SPATIAL AND TEMPORAL VARIABILITY OF THE STREAM WATER CHEMISTRY OF AN ALPINE/SUB-ALPINE CATCHMENT,

IN THE COAST MOUNTAINS OF

BRITISH COLUMBIA

· by

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ABSTRACT

The focus of this study is the hydrochemical variability of runoff events in two nested alpine/sub-alpine basins. More specifically, the aim is to link hydrograph interpretations to results of hydrochemistry during rain storms in order to understand better short term hydrochemical fluxes and variability in solute sources.

Hydrograph separation was undertaken by using four hydrological tracers; electrical conductivity, concentration of silica, and the stable environmental isotopes oxygen-18 and deuterium. The different methods predicted consistent high pre-storm water contribution for the lower station at peak flow (60%-90%) but less consistent results were found at the upper basin outlet (25%-90%).

The chemical characteristics of the stream water have been analyzed using three different approaches, namely; statistical, mass balance, and thermodynamic. Linear correlation was used to investigate the statistical association between discharge and the individual chemical species. The mass balance approach was used to correlate stoichiometry of the bedrock mineralogy to dissolved constituents in the stream water. Finally, a thermodynamic technique was used to evaluate to what extent the stream water could be represented as an equilibrium system and

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how this changed over the course of the storm. The results from these methods showed that the stream water variability was caused almost entirely by dilution from rain water input.

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1.1 BACKGROUND

Many alpine hydrochemical studies during the last decade have been focused on the long term fluctuations of water quality. These studies are motivated by concerns about potential impact of acid deposition on aquatic and terrestrial ecosystems (e.g. Drever and Hurcomb, 1986; Kattleman, 1989; and Baron, 1992). Relatively little attention, however, has been devoted to short term hydrochemical fluxes of alpine stream water, which is an important aspect of both acidification and transport of contaminants in these areas. The focus of this study is, therefore, to investigate the hydrochemical variability of two nested alpine/sub-alpine basins during distinct hydrological events. In particular, the study objective is to relate the hydrochemical interpretation of hydrograph separation to analysis in order to understand better short term hydrochemical fluxes and variabilities in solute sources.

1.2. CHEMICAL WEATHERING

Chemical weathering reactions in bedrock and soils are the primary source of solutes in the hydrosphere. The most important weathering process of silicate and aluminosilicate minerals is known as hydrolysis. The hydrolysis reaction consumes protons and produces other solutes while transferring primary minerals to a secondary face.

The main sources of protons in areas without anthropogenic influence on atmospheric composition are carbonic and organic ācids. Oxidation of naturally occurring sulphide, eg. pyrite, can also contribute to the acidity and hence control the hydrochemistry of stream waters (Raiswell and Thomas, 1984; Basset et al. 1992).

The thermodynamic relationship of the minerals involved in weathering reactions reveals what final water composition could be expected in a closed hydrological system experiencing equilibrium (ie. Garrels and Christ, 1965). Chemical thermodynamics is also valuable when identifying stable and unstable minerals at specified pressure, temperature and activity of individual solutes (Bricker, 1972).

Most surface waters are, however, open hydrological systems with a relatively short residence time in the subsurface environment, which prevents equilibrium or steady state conditions from being reached. Due to the reaction kinetics of the system, the highest rock dissolution rate is at the beginning of the encounter between water and minerals (eg. Trudgill, 1986). Flushing of dilute water through the hydrological reservoirs in the landscape, therefore, enables the reaction to continue at a high rate, whereas in a closed system the rock dissolution will decelerate as equilibrium is approached.

1.3. SPATIAL VARIABILITY OF HYDROCHEMISTRY

1.3.1. BASIN MORPHOLOGY

The importance of elevation on solute concentration of runoff was investigated by Drever and Zobrist (1992) by comparing the hydrochemistry of a series of small granitic gneiss catchments at different elevations in southern Switzerland. They found that the concentrations of the major cations and silica in surface waters decreased exponentially with higher elevations. Drever Zobrist hypothesized that decreased concentration of and individual species with higher elevation was the result of thinner soils, selective chemical weathering and a change in soil clay mineralogy. The findings of Drever and Zobrist (1992), that stream and lake water at high elevations are dilute corresponds well with other high altitudinal hydrochemical studies, such as those in Sweden (Degerman et al. 1992), Colorado (Mast, 1992), Sierra Nevada (Williams and Melack, 1991) and the British Columbia Coast Mountains (Gallie, 1983).

Details of water movement through the landscape are of fundamental concern when interpreting the influence of basin characteristics on runoff chemistry. The basin morphology controls the mixing of surface, subsurface and groundwater (Mcdonnell et al. 1991) and therefore controls stream chemistry. In a study carried out by Zecharias and Brutsaert (1988) both analytical results and their interpretation showed that the

parameters which most strongly controlled outflow of groundwater were total length of perennial streams, average basin slope and drainage density. Increased geochemical load downstream in stream channels has also been found in several other studies (eg. Foster and Grieve, 1984; Calles, 1985). The enhanced solute concentration in the downstream direction in these studies has been explained by increased groundwater outflow. Calles (1985) found that the portion of deep groundwater increased from 5% to 20% of the total flow, along a 500 meter reach in the downstream direction. Foster and Grieve (1984) also found a significant downslope increase in solute concentrations but discovered a large solute increase in the subsurface throughflow towards the stream channel as well.

Concavities, hollows and slope bases experience a concentration of subsurface throughflow and solute acquisition. This has been found where the travel distance for throughflow is small and the water still dilute (Crabtree and Burt, 1983). At the slope base, however, this is often not the case as the water, before it reaches the base of the slope, is already enriched with solutes and has, therefore, less weathering potential (Burt, 1986). Dixon (1986) found a large topographic influence on solute enrichment. He suggested that high topographic positions are areas of solute uptake, midslopes are areas of transport and removal, and base slopes are dominated by transport and accumulation. It has however been shown that the most rapid

solute enrichment occurs as soon as dilute meltwater and precipitation encounters sedimentary material (eg. Rainwater and Guy, 1961 and Trudgill, 1986). Dixon's model is, therefore, probably much too simplified, even though it largely follows the conclusions of Foster and Grieve (1984), who demonstrated that the geochemical load increased downstream in both channel and subsurface throughflow.

Variations in streambed topography can influence potential energy distribution at the streambed subsurface interface (Harvey and Bencala, 1993). Harvey and Bencala suggested that the potential energy variation could exert a significant control on surface-subsurface water mixing in mountain streams. Field evidence supported their hypothesis, especially where the slope discontinuity and the spacing between stepped bed units is large. The increased potential energy was found to have a significant influence on solute transport by recharging water to subchannel flow paths. Return of solute enriched substream water occurred where stream channel slope decreased.

1.3.2. SOILS

It has been found in lowland areas that the chemicalhydrological interaction in the near stream zone largely controls the solute contribution to streams (e.g. Pionke et al. 1988). Whether the near stream zone is of similar importance in

high mountain areas is questionable due to steep topography and thin soils forcing water to bypass the soil matrix as it flows downhill. In spite of the relatively limited distribution of soils in mountainous catchments, their importance in the near stream zone has been identified by Baron et al. (1992). They concluded that the largest relative influence on stream water chemistry is caused by the fact that soils in most alpine regions are concentrated on the valley floors adjacent to the stream channel. The importance of soils in contributing solutes to streams is found in the hydrological characteristics and pedochemical activity of the solum (Gallie and Slaymaker, 1984). Soils are extremely reactive due to their large specific surface area (Tan, 1993), and ion adsorption and retention are rapid enough that they can exercise a disproportionate influence on surface water chemistry.

1.3.3. VEGETATION

Although only a small percentage of most alpine and subalpine areas is vegetated, forest and meadows can be important sources and sinks for nutrient and certain non-nutrient ions (Arthur, 1992). Her conclusions conform well with those of Teti (1979) who argues that biomass in an alpine region is important not only because of spatial distribution but also because of the temporal variation of ionic release. Foster and Grieve (1984) came to similar conclusions that the relative chemical composition of precipitation chemistry is not only altered by

the biosphere, but that vegetation has a relatively high impact on solute loading. Most geochemical weathering studies hypothesize steady state elemental cycling of the vegetation (eg. Clayton, 1986). The quantification of solute release from vegetation becomes important in areas of anthropogenic influence (Paces, 1986), or sensitive alpine environments, which are forced out of steady state by climatic fluctuations. It is also not likely that steady state conditions in the vegetation can be achieved during individual hydrological events when flushing of accumulated material can be expected. The effect of CO_2 contribution from vegetation, and, hence, hydrogen production is expected to increase the chemical weathering rates below the tree line. The CO_2 partial pressure encountered in soil systems due to biological respiration often exceeds the concentration of the atmosphere by 100 times (Creasey et al. 1986).

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1.3.4. LITHOLOGY

It is apparent that the lithology has an important role in controlling stream water chemistry. This has also been shown in several mountain studies, by Reynolds and Johnson (1972) in silicate bedrock and by Basset et al. (1992) in sulphidic material. The geochemistry of the parent material determines the equilibrium concentration and reaction rates and, therefore, what elements could become available as weathering products. The bedrock geochemistry, however, is not the sole indicator of chemical weathering rates. The rate of dissociation depends also

on an array of physical bedrock characteristics. Eggelton (1986) found the structure of mineral complexes, cleavage planes and crystal shape to be of major importance for the susceptibility to chemical weathering. Differential chemical weathering is also influenced by the heterogeneity of the rock mineralogy (Sparks, 1971), and at joints, fractures and bedding planes (Clark and Small, 1982). More rapid mineral dissolution in the mentioned structures is caused by larger exposed surface areas.

1.3.5. CLIMATE

Climate could be considered the most important variable affecting chemical weathering rates due to its obvious control on the hydrological regime and vegetation. The single most important variable in the context of chemical weathering is the availability of water (Dethier, 1986). Thus, chemical weathering rates tend to be highest in areas of high runoff. Often coinciding with high chemical weathering rates and high runoff volumes are, therefore, streams with very dilute water due to short average residence time in the subsurface environment.

The temperature effect has been discussed by Colman and Dethier (1986). They suggest that a raised temperature will decrease the equilibrium concentration and hence the mineral solubility but increase the rate of chemical weathering as both the dissolution kinetics and thermodynamics of the system are affected. Ollier (1984) suggests that a 10° C rise in temperature could double

the rate of chemical weathering. However, chemical weathering and removal of solutes were found to be an important denudation factor, by Rapp (1960) in a subarctic small basin study and by Collins and Young (1981) in glacial environments. Such studies, carried out in cold environments, suggest that chemical weathering reactions are important not only in tropical and humid climates but in polar and alpine regions as well.

1.4. TEMPORAL FLUCTUATIONS IN HYDROCHEMISTRY

The temporal variability of surface water chemistry is mainly controlled by partitioning of water between surface and subsurface sources. Even though most high mountain areas have very dilute runoff water, large temporal variations in the runoff hydrochemistry occur. Large diurnal fluctuations of solutes occur during snowmelt in spring and during summers in glacierized basins (Collins, 1977, 1979) and during storm events (Kattleman, 1989). The importance of subsurface contributions in alpine areas to the runoff hydrochemistry depends, therefore, on the timing of inputs from dilute snowmelt and stormflow, not from the total outflow of highly concentrated subsurface water.

The variability of the geochemical load is caused by the partitioning of water between surface, soil and groundwater sources. Large variability in water chemistry occurs between the base flow and the storm flow components. The base flow comprises water originating mainly from the lower mineral horizons and

groundwater with long residence time. The storm flow component is produced during hydrologic events when the base flow is diluted by large volumes of precipitation or meltwater. The partitioning of water pathways can vary both seasonally (Kattleman, 1989) and during individual storm events (Creasey et al. 1986).

Alpine areas are characterized by rapid hydrological processes, caused by high hydraulic gradients, high flow velocities and fast transmission of hydraulic impulses (Šilar, 1990). The short residence time of water in alpine areas, resulting in dilute runoff, does not necessarily indicate a lower proportion of subsurface water compared with that of lowland areas. However, it does prevent chemical weathering reactions from proceeding towards steady state and equilibrium activities.

The precise hydrological pathway has important implications on residence time and hence on solute enrichment. Identification of the water pathway gives an understanding of magnitude and timing of solute fluxes from different hydrological reservoirs in the landscape (Slaymaker, 1988) and is, therefore, essential for the understanding of variations of the streamwater chemistry. Many hydrograph separation studies have been carried out in lowland areas during the last decades. Discrepancies between results from stream-oriented chemical and natural isotope separation of storm runoff into sources of storm and pre-storm water often

appear to contradict results from hillslope-based (hydrometric) studies. This has been the situation in the steep humid catchment, Maimai, on the South Island of New Zealand. Hydrometric studies by Mosley (1979, 1982), using artificial tracer monitoring and subsurface flow measurements to investigate the catchment's fast response to precipitation inputs, suggested that storm flow was controlled by rapid runoff of storm water routed through macropores. Work by Pearce et al. (1986) and Sklash et al. (1986), employing natural stable isotopes and chemical tracers, explicitly refuted Mosley's interpretation by demonstrating that the storm hydrograph volumetrically was dominated by pre-storm water during highfrequency storms. Implicit in their argument is that the large pre-storm water component is generated by near stream saturated overland flow and that macropore flow or other rapid-flux mechanisms could not explain the fast contribution of water to the stream. More recent findings, however, by McDonnell (1990), and McDonnell et al. (1991) showed that a large pre-storm water fraction (up to 95% of total runoff) is routed through preferred macropore pathways.

The problems encountered at the Maimai catchment could have important implications for many former hydrograph separations. This is true for mountain areas, in particular, where rapid hydrological response together with low solute concentrations could be used as misleading evidence for overland flow or

macropore flow contributing event water as the main component to the storm hydrograph. Unfortunately, no previous studies using hydrograph separation methods in alpine areas to analyze the proportion of event and pre-event water during storm flow were available to the author.

1.5 SUMMARY

Surface water hydrochemistry is the end product of interacting biogeochemical processes in the drainage basin. Chemical weathering processes are the main solute contributors to runoff in areas of limited anthropogenic influence. However, cation exchange reactions in soils, and leaching of organic material, can form variable sources and sinks of individual chemical species. Gallie (1983) has concluded that the hydrochemistry of runoff is a function of:

- The number and type of hydrologic reservoirs in the landscape;
- ii) The net chemical reactivity of each hydrologic reservoir; and,
- iii) The volume flux rate of water within each hydrologic reservoir.

Consequently, stream water chemistry is a function of the mean residence time of the water and the chemical reactivity of each reservoir. Reservoir contributions to the flux and magnitude of

solutes, therefore, can be evaluated by studying sources and sinks of solutes in the system and principal pathways of water in the catchment.

CHAPTER 2 - STUDY AREA

2.1 LOCATION

The study site comprises a west-facing catchment, straddling the alpine-subalpine ecotone in the Pacific Ranges of the Coast Mountains, about 120 km north of Vancouver, British Columbia (figure 2.1). The 0.36 km² watershed is situated 1525 to 1950 meters (5000-6400 feet) above sea level. The catchment is divided into two sub-basins: upper and lower basin, with areas of 0.29 km² and 0.07 km² respectively (figure 2.1). The study basin has a marked valley asymmetry with a steep, 25-40° north-facing talus slope and with more gentle, 5-15° vegetated south-and west-facing slopes.

2.2 CLIMATE

The meso-scale climate in the study area is cold, perhumid. The Pacific Ranges are oceanic and therefore receive large amounts of winter precipitation, making up more than 70% of total precipitation (Gallie, 1983). The cold, oceanic climate maintains alpine glaciers in the area with local glacial equilibrium line altitude fluctuating around 2100 m.a.s.l. Individual years have experienced twelve months of snow cover in the upper basin but the winter snowcover does not usually persist beyond September (Slaymaker, personal communication, 1993).



Figure 2.1. Map of British Columbia showing study location (upper panel) and basin geology and basin topography (lower).





Figure 2.2. Vegetation map (upper panel) and location of monitoring stations and bulk precipitation gauges (lower).

2.3 GEOLOGY

Regional bedrock geology consists of Coast Mountains Complex quartz diorite, which is overlain by a roof pendant of Cretaceous Gambier Group metasediments on the south ridge (Journeay, in press) (figure 1). A detailed geochemical survey was carried out by Gallie (1983) in the upper most part of the study area, Goat Meadows. He suggested that the mineralogy of the quartz diorite complex consists of; quartz 30%, plagioclase (An 40) 20%, K-feldspar 15%, hornblende 10% with a number of accessory minerals, and the metasediments of quartz 60%, actinolite 21%, chlorite 13% and accessory minerals. Gallie (1983) also found dyke swarms of vesicular basalt and traces of a feldspar porphyry. Pyrite in small amounts was found to be ubiquitous in the study basin.

Visible bedrock outcrops in the study area are heavily fractured. Fractures range in size from microscale features to several meters deep, and hundreds of meters long. The larger fractures, evident on the southern divide of the basin, are interpreted as toppling features (Slaymaker, personal communication, 1995).

2.4 VEGETATION

South- and west-facing slopes range in surface cover from alpine fir (Abies lasiocarpa) and mountain hemlock (Tsuga mertensiana) with understory of predominantly heather (notably, Cassiope

mertensiana and Phyllodoce glanduliflora) and rhododendron (Rhododendron albiflorum) to sedge (ie. Carex nigricans and Carex spectabilis), moss (ie. lycopodium sp.), lichens (ie. Cladonia sp.) and bare soil (see table 2.1). The steep northfacing valley-side consists predominantly of unvegetated talus slopes and rock bluffs (figure 2.2).

Table 2.1. Surface cover in the study area.				
Surface [•] cover	Upper basin	Lower basin		
Bedrock and talus	48%	48%		
Stands of conifers	.13%	37%		
Heather, lichens and moss	29%	12%		
Grassy-sedge meadow	2%	2%		
Bare soil	7%	<1%		
Ponds	1%	<1%		

2.5 SOILS

In the upper basin, soils have been described according to the Canadian system of classification (Canadian Soil Survey Committee, 1978) by Gallie (1983) and Souch (1984). In tree stands soils are Orthic Humo-Ferric Podzols. In grass and heather areas soils are dominated by Orthic Dystric and Orthic Sombric Brunisols and Cumulic Regosols. Owens (1990) suggests that soils in the Lower Basin, in general, are similar to soils described by Gallie (1983) and Souch (1984). Barrett (1981) and Barrett and Slaymaker (1989) found hydrophobicity in many of the soils in the study area.

2.6 HYDROLOGY

The outlet of a small oligotrophic pond, Middle Lake, defines the boundary between the two study basins. The elevation of Middle Lake is approximately 1680 meter above sea level. The lake is fed by one main stream flowing primarily at the contact between the talus slope and slopes vegetated by heather, moss and lichens. Several small ephemeral streams are activated, on the north side, during precipitation and snow-melt events. The upper portion of the main stream, originating from Gallie Pond, becomes inactive during the later part of the summer, probably caused by high rates of groundwater loss through the lake floor (Gallie, 1983).

The outlet of the lower of the two study basins is located immediately prior to the confluence with the Ash Lake outlet stream. The flow path of the stream is mainly through conifer stands with a lush understory of rhododendron and subalpine flowers (species not determined). Groundwater seeps into the stream are visible in a few locations along the flow path.

2.7 PREVIOUS WORK

Previous work on the basin includes: sediment yield estimation (Slaymaker, 1977); study of surface erosion (Hart, 1978); study of soil hydrophobicity (Barrett, 1981); study of slope sediment movement (Jones, 1982); analysis of water budget and chemical weathering of Goat Meadows (Gallie, 1983); and lake sediment

investigations (Souch, 1984; Owens, 1990). In an adjacent basin research on runoff hydrochemistry has been carried out by Zeman and Slaymaker (1975); and Teti (1979). The above studies in provide a regional context for this study and are discussed in more detail where applicable.

CHAPTER 3 - FIELD AND LABORATORY METHODS

3.1 STREAM WATER MEASUREMENTS

Two 90° sharp crested V-notch weirs were installed at the outlet of the two basins during the early snowmelt season of 1994. The weirs were built in order to obtain a continuous record of hydrological and hydrochemical parameters, which were measured every 10 seconds and stored every 10 minutes in dataloggers (CR10, Campbell Scientific).

Ultrasonic Depth Gauges (UDGO1, Campbell Scientific) were used for continuous stage height recordings at the two weirs. The UDGO1's were calibrated by instantaneous discharge measurements at different water levels using, the velocity-area method (Goudie, 1990), the time-volume method (Slaymaker, personal communication, 1994) and the 90° V-notch equation (Church and Kellerhals, 1971). Air temperature (using a 107 Temperature Probe with a 6 Plate Radiation Shield, Campbell Scientific) was measured immediately adjacent to the UDGO1 in order to calibrate it with air density fluctuations.

3.1.1 ELECTRICAL CONDUCTIVITY AND pH

Electrical conductivity (EC) using 247 Conductivity Probes (Campbell Scientific) and pH using SG50CD Sensorex Electrodes with SC32A Optically Isolated RS232 Interface (Campbell Scientific), were continuously measured at the outlet of each

study basin. EC was corrected for water temperature (using 107B Temperature Probes, Campbell Scientific) to 25°C by laboratory calibration. The EC-temperature relationship was found to be linear down to 0.003 mS/cm, with an increase of 3.0% per degree Celsius. Calibration of pH electrodes was carried out daily in the field until stable and there after checked weekly.

3.1.2 STREAM WATER SAMPLES

In order to conduct chemical analysis of the stream water at the two stations a total of 28 depth-integrated hand samples was collected in 125 ml acid-washed polyethylene bottles. Samplingfrequency at the two sites was concentrated around one early September precipitation event, daily sampling prior to the storm and one sample every two to four hours during the event. The samples were immediately filtered after collection using a hand vacuum pump with 0.45 μ m filter, and stored in a dark location close to 0°C until analysis. The samples were analyzed at the Soil Science Laboratory of the University of British Columbia silica using Atomic Absorbtion cations and for major Spectrophotometry and Inductively Coupled Plasma Atomic Emission Spectrometry, and for major anions using Flow Injection Analysis. Total Inorganic Carbon (TIC) was analyzed using a Total Carbon Analyzer at the Department of Civil Engineering, University of British Columbia. Throughout this thesis, TIC is assumed to be present only in the form of HCO_3^- . Charge balance error for the samples was 0.24% with a standard deviation of

2.84% (see appendix I). All water sample results have been converted from concentration into activities by using the Debye-Hückel equation (Drever, 1988).

35 stream water samples were collected for isotopic analysis following roughly the same sampling scheme as those collected for runoff chemistry (appendix II). Samples were collected in 30 ml polyethylene bottles which were filled as full as possible and tightly sealed with parafilm wrap to prevent equilibration with air. Samples were analyzed for deuterium and oxygen-18 by Dr. Krouse at Department of Physics and Astronomy, University of Calgary.

Isotopic composition of water is expressed in per mill (‰) deviation from the Standard Mean Ocean Water (SMOW) and is calculated as:

$$\delta^{18}O(D)_{SAMPLE} = \frac{\frac{\binom{18}{0}(D)}{\binom{16}{0}(H)}}{\frac{\binom{18}{0}(H)}{(16}(H)} - \frac{\binom{18}{0}(D)}{\binom{16}{0}(H)}}{\frac{\binom{18}{0}(H)}{\binom{16}{0}(D)}}_{SMOW}$$
(1)

where ¹⁸O and D are the heavy isotopes oxygen-18 and deuterium, and ¹⁶O and H are the common isotopes of oxygen and hydrogen. A negative value of δD or $\delta^{18}O$ implies that the sample is depleted of the heavy isotope compared to the SMOW.

3.2 PRECIPITATION MEASUREMENTS

A 0.1 mm tipping bucket rain gauge (TE525M, Campbell Scientific) was used at the lower station to measure rainfall intensity. A longitudinal transect of bulk precipitation gauges, mounted 1.5 meters above ground, was established along the stream channel in order to identify fluctuations and altitudinal differences in precipitation amounts. The bulk precipitation gauges were emptied following each precipitation event when field site was occupied, otherwise as soon as possible. The five bulk precipitation gauges were placed at 1530, 1570, 1650, 1740 and 1830 m.a.s.l. respectively.

3.2.1 PRECIPITATION SAMPLES

sampled in acid-washed Precipitation chemistry was an polyethylene sampler at one site adjacent to the upper station, and is assumed to represent both wet and dry chemical fallout (Zeman and Nyborg, 1974). Emptying of the precipitation chemistry sampler was carried out concurrent with the bulk chemical analyses precipitation gauges. Storage and of precipitation samples followed the same procedure as that of stream water samples. The charge balance error was -41.85% with a standard deviation of 10.89% for the four precipitation samples analyzed (appendix I). The large charge balance error could be caused by a deficiency of cations in samples, which presumably results from the dilute precipitation water producing large analytical errors near the instrumental detection limit.

These data are, therefore, used with caution. The EC and pH of the precipitation were measured in the laboratory using a CDM2e Conductivity meter (Radio Copenhagen) and pHM62 pH meter with glass electrode (Radio Copenhagen), respectively.

Samples for the isotopic composition of rain during event #3 were collected from the bulk precipitation gauges in order to follow the temporal and altitudinal fluctuations. In total five precipitation samples were collected and analyzed following the procedure of the stream water samples for storage and analysis of isotopic composition (appendix II).

3.3 MAPPING

Maps of the study area were prepared from the following sources:

- Pemberton topographic map sheet 92 J/7, 1988 edition 2, 1:50000, Department of Energy, Mines and Resources, Canada;
- 2) Pemberton geology map sheet 92 J/7, 1995 in press, 1:50000, Geological survey of Canada, compiled by M. Journeay (in press);
- 3) Black-and-white aerial photographs, taken at 20000 feet, 1990, 30BCB90051, No. 257 and 258; and

4) Field mapping.

The topographic maps were used to locate the study area on the

British Columbia base map (figure 2.1a) and for generalized contour lines and study basin location in figure 2.1b. The discrepancy between contour lines from map sheet 92 J/7 and the study basin limits from field mapping was not resolved. The location of the contact between Quartz Diorite Complex and Metasediments in figure 2.1b was obtained from the geology map. Aerial photographs and field mapping was used for detailed delineation of the drainage pattern, vegetation complexes and the study basin boundaries in figure 2.2a and b.

CHAPTER 4 - HYDROLOGY

4.1 DISCHARGE AND ELECTRICAL CONDUCTIVITY

Continuous monitoring of discharge and electrical conductivity (EC) was carried out from August 6 to October 8, 1994 (figure 4.1). Extensive snow patches were present in the study area in early August, they finally disappeared in the beginning of October. Large diurnal fluctuations in both discharge and EC were observed throughout August and continued through the remainder of the field season with smaller and smaller amplitude as the season progressed.

During the measurement period five distinct precipitation events occurred; August 8-9 (event #1), August 16 (event #2), September 7-9 (event #3), September 10-11 (event #4) and September 30 to October 2 (event #5). These events will be discussed in detail in later sections with an emphasis on event #3.

4.2 PRECIPITATION

There was no detectable systematic altitudinal effect on precipitation. For the five bulk precipitation gauges located in a longitudinal transect the four lower gauges show consistent results, with less than 5% variation between sites. The upper most bulk gauge, located on an exposed ridge, has a much different precipitation pattern. The discrepancy of the upper gauge is probably caused by an under-catch due to windexposure


Figure 4.1. Discharge and electrical conductivity for the entire field season at the two at the two monitoring stations, and precipitation at the lower station.

and is, therefore, omitted from the results.

Good agreement, with less than 8% variation, was found between average collected bulk precipitation volumes and the tipping bucket rain gauge located at the lower station. The use of the tipping bucket rain gauge as a representative precipitation measurement for the entire study basin can, therefore, be justified.

4.3 RUNOFF RATIO

A distinct difference in both discharge and EC between the two measurement sites was observed. Although the upper basin makes up over 75% of the total study area, the discharge at the lower station was approximately 150% higher than the upper station during August and about twice as high during the remaining field season. The EC was found to be between 30% to 60% higher at the lower station compared to the upper one during the early field season but the difference decreased continuously to about 10% approaching the end of September. The upper station also displayed a more random EC signal.

Comparison of storm runoff ratios suggests that 13% to 27% of all incoming precipitation at the lower station left the lower basin during individual precipitation events, while only 2.8% to 7.7% of precipitation left the upper basin (table 4.1).

Table 4.1. Storm runoff ratio for precipitation events.						
	Precipitation	Basin	Upper	Lower		
Event #1	31.3mm	9.5%	5.3%	27.0%		
Event #2	11.0mm	10.2%	6.3%	26.9%		
Event #3	25.7mm	. 8.5%	5.0%	23.0%		
Event #4	10.4mm	4.8%	2.8%	13.4%		
Event #5	24.3mm	7.7%	4.0%	23.0%		

There are a number of potential grounds for the inconsistency between the two sites. One potential explanation of the discrepancy could be that a large fraction of water draining from the upper basin does not enter the surface drainage network until after the upper measuring site. This would result in a larger proportion of groundwater at the lower station which could explain the differences in EC between the sites, as discussed above. This agrees well with the conclusions of Gallie (1983) in the Goat Meadows Basin were he found that a large proportion of water left the drainage basin through the groundwater system. This process could be enhanced by the heavily fractured bedrock in the area, visible at exposed outcrops, which could act as efficient hydrological conduits in the subsurface environment.

The discrepancy in discharge between the two sites could also be explained by measurement inaccuracies. It is possible that water draining the upper basin bypassed the weir under or on the side of the V-notch. Errors can also be associated with calibration

of the V-notch weirs at each site. Approximate error during peak flow in discharge measurements at the upper station is 2% (estimated from the difference in discharge measurements methods, see chapter 3). The calculated error at the lower station at peak flow is approximately 20%. The most plausible cause of this large error is shooting flow through the weir at high water levels. This would lead to an underestimation of the discharge using the V-notch equation and hence increase the discrepancy between runoff ratios at the two stations even further.

It is further possible that the subsurface divides do not follow their surface counterparts or that drainage basin areas were not accurately delineated. Errors could also be introduced when mapping the study basins from aerial photographs due to distortion (Avery and Berlin, 1985), although these maps where checked in the field. The stepped topography of the area is a further source of inaccuracy.

4.4 SUMMARY

The continuous record of discharge and EC (depicted in figure 4.1) demonstrate a large difference between the two monitoring sites. Discharge was found to be between 100% and 150% higher at the lower station although the upper basin makes up over 75% of the total study area. EC was also much higher at the lower station. The contrast between the two sites is amplified by the

runoff ratios for the two basins. The lower basin had a runoff ratio of 13% to 27% for the five monitored storms, whereas only 2.8% to 7.7% of the precipitation could be accounted for at the upper basin outlet.

The most plausible explanation of the discrepancy between the two basins is that the upper basin is not hydrologically tight. Water could potentially leave the basin through the groundwater system. This process could be enhanced by the heavily fractured bedrock in the area acting as efficient hydraulic conduits. Reentering groundwater between the two stations could explain the higher EC-signal at the lower monitoring site.

CHAPTER 5 - HYDROGRAPH SEPARATION

5.1 INTRODUCTION

The storm flow generation at the outlet of each study basin is evaluated and compared in this chapter. The goal is to separate the storm runoff into its components of storm and pre-storm water. The relative proportion of these contributions during the different stages of the storm hydrograph is useful in understanding the variation of stream water chemistry during storm events and between monitoring sites. The question of spatial and temporal variability of solute composition in runoff is further discussed in chapter 6.

The separation of the hydrograph is pursued for event #3 by using the stable environmental isotopes, oxygen-18 and deuterium, silica and EC. Except for a few minor snow patches generating a weak diurnal discharge signal, the stream was at baseflow condition prior to the storm which culminated after four rainless days. During the event 22 mm of rain fell over the basin with a maximum intensity of 3 mm per hour.

The results using the three methods, isotopes, silica and EC, are extrapolated to events #1, #2, #4 and #5. Only continuous measurements of EC and discharge are available for these events. The extrapolation is carried out in order to examine (1) if the results from event #3 are unique or (2) if the findings are

typical for other antecedent conditions as well.

5.2. SEPARATION MODELS

Traditional graphical separation methods of the storm hydrograph by extrapolation of the groundwater recession curve can not explain the dynamic process of hydrological systems, due to the arbitrary and subjective estimations needed for the use of the method (Hermann and Stichler, 1980). Growing attention to hydrochemical variability, therefore, led Pinder and Jones (1969) and Hall (1970, 1971) to present a series of simple chemical mixing models. The dynamic mixing model presented by Hall is concerned with the relationship between discharge and total solute load. As the solute concentration varies independently with time from different discharge sources the two-component mixing model described by Pinder and Jones (1969) to determine relationship between used the tracer is concentrations and discharge volumes for two different runoff components (equation 2). It can be written as:

$$Q_t * C_t = Q_s * C_s + Q_p * C_p$$
(2)

where Q is discharge, C is concentration of applicable tracer and the subscripts t, s and p refer to total, storm and prestorm water components respectively.

5.3 HYDROGRAPH SEPARATION USING STABLE ISOTOPES

The use of stable natural isotopes to separate storm and prestorm water with the two component mixing model is possible due to isotopic fractionation of air masses during evaporation and condensation phases (Mazor, 1991). A preferential accumulation of the lighter isotope in the liquid phase is caused by less efficient evaporation and more rapid condensation of the heavier isotopes. The fractionation of isotopes gives rise to altitudinal dependence, seasonal fluctuations and variations between individual storms (McDonnell et al. 1990).

Hydrograph separation based on stable isotopes started with studies by Dincer et al. (1970), Martinec (1975) and Fritz et al. (1976) and has been used mainly in humid temperate regions. Most work employing isotope hydrograph separation has shown a large pre-storm water component, frequently greater than 70%, during precipitation events (eg. Sklash and Farvolden, 1979a; Hermann and Stichler, 1980; Bishop, 1990). Both Rhode (1981) and Hooper and Shoemaker (1986) calculated that a precision of between $\pm 10\%$ to $\pm 15\%$ can be achieved using natural stable isotopes under favorable conditions.

5.3.1 RESULTS

A significant difference between isotopic composition of the storm and pre-storm component is necessary for the use of ^{18}O and D in hydrograph separation. The weighted mean values of δD and

 δ^{18} O for precipitation during event #3 was -71.8 % with standard deviation of 4.12 % and -10.6 % with standard deviation of 0.58 %, respectively (appendix 2). Average baseflow isotopic composition at the lower station, estimated from 3 samples taken 101, 74.5 and 2 hours before the outbreak of the rain, was -124 % with standard deviation of 4.4 % and -17.1 % with standard deviation of 0.17 %, respectively for δ D and δ^{18} O. For the upper station average baseflow composition of δ D and δ^{18} O was -127 % with standard deviation of 1.7 % and -17.1 % with standard deviation of 3.7 % and -17.1 % with standard deviation of 0.26 % respectively, estimated from 3 samples taken 103.5, 75.5 and 31 hours prior to the start of the rain storm.

Figure 5.1 illustrates the pre-storm water fluctuations as the discharge increased over 200% at the two stations as estimated with D and ¹⁸O. Appendix II presents the temporal variations in D and ¹⁸O and the calculated values for the old water component in the storm hydrograph using equation 2. The pre-storm water contribution calculated using an averaged value of D and ¹⁸O, is also depicted in figure 5.1. Average old water contributions using deuterium and oxygen-18 are between 65% and 89% during peak flow at both sites.

5.3.2 VALIDITY OF METHOD

When using natural stable isotopes for hydrograph separation a number of assumptions or requirements are implicit in the use of equation 2. Assumptions commonly made have been summarized by



Figure 5.1. Hydrograph separation using natural stable isotopes.

Sklash and Farvolden (1979b) as:

- Rain or snowmelt isotopic content can be characterized by a single isotopic value, or variation in isotopic content must be documented;
- ii) Pre-storm component, groundwater and vadose water, can be characterized by the baseflow with a single isotopic content;
- iii) Isotopic content of precipitation or snowmelt are significantly different from pre-storm values; and
- iv) Contribution of stored surface water to the stream is insignificant.

The validity of the isotope hydrograph separation assumptions has been explicitly questioned by Kennedy et al. (1986). Their criticism is based on one exceptionally large storm over the Mattole River basin of northwestern California, where both oxygen-18 and deuterium data suggested that the pre-storm contribution to the storm hydrograph by far exceeded the storage capacity of the watershed. In their discussion of assumption (i), Kennedy et al. (1986) suggest that the average isotopic composition of the rain does not necessarily correspond to that of the average surface runoff water. Light to moderateintensity rain may infiltrate completely whereas heavy rain with a different isotopic composition may run off, at least partly, on the surface. The hydrophobicity of the soil in the field area

described by Barrett (1981) and Barrett and Slaymaker (1989) probably prevents the potential problem of rain water partitioning due to different precipitation intensities. All rain water falling on vegetated areas in the basin will travel as overland flow until it can enter the subsurface environment relatively through the macropore system. The constant precipitation intensity of event #3 further reduces the probability of partitioning of surface and subsurface runoff (figure 5.1).

The validity of assumption (ii), that the isotopic content of the baseflow reflects stored water in the soil and groundwater reservoirs, can also be debated. DeWalle et al. (1988) found a significant difference in isotopic content between groundwater and vadose water in a small Appalachian forested catchment. Instead of a general critique of the method, they further subdivided the stormflow, using a three-component mixing model, into groundwater, soil water and direct channel precipitation. Although the study by DeWalle et al. (1988) does not explicitly refute the two-component model, their findings raise questions about possible erroneous pre-storm component calculations when using a two component mixing model. No attempt was made to use the three component mixing model in this study. It does not seem likely that a large fraction of water will be contributed from the vadose zone in the study area as most of the soil horizon is believed to be bypassed due to its compact and hydrophobic

nature. It is possible, however, that there could be a change in partitioning between deep and more shallow groundwater components with different isotopic composition, during the hydrologic event.

The last assumption, that the isotopic composition of surface storage could be affected by evaporation, may be a source of error in the storm hydrograph separation calculations. The surface storage in the small ponds in the basins are considered negligible due to the small storage capacity, but a few small snow patches contributed an unknown volume of water during the event. It is, however, not likely that the melt water contribution prior to the event was significantly different from that during the rain storm and was, therefore, accounted for in the sampling scheme of the baseflow isotopic composition.

A further problem with the isotopic separation method is that the ratio between the heavy and the normal isotopes is not perfectly conservative. It is possible that the oxygen ratio can change as a result of both isotopic fractionation and molecular exchange (Bishop, 1990). Molecular exchange occurs as a consequence of atom substitution between water and other oxygenrich molecules in the subsurface environment. According to Bishop (1990), Rhode (1987) calculated that the effect of molecular substitution is negligible during rain fall events, but can possibly be significant during spring-melt runoff.

Isotopic fractionation results from differential evaporation of isotopically lighter molecules, thus leading to an enrichment of the remaining water with heavy isotopes and, therefore, to an overestimate of the pre-storm component in runoff. The isotope ratios of deuterium and oxygen-18 of the collected isotope samples fall close to the meteoric water line for the northern hemisphere (Dansgaard, 1964), see figure 5.2. This supports the assumption that the isotopic composition has not been changed due to secondary processes, such as evaporation prior to infiltration or of water stored in aquifer, or molecular exchange between water and bypassed soil and rock material.

5.4 HYDROGRAPH SEPARATION USING SILICA

The use of specific ion concentrations in order to identify different water sources contributing to the runoff hydrograph has been successful in many cases. Depending on bedrock geochemistry, soil characteristics and precipitation chemistry, different chemical species can be utilized. One of the most commonly used ions for hydrograph separation is silica (ie. Maulè and Stein, 1990).

Kennedy (1971) showed that precipitation, which has a silica content close to zero, or at least below the analytical detection limit, will reach equilibrium concentrations with regards to silica within a few minutes to hours of contact time



Figure 5.2. Meteoric isotope line for northern hemisphere.

with the mineral matrix. Kennedy concluded that because its rapid equilibration, silica could potentially be used as a hydrological tracer. Zeman and Slaymaker (1975) confirmed Kennedy's conclusions, but it was not until the mid 1980's that silica was tested against natural stable isotopes (Hooper and Shoemaker, 1986).

5.4.1 RESULTS

Implicit in Kennedy's (1971) findings, is that the use of silica is based on the assumptions that the storm water silica concentration is equal to zero and the pre-storm concentration is equal to that of baseflow. The silica concentration in precipitation was found to be below the detection limit (< $3.0*10^{-6}$ M) for the four rain samples collected. The average baseflow concentration of silica at the upper station was $1.09*10^{-4}$ M sd $3.60*10^{-6}$ M, for three samples taken 127.5, 75.5 and 31 hours before the rain fall started. The average silica concentration of baseflow for the lower station was $1.05*10^{-4}$ M sd $5.77*10^{-7}$ M estimated from three samples collected 73.5, 29, and 2 hours prior to the onset of rain storm (figure 5.3).

At the upper basin outlet the silica tracer indicated a 50% to 68% pre-storm water contribution (figure 5.3) at peak flow. The pre-storm contribution calculated using silica as a tracer shows an approximately 20% lower value than when using isotopes for the same site. At the lower station the pre-storm



Figure 5.3. Hydrograph separation using electrical conductivity, silica and stable isotopes.

contribution at peak flow is nearly consistent with the result using oxygen-18 and deuterium, namely 67% to 89% pre-storm water.

5.4.2 VALIDITY OF METHOD

In studies comparing chemical and isotopic tracers both Hooper and Shoemaker (1986) and Wels at al. (1991) achieved a consistent higher pre-storm component with silica than with oxygen-18 and deuterium. Neither set of researchers suspected an overstatement of the pre-storm water with the silica tracer, rather they assumed an underestimate using isotopes. Wels and his companions justify their discrepancy as a result of

incomplete mixing in the soil/groundwater reservoir, whereas Hooper and Shoemaker found no physical explanation.

The rapid equilibration of water can potentially lead to an increased dissolved silica load after a brief contact with mineral and organic material. An overstatement of the pre-storm component could, therefore, result from precipitation water entering the stream via overland flow. Another problem with using silica as a hydrological tracer may be found in biologically productive water due to dissolved silica uptake by diatoms (Hooper and Shoemaker, 1986), which would lead to an underestimate of the pre-storm component. This is not likely to be a problem in the study basin under consideration due to the dilute character and low biological productivity of the

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alpine/sub-alpine stream water in the study area.

Underestimates of the pre-storm component at the study sites could, however, arise from failure of the pre-storm water to reach near equilibrium or steady state activity with regard to silica prior to the hydrological event. Even though Kennedy (1971) proposed very rapid equilibration reactions, this could be a potential problem in coarse material such as the talus slope, on the north side of the study basin, where the mineral surface area is comparably small. This could explain the discrepancy between the study sites, with an underestimate of the upper station flowing along the bottom of the south-facing talus slope concurrent with an agreement between silica and isotope separation for the lower stream which flows mainly through vegetated areas.

5.5 HYDROGRAPH SEPARATION USING ELECTRICAL CONDUCTIVITY

Pinder and Jones (1969) and Nakamura (1971) were among the first to involve chemical tracers in the analysis of hydrographs. In their work they used EC as an indicator of relative amount of storm and pre-storm water. The theory behind this hydrograph separation method is that the concentration of solutes in direct channel precipitation and surface runoff is very low in comparison to the subsurface component. Due to the difference in concentration between storm and pre-storm water, the twocomponent mixing model can be applied (equation 2).

5.5.1 RESULTS

The electrical conductivity of the rain water was 6.15 μ S/cm with a standard deviation of 1.57 μ S/cm estimated from four rain water samples taken during the duration of the field season. The EC of the baseflow for the upper station immediately prior to the onset of the storm was 21.1 μ S/cm. The average baseflow EC for the four days prior to the rain was 28.45 μ S/cm with a standard deviation of 4.36 μ S/cm. The lower reading for EC was chosen as a representative value for baseflow, at the upper station, due to the better fit to the pre-storm estimates achieved using the more conservative tracers of specific silica concentration and the natural isotopes (figure 5.3). The calculated pre-storm component using EC demonstrates a very random contribution and does not correspond well with the results achieved using isotopes and silica as hydrograph separation tracers.

At the lower station the average EC for the four days preceding event #3 was 39.00 μ S/cm with a standard deviation of 1.39 μ S/cm which was taken as a representative pre-storm value. This is close to the EC value 39.39 μ S/cm immediately prior to the storm. The hydrograph separation at the lower station followed the general pre-storm contribution trend calculated with stable isotopes and silica concentration, but demonstrated a 10% to 20% lower pre-storm contribution (figure 5.3 see also appendix IV).

5.5.2 VALIDITY OF METHOD

As with the other hydrological tracers discussed above, Pinder and Jones (1969) and Nakamura (1971) concluded from their studies that dilution smaller than expected during storm peak flow results from a large pre-storm contribution. Similar results, but with different conclusions, were presented by Pilgrim et al. (1979). They suggested that the constant high conductivity was a consequence, due not only to increased groundwater discharge, but also to a substantial dissolved load obtained by the storm component during its brief contact with the soil surface. This could be a problem in the study area since much of the storm water is believed to move, at least partly, as overland flow (Barrett, 1981). A flushing effect overland flow during initiation of the caused by the could conceivably explain precipitation event why the correspondence between EC and the other tracers used in this study is better at the onset of the storm than at peak flow.

The use of EC is further limited as variations in specific ion concentration may change individually throughout different stages of the storm (De Boer and Campbell, 1990). An additional complication is caused by the fact that EC is a measure of the total charge strength of water and not of the total activity. A monovalent species will, therefore, contribute only half that of an equivalent concentration of a divalent species to the ECsignal. Problems arising from differential changes in individual

ion concentrations were, however, overcome in this study by analyzing all major ions at different stages of event #3 (see appendix I).

Due to the kinetics of rock dissolution, EC is not likely to reach near equilibrium or steady state activities for all the different ions in the macropores and in the coarse talus material, which characterizes much of the drainage basin, during the relatively short residence time of water in the subsurface environment. This potentially explains the discrepancy between the calculated pre-storm contribution compared to the other tracers discussed in this paper.

The advantage of EC, compared to other tracers used in this study, is that it can be measured continuously. By calibrating EC against more conservative tracers it can be utilized for hydrograph separation when hand or automatic sampling is not possible (Sklash and Farvolden, 1979a; De Boer and Campbell, 1990). The next section will discuss the reliability of using EC for hydrograph separation at the two study sites and if it is possible to extrapolate the results from event #3 to other precipitation events.

5.6 EXTRAPOLATION OF HYDROGRAPH SEPARATION

In order to determine whether the large pre-storm water contribution during event #3 was a unique occurrence or whether

the same contribution could be expected from a range of antecedent conditions the possibility of extrapolating the tracer data was tested for storms when only EC and discharge was monitored. Because of the non-uniformity of the data and the relatively small sample size, the Friedman analysis of variance ranking was used to examine if there were any systematic variations between using EC and silica/stable isotopes as hydrological tracers (table 5.1).

It is apparent from table 5.1 that EC can not be used as an alternative tracer for stable isotopes and silica in hydrograph separation for the upper basin. At the lower basin, however, the

Table 5.1. Comparison between hydrological tracers using Friedman analysis of variance.					
	electrical conductivity	Significance at the 95% level			
UPPER STATION					
silica	0.89*	NO			
isotopes	0.76*	NO			
LOWER STATION					
silica	0.94*	YES			
isotopes	0.94*	YES			
* Kendall Coefficient of Concordance					

significance at 95% level between silica/stable isotopes and EC enables the use of EC as a tracer in hydrograph separation at this site (figure 5.4a and b). Due to the equilibration constraints of EC discussed above and the fact that EC showed 10% to 20% lower pre-storm contribution for event #3, we can assume that EC gives a conservative measure of the pre-storm contribution during peak flow. It is, however, possible that flushing of readily soluble material at the soil/vegetation surface during overland flow (as discussed above) could lead to a somewhat overestimated pre-storm water contribution at the commencement of the storm event.

By using EC as a hydrological tracer for the four remaining hydrological events monitored it suggested that the large prestorm component found at event #3 is typical (figure 5.4a and b).

The hydrograph separation covers a range of precipitation events from early August with baseflow close to 20 1/s to end of September with base flow less than 2 1/s. All events depict a large pre-storm component (above 50% and up to 80%), especially notable at the onset of peak flow. The increased storm water component in the later part of the peak flow could result from depletion of hydrological storage in the basin.

5.7 SUMMARY

The old water contribution during event #3 using the stable environmental isotopes, oxygen-18 and deuterium, silica and EC was 56% to 86% during peak flow at the lower station. At the



Figure 5.4a. Hydrograph separation of event #1 and #2 at the lower monitoring station using electrical conductivity.



Figure 5.4b. Hydrograph separation of event #4 and #5 at the lower monitoring station using electrical conductivity.

upper station the old water contribution was 50% to 87% at peak flow using isotopes and silica and down to 24% for EC for the same event.

When comparing the four tracers used in the hydrograph separation at the study site, two features are immediately apparent. First, the predictions of pre-storm contribution by different tracers agree well at the lower site but disagree at the upper basin. Secondly, pre-storm water contribution predicted by isotope calculations is consistent for both sites.

It is apparent from the discordant pre-storm water contribution results between isotopic and chemical tracers at the upper station that the water in the subsurface environment does not reach equilibrium or steady state activities with surrounding mineral phases. There are two possible physical explanations of this phenomenon:

- 1) Pre-storm water residence time is too short; or
- Pre-storm water reservoirs consist of very coarse material with a relatively small surface area.

As was noted in the introduction, residence time of water in hydrological reservoirs is often short in mountainous environments, due to steep slopes, shallow and compacted soils and coarse material. This is further enhanced in the upper basin

where the main stream flows primarily on the boundary between hydrophobic soils and a coarse talus slope. The lower basin stream on the other hand flows through primarily vegetated areas with more permeable soils. The differences in the near stream zone between the basins could explain the discrepancy between results using chemical tracers at the two sites.

The results using the three methods, isotopes, silica and EC, were further extrapolated for the rain storms when only EC was monitored. It was found that EC was a useful alternative tracer at the lower station but could not be used at the upper one. The extrapolation showed that a large pre-storm component could be expected for other antecedent conditions than those of event #3.

CHAPTER 6 - CHEMICAL CHARACTERISTICS

6.1 INTRODUCTION

The purpose of this chapter is to investigate the temporal and spatial variability of the stream water chemistry at the two study basins. The chemical characteristics of the stream water will be analyzed using three different approaches; mass balance, statistical and thermodynamic.

The mass balance approach is used to correlate stoichiometry of the bedrock mineralogy to dissolved constituents in the stream water. Following, the approach of Garrels and Mackenzie (1967), mass balance calculations are here used to interpret relative solute contributions from different mineral sources.

Linear correlation is used to investigate the statistical association between discharge and individual chemical species. Statistical relationships between natural waters and environmental parameters are useful tools when identifying biological, chemical and hydrological processes within drainage basins (e.g. Eriksson, 1985), but do not establish any causeand-effect correlations.

Finally, a thermodynamic technique is used to evaluate the extent to which stream water could be represented as an equilibrium system and changes over the course of the storm. An attempt is also made to find a theoretical hydrochemical

evolution path of the stream water chemistry and secondary mineral formation.

6.2 MASS-BALANCE APPROACH

Mass balance calculations can be applied to hydrochemical data in order to interpret the relative stoichiometry of rock material encountered. In general terms the stream water chemistry can be characterized by the simple mass balance equation;

Material in solution - Atmospheric input
 = Rock material - Solid residue
 t cation exchange t biomass

Garrels and Mackenzie (1967) were among the first to test the mass-balance technique on the hydrochemistry of natural waters in order to interpret the origin of the chemical composition. The approach has since been used in several studies for interpreting both chemical weathering mechanisms and rates of mineral weathering (eg. Andersson-Calles and Eriksson, 1979; Velbel, 1986 and Mast et al. 1990).

A mass-balance calculation can be made to find the origin of the total activities along a reaction path if the water composition of the initial (ie. precipitation) and final (ie. baseflow) hydrochemical composition are monitored together with a defined set of geochemical reactants and products. In order for this to work satisfactorily it is necessary to consider only a few idealized minerals representing a known range of mineral stoichiometry in the basin (Plummer and Back, 1980). In addition to the problem of mineral stoichiometry the kinetics of the system must be evaluated including very reactive minerals in small quantities and excluding inert minerals. Knowing that the majority of the study area is underlain by quartz diorite (Gallie, 1983 and Journeay, in press) a simplified geological bedrock composition can be assumed (table 6.1).

Table 6.1. Assumed major minerals contributing to hydro- chemistry.					
Minerals	Stoichiometry	Solutes			
Hornblende	$Ca_2Na_2Mg_2Al_2Si_6O_{22}(OH)_2$	Ca ²⁺ , Na ⁺ , Mg ²⁺			
K-Feldspar	KAlSi ₃ O ₈	K+			
Anorthite	CaAlSi ₂ O ₈	Ca ²⁺			
Albit	NaAlSi ₃ O ₈	Na⁺			
Quartz	SiO ₂	Inert			
Pyrite	FeSO ₄	SO42-			

6.2.1 RESULTS

Three important assumption were made applying the mass balance approach in this study. First, the secondary mineral formation was proposed to be kaolinite $(Al_2Si_2O_5(OH)_4)$. The assumption that kaolinite was the major secondary product is consistent with the prediction based on thermodynamic stability (figure 6.1). Second, release from cation exchange reactions in soils is assumed small compared to the net cation flux in the study area. The third assumption is that biomass represents steady state elemental cycling. The last two assumptions are further discussed in section 6.3 where I will argue that although cation exchange reactions in soils and biomass cycling can not be entirely disregarded their contribution during the monitored storm event is insignificant.

Back-reacting the solid residue with the hydrochemistry enables the relative contribution of individual minerals to be calculated (table 6.2). First, precipitation chemistry was subtracted from the stream water chemistry. Second, all Mg was back-reacted with kaolinite and other species necessary to balance the reaction in order to produce hornblende. Third, remaining K, Na and Ca was back-reacted with kaolinite to make K-feldspar, albite and anorthite respectively. Finally, sulphate was used to produce pyrite.

Table 6.2. Mass-balance reactions.		
Kaolinite + $5Mg^{2+}$ + $2Ca^{2+}$ + $2Na^{+}$ + $16HCO_{3}^{-}$ + $4H_{4}SiO_{4}$ = . Hornblende + $16CO_{2}$ + $17H_{2}O$		
Kaolinite + $2K^+$ + $2HCO_3^-$ + $4H_4SiO_4^-$ = $2K$ -feldspar+ $2CO_2$ +11H ₂ O		
Kaolinite + Ca^{2+} + 2HCO ₃ ⁻ = Anorthite + 2CO ₂ + 3H ₂ O		
Kaolinite+ $2Na^+$ + $2HCO_3^-$ + $4H_4SiO_4^-$ = $2Albite$ + $2CO_2^-$ + $11H_2O_2^-$		
$Fe^{2+} + SO_4^{2-} = Pyrite$		

It was found from the mass-balance calculations that close to 50% of stream flow hydrochemical load in the study area originated from weathering of anorthite (table 6.3). The high

anorthite contribution of solutes is much higher than the proportion of anorthite found in the study site bedrock, which was less then 10% (Gallie, 1983). It does, however, agree well with other hydrochemistry studies in both lowland areas (Clayton, 1988) and in mountain environments (Williams et al. 1993 and Brown personal communication, 1995). Clayton (1988) suggests that such discrepancy could be a result of incongruent release of cations from anorthite, which may result from heterogeneities within minerals. Preferential release of cations from the solid phase could also be a result of disproportionate dissolution from exchange reactions with hydrogen ions in solution (Chou and Wollast, 1985). Chou and Wollast observed in laboratory studies that nonstoichiometric dissolution was an initial transient state lasting of the order of minutes to days before a steady state, stoichiometric dissolution, took over. The process described by Chou and Wollast (1985) could, therefore, be responsible for the large Ca activities present in the study area where the water residence time is low and physical weathering is actively producing fresh new mineral surface areas. Although calcite often is not observed in geochemical analysis it is possible that very small amounts (much less than 1%) could be the main origin of large Ca activities (Mast et al. 1990). They further suggest that eolian dust of calcium carbonate could be another plausible source of dissolved calcium in surface waters.

Small amounts of pyrite are ubiquitous in the basin, and hence

the probable source of the large sulphate activities in the runoff. Oxidation of pyrite generates hydrogen ions, which potentially provides the driving force for chemical weathering in the study area.

• • •

The small standard deviation through-out event #3 (table 6.3, see also appendix V) demonstrates that there is little temporal variation in minerals contributing solutes

Table 6.3. Relative contribution of minerals to hydro- chemistry.					
Mineral	Upper basin	Standard deviation	Lower basin	Standard deviation	
Anorthite	47%	1.3%	47%	1.0%	
Albite	14%	1.0%	13%	0.3%	
K-feldspar	5%	0.2%	5%	0.2%	
Hornblende	10%	0.3%	10%	0.3%	
Pyrite	24%	1.2%	25%	0.9%	
Error % *					
H4Si04	17%	6.2%	13%	5.2%	
HCO3-	-36%	7.4%	-50%	5.4%	
HCO ₃ ^{- i)}	-30%	7.6%	-45%	5.5%	
HCO ₃ ^{- ii)}	22%	6.0%	16%	5.4%	

* Quantification of errors is made by comparing silica and bicarbonate residual activities with those of the hydrochemistry. Bicarbonate is needed for charge balance mass-balance equations, however, charge balance can also be justified by buffering hydrogen ions contributed from ⁱ⁾ rain, and ⁱⁱ⁾ oxidation of pyrite.

(sample B11 has been omitted from calculation as it was assumed an outlier). Although there is a significant dilution effect

during the event the mass-balance approach suggests that the relative proportion of contributing minerals is constant throughout the storm. There is, further, an insignificant difference between the upper and lower station in minerals responsible for the hydrochemical characteristics of the runoff.

6.2.2 VALIDITY OF APPROACH

The mass-balance approach assumes that observed pre-storm water composition is due to weathering of primary minerals and production of a secondary phase. This implies that solute contribution from soils and biota is insignificant, which can only be considered correct if the soil column is bypassed and vegetation experiences steady state conditions. This will be discussed further in the next section.

The quantification of errors in table 6.3, suggests that the calculations predict a residue of both silica and hydrogen ions. The underestimation of silica in the mass-balance for the upper and lower basin of 17% and 13% respectively, could be a result of kinetic barriers forming silica depleted phases such as gibbsite $(Al(OH)_3)$ instead of always producing kaolinite as a secondary mineral. This could further explain the difference between the two sites, where the upper basin depicts a larger silica residue but also experiences more dilute water. The underestimation in the charge balance after bicarbonate, hydrogen ions from rain and from oxidation of pyrite have been

accounted for is not well understood.

The significance of the assumed mass-transfer reactions is reduced by the fact that other minerals, or the same minerals with slightly different stoichiometry, may be involved in weathering. This problem is enhanced at the study site due to the geological complexity of the basin. Although metasediments compose only a small percentage of the north-facing slope, much mixing of this rock type has potentially occurred in the talus. The primary mineralogical difference between the two main rock types is the large proportion of actinolite and chlorite in the metasediments (Gallie, 1983). Actinolite is stoichiometrically close to hornblende, but does not contain Na, chlorite is a potential source for Mg.

A further problem is that the mass-balance calculations above infer a closed system with respect to carbon dioxide. This can be an erroneous assumption in the study area, especially in the coarse talus material where much air can interact with water in the subsurface environment. An open system, however, would increase the production of hydrogen ions in the runoff and thus increase the charge balance error.

6.3 STATISTICAL APPROACH

The statistical relationship between solute activity and stream discharge is useful when identifying biological, chemical and
hydrological processes within drainage basins. In a lowland study in central Sweden, Grip (1982) found interdependence between flow rate and different chemical elements. His statistical analysis showed positive correlation between the concentration of weathering products and low discharge during base flow, and between high discharge during storm flow and the concentration of biologically essential species.

Similar findings to those of Grip (1982) have been observed in mountain environments by Zeman and Slaymaker (1975); Miller and Drever (1977a); Stednick (1987) and Diez et al. (1991). They generally found that the sources of different elements and their concentrations responded differently to changes in flow. With increasing streamflow those elements of lithic origin, such as sodium, magnesium, and silica decrease in concentration. Species associated with organic materials increased in concentration with raised discharge, while species with several sources, such as potassium and calcium, changed according to the main source prevailing under each runoff condition.

6.3.1 RESULTS

Linear correlation between solute activities for individual chemical species and discharge were calculated to investigate the existence of significant relationships between the discharge and the chemical parameters in the study area. The results from the correlation analysis are shown in table 6.4. In general all

constituents except hydrogen ions, exhibit a significant flow dilution relationship. The positive correlation between hydrogen ions and discharge is probably caused by direct channel precipitation and overland flow introducing acid rain water into the stream, hence lowering pH of the stream water during the storm event. Prior to the onset of the precipitation event stream pH was between 7.3 and 7.6. The introduction of acid rain water (pH=5.04) lowered the pH of the stream water to a lowest point of 6.96.

Table 6.4. Correlation between discharge and individual solutes.							
Species	Upper Significance Lower basin at 95% level basin		Lower basin	Significance at 95% level			
K⁺	-0.63	YES	-0.57	YES			
Na⁺	-0.44	NO	-0.81	YES			
Ca ²⁺	-0.76	YES	-0.79	YES			
Mg ²⁺	-0.77	YES	-0.81	YES			
H ₄ SiO ₄	-0.84	YES	-0.83	YES			
S04 ²⁻	-0.77	YES	-0.82	YES			
HCO3-	-0.67	YES	-0.72	YES			
H⁺	+0.67	YES	+0.78	YES			
EC	-0.74	YES	-0.74	YES			

At the upper station the Na activity is behaving somewhat differently from other measured major ions. The lower dilution of Na may be caused by incongruent weathering of the glass fraction of volcanic ash, which is well distributed in Goat Meadows soils (Gallie, 1983). This could suggest that the water

flow path in the upper basin does not entirely by pass the soil column. Gallie (1983) suggests that water in the Goat Meadows Basin partly flows through saturated fingers, which may develop due to spatial variability in surface water-repellency or dynamic instability caused by hydraulic conductivity differences.

At the lower station K experiences somewhat less dilution during high flow than do other major ions. This could potentially be an effect of leaching of organic material during overland flow. The lower dilution of Na at the upper and K at the lower basin suggests that sources other then bedrock are likely contributing certain solutes to the streams in the study area. The effect of Na and K are, however, not statistically significant and should, therefore, be interpreted with caution.

6.4 THERMODYNAMIC APPROACH

Thermodynamics of chemical weathering reactions are used here to examine the extent to which sampled stream water data is in equilibrium with the minerals present in the study area. The approach of graphical representation using chemical thermodynamics in order to identify the stability relationship between solutes and minerals in natural waters has been used frequently in the literature (eg. Miller and Drever, 1977b, Williams et al. 1993).

Recently the interpretation of more complex chemical processes in aqueous systems has been carried out using computer modelling programs, which allow the user to simulate various processes occurring between waters and minerals. Examples of such programs are GEOL PATH (Brown and Perkins, 1978), SOLGASWATER (Eriksson, 1979) and SOLMINEQ.88 (Perkins, 1988) but more than 50 other programs are available that calculate chemical equilibrium in natural waters (Nordstrom and Ball, 1984). An attempt will be made here to find a theoretical hydrochemical evolution path of the stream water chemistry and secondary mineral formation using the program GEOL PATH.

6.4.1 RESULTS

Mineral stability diagrams (figure 6.1) based on thermodynamic relationships from, Brown and Perkins (1978), show that stream waters for event #3 plot in the kaolinite stability field. Stability diagrams are plotted assuming Al is inert and that water temperature is 25° C. $K/H-H_4SiO_4$ and $Na/H-H_4SiO_4$ stability diagrams show similar results to the $Ca/H_2-H_4SiO_4$ diagram depicted in figure 6.1.

The field data plotted in the stability diagram depict an elongated pattern for the two stations. The plotted samples to the right are from base flow whereas those to the left are from peak discharge.

6.4.2 MODEL CALCULATIONS

The theoretical hydrochemical evolution pathway depicted in figure 6.1 is estimated using the reaction-path program, GEOL PATH (Brown and Perkins, 1978). GEOL PATH is a modification of the pioneering program, PATHI (Helgeson et al, 1970). The program calculates the distribution of species in an aqueous solution, assuming that chemical equilibrium is maintained between the solution and secondary minerals. The program further uses irreversible mass transfer between solution and reactant minerals not in equilibrium to calculate the evolution pathway of a set of initial constraints.

A number of assumptions were made regarding initial constraints in the model calculations. First, major ions in the initial solution are considered equal to the precipitation chemistry in the study area. For solutes below the detection limit, an activity of 50% of the limit was chosen. Second, pH of the initial solution was calculated by adding hydrogen ions from i) rain water, and ii) oxidation of pyrite (derived from mass balance calculations). Third, initial reactants are set to the ratio of minerals contributing solutes to runoff as calculated by the mass balance approach (except pyrite which has already been accounted for).



Figure 6.1. Activities of stream water samples from the two monitoring stations plotted on a mineral stability diagram.

6.4.2 DISCUSSION

The temporal variability observable for the two stations in figure 6.1 is caused by dilution of the base flow (data points move along the x-axis toward the gibbsite field) and by an increased hydrogen ion concentration (motivate data to move upward along the y-axis). The spatial variability between the stations is limited. The data points for the upper basin depict, however, a more scattered pattern.

A discrepancy between analyzed stream water data and calculated data was found (see figure 6.1). The inconsistency between actual data and theoretical geochemical pathway may be caused by a number of limitations in the assumptions. These limitations can be summarized as:

- Mass balance approach gave erroneous results leading to faulty initial constraints.
- Due to kinetic barriers, equilibrium between natural waters and minerals is not always achieved
- 3) The thermodynamic data base is inconsistent.
- 4) Theoretical calculations were assuming closed system concerning carbon dioxide, which can lead to an underestimation of hydrogen ions present.

In spite of the many limitations of the thermodynamic approach it is reassuring to note that the field data do approximate

calculated data from the theoretical approach. If nothing else, the field data show that the assumption made in the mass balance approach that kaolinite forms as a secondary mineral in the stream is correct.

6.5 SUMMARY

Three approaches were used in order to analyze the chemical characteristics of the stream water; mass-balance, statistical and thermodynamic. The mass balance approach suggested that approximately 50% of the hydrochemical load originated from anorthite weathering. It further showed that close to 25% of the solutes came from pyrite and the remainder from albite, hornblende and K-feldspar in order of importance. The high anorthite contribution of solutes agrees well with other mountain studies, but is much higher than the proportion of anorthite in the bedrock. Almost no temporal and spatial differences in minerals contributing solutes were observed.

The statistical approach showed that a small difference occurred between the activities of Na at the upper site and K at the lower station and that of other major ions, with increased discharge. The relatively smaller dilution of Na at the upper station compared to that of other major ions at high flow could result from incongruent weathering of the glass fraction of volcanic ash. At the lower basin the smaller dilution of K could be an effect of leaching of organic material during overland

flow. The difference in response is, however, so small that it may be the result of analytical errors.

The stability diagrams, using thermodynamic relationships, showed that the stream water during event #3 was in equilibrium with kaolinite. The temporal variability visible in the stability diagram is caused mainly by dilution during storm flow. Theoretical modelling using GEOL PATH and initial constraints similar to those derived from the mass balance approach approximate the field data. CHAPTER 7 - CONCLUSIONS AND IDEAS FOR FUTURE RESEARCH

Hydrograph separation of rain-driven storm flow into its storm and pre-storm components at the two study sites depicted a much larger pre-storm water fraction (60%-90%) than previously had been expected. Although most lowland studies using stable isotope separation have suggested a pre-storm water fraction of up to 90% during precipitation events it was believed that the steep slopes in combination with hydrophobic soils and coarse talus material would produce a storm water controlled runoff hydrograph. The rapid influx of previously stored water in the study basin during precipitation events is most likely caused by pressure propagation of water from the macropore system. In the hydrophobic soils water is believed to run off as overland flow until it enters the subsurface environment. The displacement effect of water from the macropore system could be enhanced in the subsurface environment by the heavily fractured bedrock in the area acting as efficient hydrological conduits.

The large pre-storm water component generates a relatively long average residence of water in the subsurface environment. This has important implications for the buffering of incoming acid rain water which is mainly controlled by chemical weathering reactions in the soil and bedrock systems. The acid buffering capacity of rain water is noticeable in the comparably small decrease in stream water pH during the precipitation events. The buffering of acid is further observed by the neutralization of the relatively large production of acid due to the oxidation of pyrite in the study area. Hence the study area is not very susceptible to periodic acidification during rain-driven events.

The study suggests that silica and EC can be used as alternative hydrological tracers under certain hydrological and lithological conditions. These alternative tracers should, however, be verified against stable isotope tracers before use, as the conservative behavior depends on specific characteristics of each basin. At the upper basin outlet both EC and silica underestimated the pre-storm contribution. This is probably caused by the coarse talus slope intercepting much of the main stream in the upper basin preventing equilibrium or steady state conditions to be reached. At the lower station silica and EC showed a similar pattern to that of the more conventional The calculated pre-storm deuterium and oxygen-18 tracers. component using EC was, however, 10%-20% lower than the calculated values from the other three tracers. The advantage of using these alternative tracers is that hydrograph separation results can a priori be anticipated. A further advantage of using EC is that it can be continuously measured and stored in dataloggers.

In this study it was hypothesized that a spatial and temporal variability in the hydrochemistry between the two monitoring

sites and during individual rain storms could be recognized. As the hydrochemical variability is a function of the average residence time of water in the unique combination of hydrological reservoirs in each basin it was assumed that the interpretation of short hydrochemical fluxes could help in the interpretation of the variability in solute sources.

The temporal variation in hydrochemistry of the two sites was found to be mainly controlled by the input of dilute event water. However, a marginal difference in response was observed in the activity of Na at the upper and K at the lower station compared to other major ions at increasing discharge. The relatively smaller decrease in Na activity at high flow could result from incongruent weathering of the glass fraction of volcanic ash. For K a similar response could be caused by leaching of organic material during overland flow. The difference in response for Na and K is, however, so small that it could be an effect of analytical uncertainties.

The spatial variation between the two sites is mainly generated by the more dilute character of the upper basin runoff. The more concentrated stream water at the lower basin is probably caused, partly, by re-entering groundwater from the upper basin and partly also by longer average residence time and a more reactive subsurface environment motivated by a more soil covered and lush riparian zone.

Due to the heterogeneity of the studied drainage basins it is difficult to quantify the contribution of water and solutes from the different hydrological reservoirs at a desirable scale. In order to achieve a more complete understanding of individual hydrological reservoirs contribution it would be desirable to study more homogenous drainage basins in order to increase the control over geomorphological and lithological characteristics. Such a study should preferably combine hydrochemical and hydrological tracer data with hydrometric observations in order to achieve a more complete representation of the hydrological pathways and solute sources.

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Appendix I. Activities of stream and precipitation samples.

SAMPLE	DATE	TIME	AK+	aNa+	aCa2+	aMg2+	aH4SiO4	aSO42-	aHCO3-	рН	Charge
			(171)	(101)	(171)	(M)	(111)	(M)	(M)		balance%
P1	6/9	12.00	7.67E-07	3.88E-06	3.46E-06	7.93E-07	B.D.	2.64E-05	B.D.	4.85	-31.8
P2	9/9	14.00	B.D.	3.02E-06	9.90E-07	1.59E-06	B.D.	2.19E-05	B.D.	5.04	-43.4
P3	18/9	14.10	2.30E-06	4.31E-06	9.89E-07	7.94E-07	B.D.	2.69E-05	B.D.	5.32	-56.5
P6 .	6/10	19.00	2.30E-06	1.21E-05	9.89E-07	7.92E-07	B.D.	2.81E-05	B.D.	5.06	-35.7
SAMPLE	DATE	TIME	aK+	aNa+	aCa2+	aMg2+	aH4SiO4	aSO42-	aHCO3-	Ha	Charge
			(M)	·	balance%						
B4	2/9	10.20	1.10E-05	3.56E-05	1.18E-04	1.29E-05	1 08F-04	5 59E-05	2 19E-04	7 37	-3.6
B6	4/9	14.30	1.22E-05	3.77E-05	1.22E-04	1.37E-05	1.13E-04	5.46E-05	2 11F-04	7.32	0.3
B7	6/9	11.00	1.10E-05	3.56E-05	1.14E-04	1.33E-05	1.06E-04	5.16E-05	2.03E-04	7.31	-0.8
B9	7/9	21.00	1.02E-05	3.23E-05	9.85E-05	1.16E-05	9.15E-05	4.93E-05	1.79E-04	7.28	-27
B10	7/9	23.00	7.51E-06	2.72E-05	7.51E-05	8.30E-06	6.73E-05	3.85E-05	1.39E-04	7.18	-3.4
B11	8/9	03.00	1.07E-05	4.42E-05	8.03E-05	9.38E-06	6.98E-05	4.26E-05	1.63E-04	7.10	-2.8
B12	8/9	07.00	8.26E-06	2.85E-05	7.39E-05	8.68E-06	6.44E-05	3.32E-05	1.55E-04	7.03	-4.6
B13	.8/9	11.00	7.02E-06	2.47E-05	6.74E-05	7.97E-06	6.27E-05	3.20E-05	1.22E-04	7.06	-1.0
B15 ·	8/9	19.00	7.51E-06	2.64E-05	7.39E-05	8.30E-06	7.01E-05	3.95E-05	1.39E-04	7.18	-4.6
B16	8/9	23.00	9.01E-06	2.64E-05	7.81E-05	9.04E-06	7.26E-05	3.79E-05	1.55E-04	7.02	-4.7
B17	9/9	03.00	7.51E-06	2.55E-05	7.85E-05	9.06E-06	7.51E-05	3.29E-05	1.47E-04	7.09	-1.0
B19	9/9	13,00	9.98E-06	3.31E-05	9.82E-05	1.19E-05	9.44E-05	4.93E-05	2.03E-04	7.22	-6.8
		·									
SAMPLE	DATE	TIME	aK+	aNa+	aCa2+	aMg2+	aH4SiO4	aSO42-	aHCO3-	ρН	Charge
			(M)		balance%						
A5	4/9	15.30	1.29E-05	4.10E-05	1.31E-04	1.43E-05	1.05E-04	6.56E-05	2.10E-04	7.48	0.3
A7	6/9	12,45	1.24E-05	3.93E-05	1.27E-04	1.36E-05	1.05E-04	6.62E-05	2.11E-04	7.66	-1.5
A8	7/9	16.00	1.34E-05	3.98E-05	1.29E-04	1.36E-05	1.06E-04	6.19E-05	2.11E-04	7.24	0.6
A9 -	7/9	20.15	1.27E-05	3.69E-05	1.11E-04	1.19E-05	9.76E-05	5.86E-05	1.95E-04	7.09	-27
A10	7/9	23.15	1.32E-05	3.47E-05	1.24E-04	1.29E-05	9.76E-05	5.61E-05	2.11E-04	7.02	-0.3
A11	8/9	01.15	1.07E-05	3.22E-05	1.01E-04	1.15E-05	9.08E-05	5.42E-05	1.87E-04	6.99	-4.9
A12	8/9	03.15	1.07E-05	3.27E-05	1.04E-04	1.15E-05	8.65E-05	5.23E-05	1.79E-04	6,96	-1.7
A13	8/9	05.15	1.05E-05	3.18E-05	1.01E-04	1.12E-05	8.40E-05	5.01E-05	1.71E-04	6.96	-0.8
A14	8/9	07.15	1.02E-05	2.97E-05	9.62E-05	1.05E-05	8.08E-05	4.96E-05	1.63E-04	6.96	-1.6
A15	8/9	09.15	8.74E-06	2.85E-05	8.75E-05	9.74E-06	7.76E-05	4.93E-05	1.46E-04	6.96	-2.8
A17	8/9	13.15	8.99E-06	2.89E-05	8.92E-05	9.36E-06	8.15E-05	5.01E-05	1.46E-04	7.04	-2.4
A18	8/9	15.15	8.49E-06	2.80E-05	9.02E-05	9.74E-06	8.12E-05	4.75E-05	1.46E-04	7.08	-1.0
A21	9/9	03.15	9.97E-06	3.22E-05	1.07E-04	1.11E-05	9.01E-05	5.42E-05	1.87E-04	6.98	-2.8
A22	9/9	07.15	9.73E-06	3.22E-05	1.05E-04	1.19E-05	9.22E-05	5.21E-05	1.79E-04	7.00	-1.3
A23	9/9	13.15	1.05E-05	3.52E-05	1.12E-04	1.26E-05	9.22E-05	5.68E-05	1.87E-04	7.19	-0.9
A24	9/9	19.10	1.32E-05	3.89E-05	1.28E-04	1.40E-05	1.01E-04	6.20E-05	2.02E-04	7.12	1.3

B.D.=below detection limit

Precipitation samples

SAMPLE	Date	Time	mm	Deterium	Oxygen-18
P2 (3)	8/9	07.30	1.5	-70	-10.1
P3 (1)	8/9	18.10	21.2	-74	-10.4
P4 (2)	8/9	18.20	21.4	-70	-10.5
P5 (3)	8/9	18.30	20.8	-71	-10.7
P6 (3)	9/9	13.00	3.4	-81	-11.8

Stream water samples from upper station

SAMPLE	Date	Time -	Qt	Deterium	Oxygen-18	Qp (det)	Qp (ox)	Qp (avg)
			4.05	105	16.0	1 02	1 89	1.90
B5	3/9	12.30	1.95	-120	-10.9	1.92	0.40	0.11
B6	4/9	14.30	2.08	-126	-17.4	2.05	2.18	2.11
B7	6/9	11.00	1.95	-129	-17.0	2.01	1.93	1.97
B8	7/9	18.50	3.03	-124	-17.0	2.87	2.98	2.93
B9	7/9	21.00	4.41	-121	-16.6	3.94	4.07	4.01
B10	7/9	23.00	4.74	-117	-16.1	3.89	4.02	- 3.96
B11	8/9	03.00	5.09	-114	-16.1	3.90	4.32	4.11
B12	8/9	07.00	5.21	-112	-15.8	3.81	4,18	3.99
B13	8/9	11.00	6.50	-110	-15.4	4.51	4.82	4.66
B14	8/9	15.00	4.86	-109	-15.3	3.28	3.52	3.40
B15	8/9	19.00	3.88	-114	-15.8	. 2.97	3.11	3.04
B16	8/9	23.00	3.49	-114	-15.8	2.67	2.80	2.73
B17	9/9	03.00	3.39	-115	-16.0	2.66	2.82	2.74
B18	9/9	07.00	2.69	-119	-16.1	2.31	2.28	2.29
B19	9/9	13.00	2.45	-119	-16.6	2.10	2.27	2.18
B20	9/9	19.00	2.38	-112	-16.6	1.73	2.19	1.96

Stream wa	ater samples t	from lower sta	ation			,	7	
A6	3/9	13.00	4,24	-122	-17.0	4.08 ,	4.18	4.13
A5	4/9	15.30	4.48	-121	-17.3	4.23	4.62	4.42
A8	7/9	16,00	4.36	-129	-17.0	4.77	4.29	4.53
A9	7/9	20.15	8.12	-122	-16.6	7.82	7.50	7.66
A10	7/9	23.15	9.86	-116	· -16.3	8.35	8.65	8.50
A11	8/9	01.15	10.48	-120	-16.1	9.69	8.88	9.28
A12	8/9	03.15	10.70	-116	-15.9	9.06	8.74	8.90
A13	8/9	05.15	12.28	-113	-15.6	9.69	9.46	9.58
A14	8/9	07.15	10.91	-111	-15.6	8.10	8.41	8.25
A15	8/9	09.15	11.58	-102	-15.3	6.70	8.40	7.55
A16	8/9	11.15	13.00	-109	-15.4	9.27	9.62	9.44
A17	8/9	13.15	12.04	-111	-15.3	9.05	8.73	8.89
A18	8/9	15.15	9.86	-112	-15.4	7.59	7.30	7.45
A19	8/9	19.15	7.94	-109	-15.5	5.66	6.00	4.62
A20	8/9	23.15	7.42	-107	-15.7	5.00	5.83	4.41
A21	9/9	03.15	7.08	-110	-16.0	5.18	5.89	5.54
A22	9/9	07.15	5.83	-117	-16.1	5.05	4.94	5.00
A23	9/9	13.15	5.00	-123	-16.3	4.90	4.39	4.64
A24	9/9	19.10	5.00	-122	-16.6	4.81	4.61	4.71

Appendix III. Hydrograph separation using silica.

SAMPLE	Date	Time	Qt	Si (M)	Qp (Si)
B4	2/9	10.20	2.15	1.08E-04	2.13
B6	4/9	14.30	2.08	1.13E-04	2.16
B7	6/9	11.00	1.95	1.06E-04	1.89
B9	7/9	21.00	4.41	9.15E-05	3.70
B10	7/9	23.00	4.74	6.73E-05	2.93
B11	8/9	03.00	5.09	6.98E-05	3.26
B12	8/9	07.00	5.21	6.44E-05	3.08
B13	8/9	11.00	6.50	6.27E-05	3.74
B15	8/9	19.00	3.88	7.01E-05	2.50
B16	8/9	23.00	3.49	7.26E-05	2.32
B17	9/9	03.00	3.39	7.51E-05	2.34
B19	9/9	13.00	2.45	9.44E-05	2.12

Stream water samples from upper station

Stream water samples from lower station

A5	4/9	15.30	4.48	1.05E-04	4.47
A7	6/9	12.45	4.24	1.05E-04	4.23
A8	7/9	16.00	4.36	1.06E-04	4.38
A9	7/9	20.15	8.12	9.76E-05	7.53
A10	7/9	23.15	9.86	9.76E-05	9.13
A11	8/9.	01.15	10.48	9.08E-05	9.04
A12	8/9	03.15	10.70	8.65E-05	8.79
A13	8/9	05.15	12.28	8.40E-05	9.80
A14	8/9	07.15	10.91	8.08E-05	8.38
A15	8/9	09.15	11.58	7.76E-05	8.54
A17	8/9	13.15	12.04	8.15E-05	9.33
A18	8/9	15.15	9.86	8.12E-05	7.60
A21	9/9	03.15	7.08	9.01E-05	6.06
A22	9/9	07.15	5.83	9.22E-05	5.11
A23	9/9	13.15	5.00	9.22E-05	4.38
A24	9/9	19.10	5.00	1.01E-04	4.78

Silica in precipitation was below detection limit

Appendix IV. Hydrograph separation using EC.

SAMPLE	Date	Time	Qt	EC	Qp (EC)
B8	7/9	18.50	3.03	0.0211	3.05
В9	7/9	21.00	4.41	0.0197	4.02
B10	7/9	23.00	4.74	0.0141	2.55
B11	8/9	03.00	5.09	0.0142	2.76
B12	8/9	07.00	5.21	0.0121	2.09
B13	8/9	11.00	6.50	0.0120	2.58
B14	8/9	15.00	4.86	0.0101	1.30
B15	8/9	19.00	3.88	0.0121	1.55
B16	8/9	23.00	3.49	0.0130	1.60
B17	9/9	03.00	3.39	0.0123	1.40
B18	9/9	07.00	2.69	0.0164	. 1.85
B19	9/9	13.00	2.45	0.0180	1.95

Stream water sample from upper station

Stream water sample from lower station

A5	4/9	15.30	4.48	0.0401	4.58
A7	6/9	12.45	4.24	0.0394	4.24
A8	7/9	16.00	4.36	0.0391	4.33
A9	7/9	20.15	8.12	0.0371	7.55
A10	7/9	23.15	9.86	0.0325	7.82
A11	8/9	01.15	10.48	0.0310	7.85
A12	8/9	03.15	10.70	0.0294	7.47
A13	8/9	05.15	12.28	0.0281	8.10
A14	8/9	07.15	10.91	0.0268	6.78
A15	8/9	09.15	11.58	0.0255	6.74
A16	8/9	11.15	13.00	0.0262	7.83
A17	8/9	13.15	12.04	0.0250	6.81
A18	8/9	15.15	9.86	0.0251	5.62
A19	8/9	19.15	7.94	0.0284	5.31
A20	8/9	23.15	7,42	0.0299	5.29
A21	9/9	03.15	7.08	0.0305	5.20
A22	9/9	07.15	5.83	0.0306	4.30
A23	9/9	13.15.	5.00	0.0332	4.06
A24	9/9	19.10	5.00	0.0367	4.59

Appendix V. Mass balance calculations.

r reportion of minerals contributing to upper station hydrochemistry						Residuais in %		subtract		
SAMPLE	Anorthite	Albite	K-spar	Hornblend	Pyrite	.'			`H+ rain	H+ pyr
							Si	HCO3-	HCO3-	HCO3-
B4	0.48	0.13	0.05	0.10	0.24		21.98	-35.02	-30.85	20.25
B6	0.49	0.13	0.05	0.10	0.23		19.44	-46.91	-42.58	9.24
B7	0.48	0.13	0.05	0.11	0.23	•	20.44	-42.45	-37.95	12.93
B8	0.45	0.15	0.05	0.10	0.25	r_{i}	6.89	-43.77	-38.15	21.29
B9	0.47	0.14	0.05	0.10	0.24	. *	17.53	-40.17	-35.06	20.14
B10	0.46	0.15	0.05	0.10	0.25	1.1	13.00	-36.64	-30.06	25.51
B11	0.41	0.22	0.06	0.09	0.23		-42.49	-36.54	-30.95	21.39
B12	0.46	0.16	0.05	0.10	0.22		2.58	-22.62	-16.75	26.19
B13	0.46	0.15	0.05	0.10	0.23		16.43	-39.14	-31.71	20.56
B15	0.45	0.15	0.05	0.10	0.25		18.96	-34.38	-27.80	29.26
B16	0.46	0.14	0.06	0.10	0.24		17.20	-27.63	-21.76	27.25
B17	0.49	0.14	0.05	0.11	0.21		26.15	-33.60	-27.39	17.53
B19	0.46	0.14	0.05	0.11	0.24		18.61	-23.67	-19.18	29.38

Proportion of minerals contributing to upper station hydrochemistry

Proportion of minerals contributing to lower station hydrochemistry

A5	0.47	0.13	0.05	0.10	0.25	5.12	-57.60	-53.26	9.09
A7	0.47	0.13	0.05	0.09	0.26	9.57	-52.36	-48.00	14.94
A8	0.48	0.13	0.05	0.10	0.24	7.49	-54.77	-50.44	8.39
A9	0.46	0.14	0.05	0.09	0.25	7.99	-45.61	-40.93	19.26
A10	0.49	0.12	0.05	0.10	0.23	10.89	-46.52	-42.21	11.05
A11	0.46	0.13	0.05	0.10	0.26	15.84	-36.80	-31.94	26.11
A12	0.47	0.13	0.05	0.10	0.25	10.70	-46.31	-41.23	17.30
A13	0.47	0.13	0.05	0.10	0.24	10.81	-48.94	-43.62	15.08
A14	0.47	0.13	0.05	0.10	0.25	13.50	-48.36	-42.78	18.23
A15	0.46	0.13	0.05	0.10	0.27	17.39	-49.90	-43.71	23.59
A17	0.46	0.13	0.05	0.09	0.27	19.93	-52.27	-46.06	22.43
A18	0.47	0.13	0.05	0.10	0.26	22.69	-53,14	-46.93	17.96
A21	0.48	0.13	0.05	0.09	0.25	17.07	-42.88	-38.02	20.07
A22	0.47	0.13	0.05	0.10	0.25	19.13	-47.42	-42.34	16.00
A23	0.47	0.13	0.05	0.10	0.25	10.81	-51.41	-46.53	14.32
A24	0.48	0.13	0.05	0.10	0.24	4.90	-59.53	-55.03	6.26