hydrological responses can be established then it might be possible to predict streamflow responses in ungauged basins within a region of interest.

A new approach is presented, by applying a new method to separate baseflow from streamflow using a web-based analytical tool (Chapter 3 and 4). Data preparation for current automated hydrograph separation techniques is often time consuming as the use of this technique often requires both model parameterization and regionalization. Further, the reliability of hydrograph separation techniques relies primarily on the assumption that the tracer used can be treated conservatively and concentrations of the different components remain constant during a storm event. This, however, provides

the largest uncertainty in applying this technique. Other common separation techniques are either graphical, which tend to focus on defining the points where baseflow intersects the rising and falling limbs of the quickflow response, or they involve filtering, where data processing of the entire stream hydrograph derives a baseflow hydrograph. Data filtering was used in this study to separate quickflow from stormflow employing the Web version of the WHAT system. Daily stream flow data was formatted to fit the model requirements and were subsequently uploaded to the WHAT server. The WHAT system allows the user to choose among three baseflow separation techniques, one of which was used in this study (Chapter 3). Manual separation of baseflow from stream flow can lead to inconsistencies in the results, while the WHAT system provides consistent repeatable results free of subjective irregularity. The separation of baseflow from stormflow was used to quantify direct runoff and to calculate runoff coefficients.

From there, a new method was developed to quantify antecedent moisture conditions within a catchment (Chapter 3). Average springflow over a 21 year period was used to calculate a standard value to estimate overall wetness within a catchment followed by an analysis of the relationship between precipitation input and basin response under a range of varying antecedent moisture across basins. Antecedent moisture conditions within the basins are defined as a fraction of the mean spring melt flow in percent, which served as a surrogate of antecedent wetness in each basin. With the availability of a large streamflow database, this approach could be used to obtain unique hydrologic responses for each catchment to a range of identical precipitation inputs shown as runoff coefficients (Q/R). A selection of climatic differing years was

chosen to represent the greatest variety of typical climatic conditions. It could be shown that runoff coefficients spatially differ between forested basins and increase with respect to antecedent moisture conditions. Further, a second conclusion that can be drawn from this analysis is that the amount of runoff per unit precipitation differs in each basin and depends on the basin's physical characteristics. Particularly important is the predictive nature of this method to improve understanding of hydrological responses in relation to their precipitation input. The results show that streamflow responses during dry and wet states vary considerably for some basins, such as Harp 3A, 5 and 6; however, they are less variable for Harp 4, which is illustrated by statistically significant relationships (Table 5). All basins show increased runoff coefficients with smaller precipitation inputs on low antecedent moisture conditions, which could point to hydrophobicity of upper soils after dry periods (Turgeon et al., in press, Buttle and Turcotte, 1999).

A matter of debate within the scientific community has also been the question of what runoff processes operate in the Muskoka-Haliburton region, Ontario to deliver water to the stream. Scientists use a number of stream flow mechanisms to explain the rapid delivery of water to the stream such as saturation overland flow (Dunne and Black, 1970), translatory flow (Bishop, 1991), groundwater ridging (Sklash and Farvolden, 1979), and macropore flow (McDonnell, 1990, Buttle and Turcotte, 1999). All of these processes can coexist within a catchment and may vary spatially and temporally at various times as a function of rainfall intensity and duration, and catchment antecedent wetness. Each catchment may be dominated by a particular mechanism, depending on climatic conditions and physical attributes of the catchment.

This study supports the conclusion from a number of previous studies on streamflow generation in forested catchments, for example occurrence of overland flow during drought conditions after rainfall due to reduced infiltration rates (Biron et al., 1999), water transport via preferential flow pathways (Buttle and McDonald, 2000) and the degree of water delivery depending on hillslope – valley coupling (Devito et al., 1996).

Chapter 4 addresses three main aspects of hydrological processes: rainfall input, antecedent moisture conditions, and runoff generation. To determine possible seasonal controls and spatial differences of hydrological responses, hydrometric data from four years with contrasting climatic conditions were used.

Antecedent moisture is characterized by a clear temporal pattern evidenced by the observed moisture deficient periods in summer and to a lesser extent in winter. During the dry periods in summer, runoff events tend to occur as a result of short-duration storms over dry soils and deep water tables causing low runoff coefficients (Chapter 3 and 4). In the case of PC 1-08, summer rainfall events are not sufficient to cause runoff due to bedrock depressions acting as storage reservoirs, which need to be filled first in order to produce runoff (Buttle et al., 2004). PC 1 does not generate runoff because of its wetland proportion, which acts as a reservoir. Also, HP 3A did not produce any runoff during the summer months suggesting that subsurface flow ceased causing the spatial patterns of soil moisture to change. Streamflow of these catchments was controlled by the state of antecedent moisture and the hydrological response showed a clear seasonal pattern. At the end of the dry periods, when evaporation rates drop and storage capacity of soils decline, areas are more likely to become saturated over time, thus generating significant amounts of runoff in some basins. HP 3A, for

example, shows a flashy response indicated by high runoff coefficients. Runoff production in HP 4-21, although elevated during that time, is smaller due to thicker soils, and thus higher water storage capacity, in addition to a deeper water table compared to HP 3A. Further, smaller hydraulic conductivity in deeper soils results in lower runoff coefficients even during wetter conditions as some of the rainfall input will be retained and released only slowly throughout the year. Runoff of PC 1-08 exceeds runoff of PC 1 until the wetland storage capacity is exhausted. As the contributing area expands more runoff is produced in PC 1. Hence, wetlands have a significant effect on hydrological response patterns due to their ability to store water, and as a result exert a time lag effect on runoff production.

The evident seasonal pattern of antecedent moisture may also be influenced by seasonally changing evapotranspiration rates in addition to temporal patterns of precipitation. Precipitation increases during fall but decreases during the summer months; however, statistical analyses indicate a relative similar distribution of rainfall inputs across basins throughout the studied years (Chapter 4).

The temporal pattern of antecedent moisture conditions suggests a significant influence on hydrological processes during the dry period in summer, which starts in mid- June, after spring melt has ceased, and ends between mid and late October, when larger rainfall events refill soil storage and the wet season begins. Governed by the temporal patterns of antecedent moisture conditions, streamflow responses shift between a dry and a wet state and are likely produced by different processes. During the summer months soil surface conditions determine whether runoff is conducted via overland flow or infiltrates and is transmitted via subsurface travel pathways. Whether

macropores are activated to transport water depends on the magnitude and duration of precipitation events as the surrounding soils of macropores must be saturated in order to move water along these flowpaths. In any case, during the dry seasons soils are drained to support baseflow or water is evapotranspired to sustain vegetation, resulting in a water deficit which needs to be refilled before hillslope drainage can occur to the greatest extent. As soils recharge and become more saturated during wetter seasons, water is routed via shallow, more conductive flow paths to the stream producing large runoff coefficients caused by the seasonal effects of higher antecedent moisture conditions within soils. Thus, hydrological response operates on two different time scales: a) event driven during the summer; and b) seasonally driven by the water storage properties of soil.

Chapter 5 considers temporal patterns of stream chemistry in two differing catchments, PC 1-08 and HP 4-21. The varying response of mass export in differing climatic years observed in this study illustrates the importance of high event discharges for the annual exports of these solutes from basins. In dry years, storm discharges in HP 4-21 exceeded 20 % of the time during a year and delivered about 65 % of Cl^-, SO_4^{2-}, SiO_2, and Ca^{2+} to the stream. In PC 1-08 discharge that exceeded 20 % of the time delivered about 80 % of Cl^-, SO_4^{2-}, SiO_2, and Ca^{2+}. During the wet year the proportion of mass export in HP 4-21 decreases with storm volume that exceeds 20 % of the time while export in PC 1-08 increases indicating a shift in HP 4-21 from mainly snowmelt driven export to increased export during high event discharges in fall. These results emphasize the importance of an adequate sampling frequency of chemical data in small basins. Concentrations of many solutes, such as Ca^{2+} and SiO_2, are reported to decrease

with increasing discharge during storms; however, fluxes clearly increase as export patterns are directly related to discharge. It is therefore crucial to develop a sampling strategy which is representative of high export events to reflect the natural variability of chemistry in forested basins.

Considering these results, climate induced shifts such as more intense and infrequent storm events as predicted by future climate scenarios (IPCC, 2001) are likely to alter flow pathways and mass export patterns. In any case, due to increased temperatures evaporation will be higher with drier or wetter climates resulting in decreased runoff and consequently altering flow paths and stream chemistry.

6.1 Outlook and implications

Current understanding of streamflow generation mechanisms is based on extensive field work, numerical as well as physical based models and laboratory experiments. However, many of the runoff mechanisms are still unclear. More data are required to study streamflow generation mechanisms, especially as each catchment delivers rain differently to the stream channel. Building models that adequately simulate real world runoff mechanisms requires large climate and region specific data sets from a significant number of basins in order to compute meaningful hydrologic responses. Current existing hydrological models are based on rather uniformly changing conditions for the movement of water between storage areas. Given the variability of possible flow pathways during an event and the heterogeneity of soils with different capacities to conduct or store water, more detailed information about these hydrological processes have to be acquired to refine existing hydrological models.

Whether a hydrological model qualifies to permit accurate simulations of current hydrological processes is dependent on the usefulness of the simplifications which have been chosen and the purpose of its application. For example, one of the key controls on runoff production as illustrated in this thesis is the antecedent moisture condition prior to a storm. However, the ability to couple this knowledge with the relevant model algorithms still has significant gaps. Mechanisms which have been verified on small scales are transferred into larger scales. Finding an appropriate algorithm to simulate antecedent moisture that occurs on such various scales conditions remains unresolved.

For hydrochemical models, hydrology, although an important signal, is only one of many signals that must be reproduced. The dominant flow path in these models is often treated as vertical flow. For the purpose of simulating stream flow generation using chemical data more detailed information is needed.

Comparison of more than one basin in the same climatic setting in this study has proven to be a useful approach for identifying differences in hydrological responses among basins. To improve current models it is necessary to resolve problems related to scale issues, including measurements, which are sampled less frequently in space than in time (e.g. precipitation is more frequently collected on a time scale than it is spatially).

Finally, as a general remark, although models provide a means to test concepts drawn from the real world system and gain a better understanding of how the catchment hydrological response behaves under different conditions, they are only a best representation of the physical processes known at present defined by a set of parameters reflecting the scientific understanding achieved at that time. Hydrological models are

useful for conceptualizing dominant hydrologic processes operating in a catchment. They help to organize and formulate unresolved problems and assist in testing hypotheses; thus they should be seen as a multi-purpose tool for additional analysis. However, it should be noted that field data are the crucial ingredient for examining hydrological processes in a real world system, and turning hydrological research into a modelling exercise only must be avoided. The combined use of both experimental field measurements and models that simulate processes in the context of what the model aims to predict will improve the understanding of hydrological processes within forested catchments and lead to new insights.

References

Abdul, A.S. & Gillham, R.W. (1984). Laboratory studies of the effects of the capillary fringe on streamflow generation. Water Resources Research, 20, 691-698.

Allan, C.J. & Roulet, N.T. (1994). Runoff generation in zero-order Precambrian Shield Catchments: The stromflow response of a heterogeneous landscape. Hydrological Processes, 8, 369-388.

Aravena, R., Schiff, S.L., Trumbore, S.E., Dillon, P.J. & Elgood, R. (1992) Evaluating dissolved inorganic carbon cycling in a forested lake watershed using carbon isotopes. Radiocarbon 34(3), 636-645

Ball, J. & Trudgill, S. (1995). Overview of Solute Modelling. In: Solute Modelling in Catchment Systems. S.T. Trudgill (Ed.), pp. 2-55.

Bazemore, D.E., Eshleman, K. & Hollenbeck, K.J. (1994). The role of soil water in stormflow generation in a forested headwater catchment:synthesis of natural tracer and hydrometric evidence. Journal of Hydrology 162: 47–75

Beven, K.J. & German, P. (1982). Macropores and Water flow in soils. Water Resources Research, 18, 1311-1325.

Beven, K.J. & Kirkby, M.J. (1979). A physical based, variable contributing area model of basin hydrology. Hydrological Sciences Bulletin, 24, 43-69.

Beven, K.J., Gilman, K. & Newson, M. (1979). Flow and flow routing in upland channel networks. Hydrological Sciences Bulletin, 24, 303-325.

Blöschl, G. and Sivapalan, M. (1997). Process controls on regional flood frequency:

Coefficient of variation and basin scale. Water Resources Research, Vol. 33, No. 12, 2967–2980.

Biron, P.M., Roy, A.G., Courschesne, F., Hendershot, W.H., Cote, B. & Fyles, J. (1999). The effects of antecedent moisture conditions on the relationship of hydrology to hydrochemistry in a small forested watershed. Hydrological Processes, 13, 1541 - 1555.

Bishop, K.H. (1991). Episodic Increases in Stream Acidity, Catchment Flow Pathways and Hydrograph Separation. Jesus College, Cambridge

Bishop, K.H., Grip, H. & O'Neill, A. (1990). The origins of acid runoff in a hillslope during storm events. Journal of Hydrology, 116, 35-61.

Bishop, K.H., Petterson, C., Allard, B. & Lee, Y.-H. (1994). Identification of the riparian sources of aquatic dissolved organic carbon. Environmental International, 20, 11-19.

Bonell, M. (1993). Progress in understanding of runoff generation dynamics in forests. Journal of Hydrology, 150, 217-275.

Bonell, M. (1998). Selected challenges in runoff generation research in forests from the hillslope to headwater drainage basin scale. Journal of the American Water Resources Association, 34, 765-785.

Borwick, J., Buttle J.M. & Ridgway, M.S. (2006). A topographic index approach for identifying groundwater habitat of young-of-year brook trout (Salvelinus fontinalis) in the land-lake ecotone. Can. J. Fish. Aquat. Sci. 63, 239-253.

Bottomley, D.J., Craig, D. & Johnston, L.M. (1984). Neutralization of acid runoff by groundwater discharge to streams in Canadian Precambrian Shield watersheds. Journal of Hydrology, 75, 1-26.

Brammer, D. and J.J. McDonnell (1995). An evolving perceptual model of hillslope hydrology at the Maimai catchment. In. M.G. Anderson, S. Brooks and T. Burt (eds). Advances in Hillslope Hydrology, John Wiley and Sons, pp. 35-60.

Brown, V.A., McDonnell, J.J., Burns, D.A. & Kendall, C. (1999). The role of event water, a rapid shallow flow component. Journal of Hydrology, 217, 171-199.

Burns, D.A., McDonnell, J.J., Hooper, R.P., Peters, N.E., Freer, J.E., Kendall, C. & Beven, K. (2001). Quantifying contributions to strom runoff through end-member mixing analysis and hdrologic measurements at the Panola Mountain Research watershed (Georgia, USA). Hydrological Processes, 15, 1903-1924.

Buttle, J.M. & House, D.A. (1997). Spatial variability of saturated hydraulic conductivity in shallow macroporous soils in a forested basin. Journal of Hydrology, 203, 127-142.

Buttle, J.M. & Leigh, D.G. (1997). The influence of artificial macropores on water and solute transport in laboratory soil columns. Journal of Hydrology, 191, 290-314.

Buttle, J.M. & McDonald, D.J. (2000). Soil macroporosity and infiltration characteristics of forest podzol. Hydrological Processes, 14, 831-848.

Buttle, J.M. & McDonald, D.J. (2002). Coupled vertical and lateral preferential flow on a forested slope. Water Resources Research, 38 (5), 18-1 - 18-16.

Buttle, J.M. & Peters, D.L. (1997). Inferring hydrological processes in a temperate basin using isotopic and geochemical hydrograph separation: a re-evaluation. Hydrological Processes, 11, 557-573.

Buttle, J.M. & Sami, K. (1992). Testing the groundwater ridging hypothesis of streamflow generation during snowmelt in a forested catchment. Journal of Hydrology, 135, 53-72.

Buttle, J.M. & Turcotte, D.S. (1999). Runoff processes on a forested slope on the Canadian Shield. Nord. Hydrol. 30, 1-20.

Buttle, J.M. (1994). Isotope hydrograph separations and rapid delivery of pre-event water from drainage basins. Process in physical Geography, 18, 16-41.

Buttle, J.M. (1998). Fundamentals of Small Catchment Hydrology. In: Isotope tracers in Catchment Hydrology, C. Kendall & J.J. McDonnell (Eds.), 1-5.

Buttle, J.M., Creed, I.F. & Pomeroy, J.W. (2000). Advances in Canadian forest hydrology. Hydrological Processes, 14, 1551-1578.

Buttle, J.M., Dillon, P.J. & Eerkes, G.R. (2004). Hydrologic coupling of slopes, riparian zones and streams: an example from the Canadian Shield. Journal of Hydrology, 287, 161 - 177.

Buttle, J.M., Hazlett, P.W., Murray, C.D., Creed, I.F., Jeffries, D.S., & Semkin, R. (2001). Prediction of groundwater characteristics in forested and harvested basins during spring snowmelt using a topographic index. Hydrological Processes, 15, 3389-3407.

Caine, N. (1989). Hydrograph separation in a small alpine basin based on inorganic solute concentrations. Journal of Hydrology, 112, 89-101.

Calles, U.M. (1984). Deep groundwater contribution to a small stream. Nordic hydrology, 45-54.

Chapman, T.G. (1991). Comment on evaluation of automated techniques for base flow and recession analyses, by RJ Nathan and TA McMahon. Water Resources Research, 27(7), 1783-1784

Choudhury, B.J., Blanchard, B.J. & Richardson, C.W. (1982). A simulation study of the recession coeffcient for antecedent precipitation index. In: International Symposium on Hydrometeorology, A. Ivan & R. A. Clark Johnson (Eds.), 69 - 71.

Christophersen, N., & Neal, C. (1990). Linking hydrological, geochemical and soil chemical processes on the catchment scale: an interplay between modeling and field work. Water Resources Research, 26, 3077-3086.

Christophersen, N., Clair, T.A., Driscoll, C. T., Jeffries, D.S., Neal, C. & Semkin, R. G. (1994). Hydrochemical Studies. In: SCOPE – Biochemistry of Small Catchments, B. Moldan and J. Cerny (Eds.) (1994).

Christophersen, N., Neal, C., Hooper, R.P., Vogt, R.D. & Andersen, S. (1990). Modelling streamwater chemistry as a mixture of soilwater end-members - a step towards second-generation acidification models. Journal of Hydrology, 116, 307-320.

Christophersen, N., Robson, A., Neal, C., Whitehead, P.G., Vigerust, B. & Henriksen, A (1990). Evidence for a long-term deterioration of streamwater chemistry and soil acidification at the Birkenes catchment, southern Norway. Journal of Hydrology, 116, 63-76.

Clarke, R.T. (1994). Rainfall-runoff models. In: Statistical Modelling in Hydrology. R.T. Clarke (Ed.), 1995, 303-351. John Wiley & Sons Ltd.

Creed, I.F. & Band, .LE. (1998). Export of nitrogen from catchments within a temperate forest: evidence for a unifying mechanism regulated by variable source area dynamics. Water Resources Research 34(11), 3079–3093

Dawdy, D.R., and Matalas, N.C., 1964, Statistical and probability analysis of hydrologic data, part III: Analysis of variance, covariance and time series, in Ven Te Chow, ed.,
Handbook of applied hydrology, a compendium of water-resources technology: New York, McGraw-Hill Book Company, p. 8.68-8.90.

Devito, K. & Hill, A.R. (1997). Sulfate dynamics in relation to groundwater surface water interactions in headwater wetlands of the southern Canadian Shield. Hydrological Processes, 11, 485-500.

Devito, K. (1995). Sulfate mass balances of Precambrian Shield wetlands: the influence of catchment hydrogeology. Can.J.Fish.Aquat.Sci., 52, 1750-1760.

Devito, K., Hill, A.R. & Dillon, P.J. (1999). Episodic sulfate export from wetlands in acidified headwater catchments: prediction at the landscape scale. Biogeochemistry, 44, 187-203.

Devito, K.J. & Dillon, P.J. (1993). The influence of hydrologic conditions and peat oxia on the phosphorus and nitrogen dynamics of a conifer swamp. Water Resources Research 29, 2675-2685.

Devito, K.J., Hill, A.R. & Roulet, N. (1996). Groundwater-surface water interactions in headwater forested wetlands of the Canadian Shield. Journal of Hydrology 181: 127–147

DeWalle, D.R., Swistock, B.R. & Sharpe, W.E. (1988). Three-component tracer model for stormflow on a small Appalachian forested catchment. Journal of Hydrology, 104, 301-310.

Dillon, P.J. & Molot, L.A. (1997) Dissolved organic and inorganic carbon mass balances in central Ontario lakes. Biogeochem. 36, 29–42

Dillon, P.J., Molot, L.A. & Scheider, W.A. (1991). Phosphorous and nitrogen export from forested stream catchments in central Ontario. J. Environ. Qual. 20, 857-864.

Dunne, T. & Black, R.D. (1970). An experiment investigation of runoff production in permeable soils. Water Resources Research, 6, 478-490.

Dunne, T. & Black, R.D. (1970). Partial area contributions to storm runoff in a small New England watershed. Water Resources Research, 6, 1296-1311.

Dunne, T. & Leopold, L.B. (1978). Water in Environmental Planning. Freeman, New York, 818 p.

Dunne, T., Moore, T.R. & Taylor, C.H. (1975). Recognition and Prediction of runoff - Producing Zones in Humid Regions. Hydrological Sciences Bulletin, 305-326.

Easthouse, K.B., Mulder, J., Christophersen, N. & Seip, H.M. (1992). Dissolved organic carbonfractions in soil and stream water during variable hydrological conditions at Birkenes, South Norway. Water Resour. Res. 28(6), 1585–1596

Eckhardt, K. (2005). How to construct recursive digital filters for baseflow separation. Hydrological Processes, 19, 507-515.

Eimers, M.C., Dillon, P.J., Schiff, S.L. (2004). Sulphate Flux from an Upland Forested Catchment in South-Central Ontario, Canada. Water, Air & Soil Pollution, 152, 3-21.

Eimers, M.C., Dillon, P.J., Schiff, S.L. & Jeffries, D.S. (2003). The effects of drying and re-wetting and increased temperature on sulfaterelease from upland and wetland material, Soil Biol. Biochem., 35, 1663.

Eimers, M.C., Dillon, P.J. (2002). Climate effects on sulfate flux from forested catchments in south-central Ontario. Biogeochemistry 61, 337-355.

Elsenbeer, H., West, A. & Bonell, M. (1994). Hydrologic pathways and storm flow hydrochemistry at South Creek, north-east Queensland. Journal of Hydrology, 162, 1-21

Evans, C. & Davies, T.D. (1998). Causes of concentration/discharge hysteresis and its potential as a tool for analysis of episode hydrochemistry.

Genereux, D. (1998). Quantifying uncertainty in tracer-based hydrograph separations. Water Resources Research, 34, 915-919.

Gillham, R.W. & Jayatilaka, C.J. (1998). Response to Comment by Jeffrey J. McDonnell and James M. Buttle on A deterministic-empirical model of the effect of the capillary-fringe on near-stream area runoff. 1. Description of the model (Journal of Hydrology Vol. 184 (1996) 299-315). Journal of Hydrology, 207, 286-289.

Gillham, R.W. (1984). The capillary fringe and its effect on water-table response. Journal of Hydrology, 67, 307-324.

Grayson, R.B., Moore, I.D. & McMahon, T.A. (1992). Physically Based Hydrologic Modeling 2. Is the concept realistic? Water Resources Research, 26, 2659-2666.

Grayson, R.B., Western, A.W. & Chiew, F.H.S. (1997). Preferred states in spatial soil moisture patterns: Local and non-local controls. Water Resources Research, 33(12), 2897 - 2908.

Gregory, K.J. & Walling, D.E. (1973). Drainage Basin Form and Process, Arnold, London, 458 p.

Hansen, J., R. Ruedy, M. Sato & R. Reynolds (1996) Global surface air temperature in 1995: Return to pre-Pinatubo level. Geophys. Research Letters 23, 1665-1668.

Hauhs, M. (1987). The relation between water flowpaths in the soil and runoff chemistry at Risdalsheia, a small headwater catchment in Southern Norway (RAIN Project). In: SCOPE – Biochemistry of Small Catchments. B. Moldan and J. Cerny (Eds.), 1994

Hewlett, J.D. & Hibbert, A.R. (1964). Factors affecting the response of small watersheds to precipitation in humid areas. In: Forest Hydrology, W.E. Sopper & H.W. Lull (Eds.), 1967, 275-29.

Hill, T. & Neal, C. (1997). Spatial and temporal variation in pH, alkalinity and conductivity in surface runoff and groundwater for the Upper River Severn catchment. Hydrology and Earth System Sciences, 1, 697-715.

Hinton, M.J. (1998). The role of groundwater flow in streamflow generation within two small forested watersheds of the Canadian Shield. University of Waterloo; PhD thesis.

Hinton, M.J., Schiff, S.L. & English, M.C. (1993). Physical properties governing groundwater flow in a glacial till catchment. Journal of Hydrology, 142, 229-249.

Hinton, M.J., Schiff, S.L. & English, M.C. (1994). Examining the contributions of glacial till water to strom runoff using two- and three-component hydrograph separartions. Water Resources Research, 30, 983-993.

Hinton, M.J., Schiff, S.L. & English, M.C. (1997). The significance of storms for the concentration and export of dissolved organic carbon from two Precambrian Shield catchments. Biogeochemistry 36(1), 67-88.

Hinton, M.J., Schiff, S.L. & English, M.C. (1998). Sources and flowpaths of dissolved organic carbon during storms in two forested watersheds of the Precambrian Shield. Biogeochemistry, 41, 175-197.

Hoeg, S. & Uhlenbrook, S. (2000). Hydrograph separation in a mountainous catchment - combining hydrochemical and isotope tracers. Hydrological Processes, 14, 1199-1216.

Hooper, R.P. & Shoemaker, C. (1985). Aluminum mobilization in an acidic headwater stream: temporal variation and mineral dissolution disequilibria. Science, 229, 463-465

Hooper, R.P. & Shoemaker, C.A. (1986). A comparison of chemical and isotopic hydrograph separation. Water Resources Research, 22, 1444-1454.

Hooper, R.P. (2001). Applying the scientific method to small catchment studies: A review of the Panola Mountain experience. Hydrologcial Processess, 15, 2039-2050.

Hooper, R.P., Christopersen, N. & Peters, N.E. (1990). Modelling streamwater chemistry as a mixture of soilwater end-members - an application to the Panola mountain catchments, Georgia, U.S.A. Journal of Hydrology, 116, 321-343.

Hornberger, G.M. & McKnight, D.M. (1994). Hydrological controls on dissolved organic carbon during snowmelt in the Snake River near Montezuma, Colorado. Biogeochemistry, 25, 147-165.

Hornberger, G.M., Scanlon, T.M. & Raffensperger, J.P. (2001). Modelling transport of dissolved silica in a forested headwater catchment: the effect of hydrological ad chemical time scales on hysteresis in the concentration-discharge relationship. Hydrological Processes, 15, 2029-2038.

Horton, R. (1933). The role of infiltration in the hydrologic cycle. Transactions of the American Geophysical Union, 14, 446-460.

Huth, A. K., Conklin, M. H., Brooks, P. D., Bales, R. C., Grimm, N. B., Haas, P. A., & Petti, J.R.. Hydrology and solute transport during floods in a semi-arid stream. In review.

IPCC, 2001: Climate Change 2001: The Scientific Basis. J.T. Houghton et al. (eds.), *Cambridge University Press,* 881pp.

Jacobs, J., Myers, D.A. & Whitfield, B.M. (2003). Improved rainfall/runoff estimates using remotely sensed soil moisture1. Journal of the American Water Resources Association, Apr. 2003.

Jeffries, D.S. & Snyder, W.R. (1983). Geology and geochemistry of the Muskoka-Haliburton study area. Data Report DR 83/2. Dorset Research Centre, Dorset, Ont..

Jeffries, D.S., Semkin, R.G., Neureuther, R. & Seymour, M. (1988). Ion mass budgets for lakes in the Turkey Lakes Watershed, June 1981-May 1983. Can. J. Fish. Aquat. Sci., 45, (Suppl. 1), 47-58.

Jenkins, A., Cosby, B.J., Ferrier, R.C., Walker, T.A.B. & Miller, J.D. (1990). Modelling stream acidification in afforested catchments: an assessment of the relative effects of acid deposition and afforestation. Journal of Hydrology, 120, 163–181.

Jenkins, A., Ferrier, R.C., Harriman, R. & Ogungkoya, Y.O. (1994). A case study in hydrochemistry: conflicting interpretations from hydrological and chemical observations. Hydrological Processes, 8, 335-349.

Jenkins, A., Kämäri, J., Norton, S. A., Whitehead, E, Cosby B. J. & Brakke, D. F. (1989). 'Models to describe the Geographic Extent and Time Evolution of Acidification and Air Pollution Damage', in Kämäri, J., Brakke, D. F., Jenkins, A., Norton S. A., and Wright, R. F. (eds.), Regional Acidification Models, Springer-Verlag, Berlin, Heidelberg, pp. 113-128.

Jenkins, A., Peters, N.E. & Rodhe, A. (1994). Hydrology. In: SCOPE – Biochemistry of Small Catchments. B. Moldan and J. Cerny (Eds.), 1994.

Johnson, N.M., Likens,G.E., Bormann, F.H. and Pierce, R.S. (1968) Rate of chemical weathering of silicate minerals in New Hampshire. Geochim. Cosmochim. Acta 32: 531-545.

Johnston, C.D. (1987) Distribution of environmental chloride in relation to subsurface hydrology. J. Hydrol. 94: 67-88. In: SCOPE – Biochemistry of Small Catchments. Chapter 9: Hydrological Processes. B. Moldan and J. Cerny (Eds.), 1994.

Jones, J. (2000). Hydrologic processes and peak discharge response to forest removal, regrowth, and roads in 10 small experimental basins, western Cascades, Oregon. Water Resources Research, 36 (9), 2621-2642.

Kendall, C. & Caldwell, E.A. (1998). Fundamentals of Isotope Geochemistry. In: Isotope tracers in Catchment Hydrology. C. Kendall & J.J. McDonnell (Eds.), 51-86.

Kendall, C. (1990). Isotope tracers of water and solute sources in catchments. In: Solute Modeling in catchment systems, 262-297.

Kendall, K.A., Shanley, J.B. & McDonnell, J.J. (1999). A hydrometric and geochemical approach to test the transmissivity feedback hypothesis during snowmelt. Journal of Hydrology, 219, 188 -205.

Kennedy, V.C., Kendall, C., Zellweger, G.W., Wyerman, T.A. & Avanzino, R.J. (1986). Determination of the components of stormflow using water chemistry and environmental isotopes, Mattole River Basin, California. Journal of Hydrology, 84, 107-140.

Kirkwood, S.E. & Nesbitt, H.W. (1991). Formation and evolution of soils from an acidified watershed: Plastic Lake, Ontario, Canada. Geochimica et Cosmochimica Acta, 55, 1295 - 1308.

Kohler, M.A. & Linsley, R.K. (1951). Predicting the runoff from storm rainfall. US Weather Bur Res Pap 34, Washington, DC.

LaZerte, B. & Scott, L. (1996). Soil water leachate from two forested catchments on the Precambrian Shield, Ontario. Can. J. For. Res. 26, 1353–1365

LaZerte, B. (1993). The impact of drought and acidification on the chemical exports from a minerotrophic conifer swamp. Biogeochemistry 18, 153-175.

Likens, G.E., Bormann, F.H., Pierce, R.S., Eaton, J.S. & Johnson, N.M. (1977). Biogeochemistry of a Forested Ecosystem. Springer-Verlag, New York, 146 pp.

Lim, K. J., Engel, B. A., Tang, Z., Choi, J., Kim, K., Muthukrishnan, S. & Tripathy, D. (2005). Automated Web GIS based hydrograph analysis tool, WHAT. Journal of the American Water Resources Association **41** (6), 1407-1416.

Linsley, R.K., Kohler, M.A. & Paulus, J.L.H. (1982). Hydrology for Engineers 3rd Ed. McGraw-Hill, New York, 508 p.

Lynch, J. A., Corbett, E. S., and Sopper, W. E.: Effects of antecedent soil moisture on stormflow volumes and timing, in: Proc. 3rd Int.Symp. in Hydrology (Colorado State University, Fort Collins, Colorado, USA), 89–99. Water Resources Publications, Colorado, USA, 1979.

Lynch, J.A. & Corbett, E.S. (1982). Relationship of antecedent flow rate to storm hydrograph components. In: International Symposium on Hydrometeorology, A. Ivan & R. A. Clark Johnson (Eds.), 73 - 77.

Lyne, V. & Hollick, M. (1979). Stochastic time-variable rainfall-runoff modelling. Institute of Engineers Australia National Conference. Publ. 79/10, 89-93.

MacLean, R.A., English, M.C. & Schiff, S.L. (1995). Hydrological and hydrochemical response of a small Canadian Shield catchment to late winter rain-on-snow events. Hydrological Processes 9, 845–863

Macrae, M.L., English, M.C., Schiff, S.L., & Stone, M.A. Temporal patterns of nutrient export from a first-order agricultural basin in Southern Ontario. Elements (Canadian Geophysical Union), June 2003.

Maule, C.P. & Stein, J. (1990). Hydrologic flow path definition and partitioning of spring meltwater. Water Resources Research, 26, 2959-2970.

McDonnell, J.J. & Taylor, C.H. (1987). Surface and subsurface water contributions during snowmelt in a small Precambrian Shield watershed, Muskoka, Ontario. Atmosphere-Ocean 25, 251-266.

McDonnell, J.J. (1990). A rationale for Old Water Discharge Through Macropores in a Steep, Humid Catchment. Water Resources Research, 26, 2821-2832.

McDonnell, J.J., Bonell, M., Stewart, M.K. & Pearce, A.J. (1990). Deuterium variations in storm rainfall: Implications for stream hydrograph separation. Water Resources Research, 26, 455-458.

McDonnell, J.J., D. Brammer, C. Kendall, N. Hjerdt, L. Rowe, M. Stewart and R. Woods 1998. Flow pathways on steep forested hillslopes: The tracer, tensiometer and trough approach, In Tani et al., (eds). Environmental Forest Science, Kluwer Academic Publishers, pp. 463-474.

McDonnell, J.J., Stewart, M.K. & Owens, I.F. (1991). Effect of catchment-scale subsurfacing mixing on stream isotope response. Water Resources Research, 27, 3065-3073.

McPhaden, M.J., 2002: El Niño and La Niña: Causes and Global Consequences. In: Encyclopedia of Global Environmental Change, Vol 1, John Wiley and Sons, Ltd., Chicester, UK, 353-370.

Moore, I.D., Coltharp, G.B. & Sloan, P.G. (1983). Predicting runoff from small Appalachian Watersheds. Trans.Ky.Acad.Sci., 44, 135-145.

Moore, R.D. (1989). Tracing runoff sources with deuterium and oxygen-18 during spring melt in a headwater catchment, Southern Laurentians, Quebec. Journal of Hydrology, 112, 135-148.

Mosley, M.P. (1979). Streamflow generation in a forested watershed, New Zealand. Water Resources Research, 15, 795-806.

Mosley, M.P. (1982). Subsurface flow velocities through selected forest soils, south island, New Zealand. Journal of Hydrology, 55, 65-92.

Mulder, J., Christophersen, N., Hauhs, M., Vogt, R.D., Andersen, S. & Andersen, D.O. (1990). Water flow paths and hydrochemical controls in the Birkenes catchment as inferred from a rainstorm high in seasalts. Water Resources Research, 26, 611-622.

Mulholland, P.J., Best, R., Coutant, C.C., Hornberger, G.M., Meyer, J.L., Robinson, P.J., Stenberg, J.R., Turner, R. E., Vera-Herrera, F. & Wetzel, R.G. (1997). Effects of climate change on freshwater ecosystems of south-eastern United States and the Gulf Coast of Mexico. Hydrological Processes, 11, 949 - 970.

Mulholland, P.J., Wilson, G.V. & Jardine, P.M. (1990). Hydrogeochemical response of a forested watershed to storms: effects of preferential flow along shallow and deep flow paths. Water Resources Research 26(12), 3021–3026.

Murray, C.D. & Buttle, J.M. (2005). Infiltration and soil water mixing on forested and harvested slopes during spring snowmelt, Turkey Lakes Watershed, central Ontario. Journal of Hydrology, 306, 1-20.

Nathan, R.J. & McMahon, T.A. (1990). Evalutation of automated techniques for base flow and recession analyses. Water Resources Research, 26(7), 1465 -1473.

McNamara, J. P., Chandler, D., Seyfried, M. & Shiva Achet (in press). Soil moisture states, lateral flow, and streamflow generation in a semi-arid, snowmelt-driven catchment. Hydrological Processes. (in press).

Neal, C., Hill, T., Hill, S. & Reynolds, B. (1997). Acid neutralization capacity measurements in surface and ground waters in the Upper River Severn, Plynlimon: from hydrograph splitting to water flow pathways. Hydrology and Earth System Sciences, 3, 687-696.

Neal, C., Robson, A.J. & Smith, C.J. (1990). Acid neutralization capacity variations for the Hafren Forest Stream, Mid-Wales: inferences for hydrological processes. Journal of Hydrology, 121, 85-101.

Novakowski, K.S. & Gillham, R.W. (1988). Field investigations of the nature of water-table response to precipitation in shallow water-table environments. Journal of Hydrology, 97, 23-32.

Ogungkoya, Y.O. & Jenkins. (1993). Analysis of storm hydrograph and flow pathways using a three-component hydrograph separation model. Journal of Hydrology, 142, 71-88.

Pearce, A.J., Stewart, M.K. & Sklash, M.G. (1986). Strom runoff generation in humid headwater catchments. 1. Where does the water come from? Water Resources Research, 22, 1263-1272.

Peters, D.L., Buttle, J.M., Taylor, C.H. & LaZerte, B.D. (1995). Runoff production in a forested, shallow soil, Canadian Shield basin. Water Resources Research, 31, 1291-1304.

Peters, N.E. & Ratcliff, E.B. (1998). Tracing Hydrologic Pathways using chloride at the Panola Mountain Research Watershed, Georgia, USA. Water, Air, and Soil Pollution, 105, 263-275.

Peters, N.E. (1994). Hydrologic Processes. In: SCOPE – Biochemistry of Small Catchments. B. Moldan and J. Cerny (Eds.), 1994.

Pionke, H.B., Gburek, W.J. & Folmar, G.J. (1993). Quantifying stormflow components in a Pennsylvania watershed when ^{18}O and storm conditions vary. Journal of Hydrology 148, 169–187.

Post, W.M., Izzaurralde, R.C., Mann, L.K. & Bliss, N. (2001). Monitoring and verifying changes of organic carbon in soil. Climatic Change, 51, 73-99.

Ponce, V. M. & Hawkins, R. H. (1996). Runoff curve number: Has it reached maturity? Journal of Hydrologic Engineering, ASCE, 1(1), 11-19.

Quinn, P.F., Beven, K.J., Chevallier, P. & Planchon, O. (1991). The prediction of hillslope flow paths for distributed hydrological modelling using digital terrain models. Hydrological Processes, 5, 59-79.

Rice, K.C. & Hornberger, G.M. (1998). Comparison of hydrochemical tracers to estimate source contributions to peak flow in a small, forested, headwater catchment. Water Resources Research, 34, 1755-1766.

Robson, A.J. & Neal, C. (1990). Hydrograph separation using chemical techniques: an application to catchments in Mid-Wales. Journal of Hydrology, 116, 345-363.

Robson, A.J. & Neal, C. (1997). Linking Mixing Techniques to a Hydrological Framework - An Upland Application. In: Solute Modelling in Catchment Systems, S.T. Trudgill (Ed.), 347-367.

Robson, A.J., Beven, K.J. & Neal, C. (1992). Towards identifying sources of subsurface flow: a comparison of components identified by a physically based runoff model and those determined by chemical mixing techniques. Hydrological Processes, 6, 199-214.

Robson, A.J., Neal, C. & Christophersen, N. (1997). Towards coupling hydrological, soil and weathering processes within a modelling perspective. In: Geochemical Processes, Weathering and Groundwater Recharge in Catchments, O.M. Saether & P. de Caritat (Eds.), 329-379.

Robson, A.J., Neal, C., Smith, C.J. & Hill, S. (1992). Short term variations in rain and stream water conductivity at a forested site in mid Wales-implications for water movement. Science of the Total Environment, 119, 1-18.

Rodhe, A. & Killingtveit, A. (1997). Catchment Hydrology. In: O.M. Saether & P. de Caritat (Eds.), Recharge in Catchments. (pp. 77-108). A.A. Balkema.

Rodhe, A. (1981). Spring flood meltwater or groundwater? Nordic hydrology, 12, 21-30.

Rodhe, A. (1998). Snowmelt-Dominated Systems. In: Isotope tracers in Catchment Hydrology, C. Kendall & J.J. McDonnell (Eds.), 391-434

Ross D.S., Bartlett R.J., Magdo? F.R. & Walsh G.J. (1994). Flow path studies in forested watersheds of headwater tributaries of Brush Brook, Vermont. Water Resources Research 30(9), 2611–2618.

Scanlon, T.M., Raffensperger, J.P. & Hornberger, G.M. (2001). Modeling transport of dissolved silica in a forested headwater catchment: Implications for defining the hydrochemical response of observed flow pathways. Water Resources Research, 37, 1071-1082.

Scheider W.A., Cox, C.M. & Scott, L.D. (1983). Hydrological data for lakes and watersheds in the Muskoka-Haliburton study area (1976-1980). Ontario Ministry of the Environment, Dorset, Ontario.

Scheider W.A., Jeffries, D.S. & Dillon. P.J. (1979). Effects of acidic precipitation on Precambrian freshwaters in southern Ontario. J. Great Lakes Res. 5, 45-51.

Scheider W.A., Moss, J.J. & Dillon, P.J. (1979). Measurement and uses of hydraulic and nutrient budgets. US EPA 440/5-79-001, Washington, DC.

Schiff, S.L., Devito, K.J., Elgood, R.J., McCrindle, P.M., Spoelstra, J., Dillon, P. (2002). Two adjacent catchments: dramatically different nitrate export. Water Resour. Res. 38, 1278-1292

Schiff, S.L., Aravena, R., Mewhinney, E., Elgood, R., Warner, B. & Trumbore, S. (1998). Precambrian Shield wetlands: hydrologic control of the sources and export of dissolved organic matter. Climatic change, 40, 167-188.

Schiff, S.L., Aravena, R., Trumbore, S.E. & Dillon, P.J. (1990). Dissolved organic carbon cycling in forested watersheds: a carbon cycle approach. Water Resources Research, 26, 2949–2957

Schiff, S.L., Aravena, R., Trumbore, S.E., Hinton, M.J., Elgood, R. & Dillon, P.J. (1997). Export of DOC from forested catchments on the Precambrian Shield of Central Ontario: Clues from 13C and 14C. Biogeochem. 36, 43–65

Searcy, J.K. (1959) Flow duration curves-Manual of hydrology, Part 2. Low flow techniques. US Geological Survey Water Supply Paper 1542-A.

Semkin, R.G., Jeffries, D.S. & Clair, T.C. (1994). Hydrochemical Method and Relationships for Study of Stream Output from Small Catchment. In: SCOPE – Biochemistry of Small Catchments. B. Moldan and J. Cerny (Eds.), 1994.

Shaman, J., Stieglitz. M. & Burns, D. (2004). Are big basins just the sum of small catchments? Hydrological Processes, 19, 3195-3206.

Shanley, J.B., Kendall, C., Smith, T.E., Wolock, D.M. & McDonnell, J.J. (2002). Controls on old and new water contributions to stream flow at some nested catchments in Vermont, USA. Hydrological Processes, 16, 589-609.

Sidle, R.C., Tsuboyama, Y., Noguchi, S., Hosoda, I., Fujieda, M. & Shimizu, T. (2000). Stormflow generation in steep forested headwaters: a linked hydrogeomorphic paradigm. Hydrological Processes, 14, 369 - 385.

Sidle, R.C., Tsuboyama, Y., Noguchi, S., Hosoda, I., Fujieda, M. & Shimizu, T. (1995). Seasonal hydrologic response at various spatial scales in a small forested catchment, Hitachi Ohta, Japan. Journal of Hydrology, 168, 227-250.

Singh, V.P. (1989). Hydrologic Systems Vol 11: Watershed Modeling. Prentice Hall.

Singh, P., Huebl, H. & Weinmeister, H.W. (2000). Use of the recession characteristics of snowmelt hydrographs in the assessment of snow water storage in a basin. Hydrological Processes, 14, 91-101.

Sklash, M.G. & Farvolden, R.N. (1979). The role of groundwater in storm runoff. Journal of Hydrology, 43, 45-65.

Sklash, M.G. (1990). Environmental isotope studies of storm and snowmelt runoff generation. In: Process in hillslope hydrology, M.G. Anderson & T.P. Burt (Eds.), 401-436.

Sklash, M.G., Farvolden, R.N. & Fritz, P. (1976). A conceptual model of watershed response to rainfall, developed through the use of oxygen-18 as a natural tracer. Canadian Journal of Earth Sciences,

Sklash, M.G., Stewart, M.K. & Pearce.A.J. (1986). Storm runoff generation in humid headwater Catchments 2. A case study of Hillslope and low -Order stream response. Water Resources Research, 22, 1273-1282.

Soulsby, C. (1995). Contrast in storm event hydrochemistry in an acidic afforested catchment in upland Wales. Journal of Hydrology, 170, 159-179.

Stieglitz, M., Shaman, J., McNamara, J., Engel, V., Shanley, J. & Kling, G. W. (2003). An approach to understanding hydrologic connectivity on the hillslope and the implications for nutrient transport. Global Biochemical Cycles, 17 (4), 16-1 - 16-15.

Sullivan, T.J., Christophersen, N., Muniz, I.P. Seip, H.M. & Sullivan, P.D. (1986). Aqueous aluminum chemistry response to episodic increases in discharge. Nature 323, 324-327.

Swistock, B.R., DeWalle, D.R. & Sharpe, W.E. (1989). Sources of acidic storm flow in an Appalachian headwater stream. Water Resources Research, 25(10), 2139-2147

Trudgill, S.T., Pickles, A.M., Burt, T.P. & Crabtree, R.W. (1981). Nitrate losses in soil drainage waters in relation to water flow rate on a deciduous woodland site. Journal of Soil Science, 32, 433-441.

Tsuboyama, Y., Sidle, R.C., Noguchi, S. & Hosoda, I. (1994). Flow and solute transport through the soil matrix and macropores of a hillslope segment. Water Resources Research, 30, 879-890.

Tsujimura, M. Onda, Y. & Ito, J. (2001). Stream water chemistry in a steep headwater basin with high relief. Hydrological Processes, 15, 1847 - 1858.

Turner, J.V., Macpherson, D.K. & Stokes, R.A. (1987). The mechanisms of catchment flow processes using natural variations in deuterium and oxygen-18. Journal of Hydrology, 94, 143-162.

Uchida, T., Kosugi, K., and Mizuyama, T.: Runoff characteristics of pipeflow and effects of pipeflow on rainfall-runoff phenomena in a mountainous watershed, J. Hydrol., 222, 18–36, 1999.

Vanni, M. J., Renwick, W.H., Headworth, J.L., Auch, J.D. & Schaus, M. H. (2001). Dissolved and particulate nutrient flux from three adjacent agricultural watersheds: A five-year study. Biogeochemistry, 54, 85-114.

Waddington, J.M. & Roulet, N.T. (1993). Runoff mechanisms in a forested groundwater discharge wetland. Journal of Hydrology, 147, 37-60.

Walling, D.E. & Webb, B. W. (1986). Solutes in river systems. In Trudgill, S. T. (Ed.): Solute Processes. Wiley-Interscience, pp. 251-327.

Ward, R.C. (1984). On the response to precipitation of headwater streams in humid areas. Journal of Hydrology, 74, 171-189.

Warfvinge, P. (1995). Basic Principles of Frequently Used Models. In: Solute Modelling in Catchment Systems, S.T. Trudgill (Ed.), 57-72.

Watmough, S.A. & Dillon, P.J. (2001). Base cation losses from a coniferous catchment in central Ontario, Canada. Wat. Air Soil Pollut. Focus. 1, 507-524.

Watmough, S.A. & Dillon, P.J. (2003). Base cation and nitrogen budgets for seven forested catchments in central Ontario, 1983-1999. Forest Ecology and Management 177, 155-177.

Wels, C., Cornett, R.J. & LaZerte, B.D. (1990). Groundwater and wetland contributions to stream acidification: an isotopic analysis. Water Resources Research 26, 2993-3003.

Wels, Ch., Taylor, C.H., Cornett, R.J. & LaZerte, B.D. (1991). Streamflow generation in a headwater basin on the Precambrian Shield. Hydrological Processes, 5, 185-199.

Welsh, D.L., Kroll, C.N., McDonnell & Burns, D.A. (2001). Topographic controls on the chemistry of subsurface stormflow. Hydrological Processes, 15, 1925-1938.

Whipkey, R. Z.: Subsurface stormflow from forested slopes, Bull. International Association Scientific Hydrology, 10, 74–85, 1967.

Whitehead, P.G. (1995). The MAGIC model approach to assessing environmental impacts of land-use change and atmospheric pollution. In: Solute Modelling in catchment systems, S.T. Trudgill (Ed.), 371-386.

Williamson, D. R., Stokes, R. A. and Ruprecht, J. K. (1987) Response of input and output of water and chloride to clearing for agriculture. *J. Hydrol.* 94: 1-28. In: SCOPE – Biochemistry of Small Catchments. B. Moldan and J. Cerny (Eds.), 1994.

Wilson, G.V., Jardine, R.J., Luxmoore, R.J., Zelazny, L.W., Lietzke, D.A. & Todd, D.E. (1991). Hydrogeochemical processes controlling subsurface transport from an upper subcatchment of Walker Branch Watershed during strom events. 1. Hydrologic Transport Processes. Journal of Hydrology, 123, 297-316.

Winter, T. C. & Woo, M.-K. (1990). Hydrology of lakes and wetlands. Pp. 159–187 In: The geology of North America. Vol. 0-1. Surface water hydrology. M. G. Wolman and H. C. Riggs (eds.). Boulder, CO: The Geologic Society of America

Wolock, D.M. (1993). Simulating the variable-source-area concept of streamflow generation with the watershed model TOPMODEL. U.S.Geological Survey. Report 93-4124

Wood, E.F., Sivapalan, M. & Beven. K. (1990). Similarity and scale in catchment storm response. Rev. Geophys. 28, 1–18

Wood, E.F., Sivapalan, M., Beven, K. & Band, L. (1988). Effects of spatial variability and scale with implications to hydrologic modelling. Journal of Hydrology 102, 29-47.

Woods, R. & Sivapalan, M. (1995). Investigating the representative elementary area concept: an approach based on field data. Hydrological Processes, 9, 291-312.

Appendix 1

Statistical calculations

Table A1: F-Test Two-Sample for variances of precipitation

	PC 86/87	HP 86/87	PC 88/89	HP 88/89	PC 89/90	HP 89/90	PC 90/91	HP 90/91	PC 91/92	HP 91/92
Mean	19.09	19.36	17.94	16.03	16.13	17.58	19.04	20.72	19.31	16.39
Variance	229.67	159.42	211.33	130.82	233.73	208.05	260.34	207.65	347.34	284.77
Observations	48	47	33	41	53	46	48	45	29	32
df	47	46	32	40	52	45	47	44	28	31
F	1.44		1.62		1.12		1.25		1.22	
P(F<=f) one-	0.11		0.08		0.35		0.23		0.29	
F Critical	1.63		1.73		1.62		1.64		1.84	

	HP 92/93	PC 92/93	HP 93/94	PC 93/94	HP 95/96	PC 95/96	PC 96/97	HP 96/97	PC 97/98	HP 97/98
Mean	25.80	29.06	18.00	19.84	22.62	21.66	23.13	22.10	15.84	14.85
Variance	479.67	473.88	226.18	130.11	365.37	313.38	386.14	283.57	286.97	254.81
Observations	27	32	39	36	54	50	49	52	47	48
df	26	31	38	35	53	49	48	51	46	47
F	1.01		1.74		1.17		1.36		1.13	
P(F<=f) one-tail	0.48		0.05		0.29		0.14		0.34	
F Critical one-tail	1.86		1.74		1.60		1.60		1.63	

Table A2: Analysis of variance for comparing means.

ANOVA: Single Factor
Testing for significantly different means of PPT during wet years
SUMMARY

Groups	Count	Sum	Average	Variance
HP 1986/87	47	909.89	19.36	159.42
PC 1986/87	48	916.48	19.09	229.67
HP 1990/91	46	945.98	20.56	204.18
PC 1990/91	48	913.70	19.04	260.34
HP 1992/93	30	754.02	25.13	444.90
PC 1992/93	34	985.31	28.98	459.28
HP 1995/96	54	1221.43	22.62	365.37
PC 1995/96	50	1082.92	21.66	313.38
HP 1996/97	53	1156.41	21.82	282.42
PC 1996/97	49	1133.34	23.13	386.14

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	3278.29	9	364.25	1.21	0.29	1.90
Within Groups	135551.80	449	301.90			
Total	138830.08	458				

ANOVA: Single Factor
Testing for significantly different means of PPT during dry years
SUMMARY

Groups	Count	Sum	Average	Variance
HP 1988/89	41	657.35	16.03	.82
PC 1988/89	33	592.06	17.94	.33
HP 1989/90	46	808.69	17.58	.05
PC 1989/90	53	854.82	16.13	.73
HP 1991/92	33	527.53	15.99	.37
PC 1991/92	29	560.07	19.31	.34
HP 1993/94	41	737.26	17.98	.96
PC 1993/94	37	738.42	19.96	.98
HP 1997/98	48	712.70	14.85	.81
PC 1997/98	47	744.56	15.84	.97

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	960.79	9	106.75	0.47	0.90	1.90
Within Groups	90587.37	398	227.61			
Total	91548.16	407				