STREAMWATER QUALITY AS AFFECTED BY SOURCE OF FLOW ON A SMALL FORESTED WATERSHED IN CENTRAL ARKANSAS

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Submitted to the Faculty of the
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Oklahoma State University
in partial fulfillment of
the requirements for
the degree of
DOCTOR OF PHILOSOPHY
July, 1993

OKLAHOMA STATE UNIVERSITY

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ACKNOWLEDGEMENTS

I am lucky to have gained a great deal of experience from the outstanding people I worked with during my doctoral research. I am especially grateful to my major advisor, Dr. Edwin L. Miller for his motivation, friendship, guidance and his confidence in me during my study at Oklahoma State University. I would also like to thank Dr. Donald J. Turton for his helpful comments, ideas and criticism. Thanks goes out to the remaining members of my committee; Dr. Arthur Hounslow and Dr. Scott W. Fargo for their advise and insightful review of my manuscript. Their input and support are highly appreciated. Thanks to Michale Kress for his help in the field.

I am grateful to fellow graduate students for their friendship and help provided throughout my tenure at Oklahoma State University. A special thanks goes to Dr. Ronald S. Beer, Vice President for student services and Dr. Jack D. Vitek, the Coordinator of Environmental Science programs for their understanding and support.

A special thanks goes to my great friend, Mike Williams and his wife, Patricia.

Finally, I would like to acknowledge the support of my family members, emotionally and financially. My family taught me to be persistent and to work hard for there is a

ray of light at the end of darkness, with faith and hope. I am grateful for my wife, Sameria, my sons, Saief and Zaied and my daughters Rawaidea and Noor, their patient and love enabled me to complete this degree.

This work was completed in the mist of a most turbulent period of my existence and even with our lives on a balance, the memory of my childhood gave me the strength, the faith and the hope to rise above these stormy periods. For these reasons, I dedicate this work to my family.

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CHAPTER I

INTRODUCTION

Purpose

Streamwater quality is dependent on many interrelated and complex factors. The major components of streamflow and chemical constituents are precipitation, throughfall, baseflow (groundwater discharge), overland flow, and subsurface flow. Steeply sloping, undisturbed, forested watersheds, such as the one in this study, can provide a significant portion of water for municipalities, fisheries, and recreational uses. Therefore, research has been conducted to determine the impacts of the various subsurface pathways of water flow on the quality of streamwater (Whipkey, 1965 and 1967; Betson and Marius, 1969; Hewlett and Nutter, 1970; Dunne et al., 1975; Glass et al., 1988; Turton, 1989).

Maintaining streamwater quality is one of the most important objectives of the Federal Water Pollution Control Act Amendment of 1972, the Safe Drinking Water Act of 1974, the 1977 Clean Water Act, and the Water Quality Act of 1987. Many state and local regulations have also emphasized the importance of protecting and improving water quality.

During the past decade, attempts have been made to understand water movement and chemical transport mechanisms in the unsaturated and saturated zones. Recently, attention has once again been focused on this area as concern over agricultural land use has stirred interest in pursuing a thorough understanding of streamflow processes.

This study seeks to relate observed variations in streamwater chemistry to runoff sources under different hydrologic conditions for an undisturbed, forested watershed in Central Arkansas. The study also seeks to contribute to a better understanding of flow processes, pollutant transport mechanisms, and water quality management. This, in turn, will aid in predicting and preventing streamwater and groundwater contamination.

Problem Statement

In field situations, water chemistry is dependent on factors such as soil chemical properties, climate, vegetation, geology of the study site, and the duration of contact of water with soil materials. A combination of field and laboratory studies is required for a comprehensive understanding of subsurface flow and chemistry. The results of field work and quantitative laboratory analysis need to be delivered to a thorough theoretical consideration if our understanding of subsurface flow and chemical transport mechanisms is to be advanced which will allow an understanding of the relationships between solute runoff and element cycling in undisturbed ecosystems.

Very little research has been conducted in describing subsurface flow and streamwater chemistry in undisturbed forested watersheds of the Ouachita mountains. The only detailed study that has been done on subsurface flow contribution to total streamflow and streamwater chemistry in the area is as presented by Turton (1989). Thus, to interpret observations that were obtained from sampling subsurface pathways of water flow, a basic understanding of the elemental transport process is needed. The changes in chemical, biological, and hydrological processes over time within each soil horizon may influence or could have significant impacts on the cycling and migration of particular elements or dissolved constituents in the soil horizons. Such understanding of elemental migration is also needed to validate explanations of how various flow horizons combine to produce streamwater chemistry.

The ultimate goal of this study is to provide information on the influence of various soil horizons on streamwater quality. Changes in the chemical properties of inputs from precipitation and throughfall, when compared with streamwater quality, allow deductions to be made on the influence of the different soil horizons.

In addition, an understanding of land use and chemical transport mechanisms through saturated and unsaturated zones to the stream and groundwater are necessary in predicting and preventing streamwater pollution and groundwater contamination (Glass et al., 1988).

Objectives

The primary objectives of this study are:

1) Characterizing and comparing the chemistry of subsurface flow from soil horizons.

2) Relating and determining the influence of subsurface flow and chemistry from the soil horizons on streamwater quality.

3) Determining inputs and outputs of selected constituents of a forested watershed.

These objectives can be accomplished by calculating:

A) The subsurface flow contribution per layer to the total streamflow.

B) The chemical concentrations and loads of the rainfall and throughfall.

C) The chemical concentrations and loads for each soil horizon.

D) The chemical concentrations and loads for streamwater at the watershed outlet.

Detailed observations of the chemical changes which occur will be used to determine the contribution of subsurface flow from different horizons to total streamwater chemistry.

Terminology

Bulk Precipitation: The combination of wetfall (rain) and dryfall (dust, debris) leaving the atmosphere and settling on a surface.

Throughfall: That part of wet precipitation falling through the canopy including water drip from wetted leaves and branches.

Subsurface Flow: The process of water flowing beneath and parallel to the soil surface toward a channel without reaching groundwater.

Baseflow: One of the contributing sources which may act as a streamflow; usually synonymous with groundwater discharge and takes place between periods of stormflow.

Streamflow: Streamflow results from a combination of overland flow, subsurface flow and baseflow produced by storm events contributing rainfall or snow. However, in most undisturbed, forested watersheds, overland flow is uncommon.

CHAPTER II

REVIEW OF LITERATURE

Streamflow Generating Processes

Many field studies have been reported on streamflow generating processes and the movement of water through forest soils. (Hewlett, 1961; Whipkey, 1965; Hewlett and Hibbert, 1967; Sloan et al., 1983). There are two generally accepted models of streamflow generation at the watershed scale:

1) The Hortonian (1933) concept of stormflow runoff generation which involves the relationship between rainfall intensities and soil infiltration and percolation rates. This concept emphasizes the importance of overland flow on the generation of streamflow and especially stormflow.

2) Hursh (1936) and Hewlett and Hibbert (1967) introduced the concepts of variable source area and subsurface stormflow, and suggested that saturation overland flow, unsaturated interflow and return flow are all important in streamflow generation.

Hydrologic processes are a function of time, space, vegetation, topography, soils, and geology (Whipkey, 1965; Hewlett and Nutter, 1970; Dunne, 1978). Consequently, the processes are complicated and difficult to quantify.

Unfortunately, there has been inadequate work dealing with undisturbed forested watersheds where the variable source area concept of flow generation applies. Much of the quantitative research on streamflow has dealt with the Hortonian concept (Horton, 1933 and 1940) as a basis for understanding the flow generating processes. According to this hypothesis, the greatest proportion of stormflow is comprised of surface runoff which occurs when rainfall intensities exceed soil infiltration rates. Even though some investigators doubt that subsurface flow can be a dominant mechanism in generating stormflow (Freeze, 1972 and Smith and Hibbert, 1983), it has been widely recognized that Horton's concept represents only one extreme of the numerous mechanisms involved in stormflow generation. Hursh (1936 and 1944) represents the other extreme which considers the process expressed in the variable source area concept as the only mechanisms involved in generating stormflow. Various field studies have reported incidents where both of these extremes have been observed either individually or in combination.

In undisturbed forested regions, overland flow generally does not occur except in saturated zones around stream channels. This is primarily because of the occurrence of highly permeable soil horizons and high infiltration rates which exceed the rainfall intensities of most storms. However, subsurface lateral flow, return flow, and saturation overland flow (expanding and shrinking saturated zones) can potentially be major contributors to stormflow. In fact the proportion of the storm precipitation that leaves forested regions as rapid subsurface flow from upper slopes to stream channels is thought to be a significant, if not predominant, component of total stormflow (Whipkey, 1965 and 1967; Hewlett and Hibbert, 1967; Weyman, 1973; Beasley, 1976; Dunne, 1978; Pilgrim et al., 1978; Mosley, 1979; Bevin and Germann, 1981 and 1982; Germann, 1986).

Various researchers have investigated the contribution of subsurface flow to total stormflow on forested watersheds. Beasley (1976) reported that during wet periods 88 to 92 percent of 75.4 cm of total rain emerged as subsurface flow. In a study conducted in the Jamieson Creek watershed (Cheng, 1988), 55 percent of a 76 mm storm was produced as subsurface flow. Recently , Turton (1989) concluded that up to 48 percent of total streamflow volume was contributed by subsurface flow, on a small forested watershed in southeastern Oklahoma.

Numerous researchers have reported that subsurface flow controls streamflow generation due to steep hillslopes, highly permeable soil horizons underlain by less permeable layers, and narrow valley bottoms. Also, saturation overland flow can account for quick release to the streamflow and an increase or decrease in response to precipitation input (Dunne and Black, 1970; Hewlett and

Nutter, 1970; Turton, 1989). In an undisturbed forested watershed, interflow represents that portion of subsurface flow beneath and parallel to the soil surface and flows downslope toward a channel. In steep watersheds, interflow may have a vertical or horizontal flow component, and it may be saturated or unsaturated.

Experimental evidence has indicated that sloping forested watersheds contribute to streamflow through variable source areas, interflow and baseflow (Hewlett and Hibbert, 1963; Whipkey, 1965; Weyman, 1973; Dunne and Leopold, 1978; Pilgrim et al., 1978). However, increasing evidence suggests that interflow from variable source areas may be diverted to saturation overland flow in water-saturated zones adjacent to riparian zones (Dunne et al., 1975; Hewlett and Troendle, 1975; O'Loughlin, 1981 and 1986; Anderson and Kneale, 1982).

Water Balance

The water balance of a watershed refers to the quantification of the major components of the hydrologic cycle. On an algebraic basis the water balance can be expressed as :

$$Pg = E_t + Q \pm \Delta S$$

where:

Pg = Precipitation
E_t = Evapotranspiration
Q = Streamflow
ΔS = Storage

When it is convenient or necessary, each of the terms in the water balance equation can be further divided into respective components. For example, evapotranspiration can be subdivided as follows:

$$E_t = T + I_t + E_s + E_o$$

where:

E_t = Evapotranspiration

T = Transpiration

I_t = Total Interception

E_s = Evaporation from soil

E_o = Evaporation from open water

The annual average precipitation at the Alum Creek watershed is about 132 cm with negligible snow and ice. During a study by Miller et al. (1988), annual total precipitation for the years 1979 to 1983 ranged from 72 to 142 percent of the long range average precipitation (132 cm). The rainfall in the watershed is seasonal, with over 50 percent of the rainfall produced during the spring (N.O.A.A., 1987). Miller et al. (1988) also reported one rainfall in excess of 34.3 cm occurred within 24 hours in December 1982. The watershed climate is classified as temperate-humid and cold during the winter with an average of 6.1 degrees Celsius (^{o}C) and hot during the summer with an average maximum temperature of 32.8^{o}C.

In order to estimate the nutrient budgets for a watershed, water balance measurements or estimates are required. This is because water is one of the primary vehicles for nutrient input to the watershed, water aids in the cycling of nutrients within the watershed system, and streamflow is the primary means by which nutrients leave the watershed (Likens 1977; Swank and Waide, 1988; Jorgensen and Wells, 1986). Rogerson (1976) reported that for the Ouachita Mountain Drainages, of an annual precipitation of 144.3 cm (56.81 inches), 14 percent was stormflow, 60 percent was lost as evapotranspiration while about 27 percent was lost as deep seepage and baseflow. Another study was done by Rogerson and Lawson (1982) in the Boston Mountains of Northern Arkansas and Eastern Oklahoma representing 1.4 million ha of low to moderate value forests. Rogerson and Lawson observed that of the annual precipitation of 82 cm falling on a watershed, about two-thirds was lost to the atmosphere as evapotranspiration. For individual storms, the water budget varied considerably from the annual percentages.

Throughfall, which represents the part of wet precipitation which reaches forest floor through the canopy, varies on the average from 80% to 95% of precipitation. The amount and variability of the throughfall in a forested ecosystem is affected by rainfall intensity and vegetative canopy density (Lawson, 1967; Likens et al., 1977; Dunne and Leopold, 1978; Clingenpeel, 1980). In Ouachita Mountain forests, Beasley et al. (1988) found that throughfall in a pine plantation watershed accounted for 83.4 percent of total gross precipitation and 87.3 percent of total gross precipitation in a mixed pine hardwood watershed. Henderson et al. (1977) reported that dormant season throughfall averaged as high as 89 percent of incident precipitation while growing season throughfall averaged 87 percent.

Evapotranspiration will tend to be a minor component of the hydrologic cycle during the cold season. Evapotranspiration increases and reaches a maximum loss during the summer season. Rogerson and Lawson (1982) reported that summer storms of short duration produce small amounts of runoff due to the high evapotranspiration levels which increase soil water deficits. Gilliam (1983) reported that mean monthly volumes of 10.9 cm of precipitation from 1976 to 1980 at Santee watershed resulted in a 8.3 cm loss due to evapotranspiration. The subsurface flow produced during the winter was observed to be higher than in summer due to the combined effects of low winter temperatures and evapotranspiration in the study area (Beasley, 1976). Evapotranspiration, which depends on the temperature and vegetation density, was reported to be 45 cm out of 380 cm of precipitation in Western Olympic Mountain (Wooldridge and Larson, 1980). During the summer season about two-thirds of precipitation was lost due to evapotranspiration in a pine spruce ecosystem with shallow soils (Niclson, 1987). Miller et al. (1988) reported that the summer stormflows from Arkansas watersheds study area were lower than the other seasons indicating high levels of evapotranspiration. This observation is similar to those of Elwood and Henderson

(1975) for Walker Branch at Oak Ridge, Tennessee where the streamflow was maximum during the wet periods due to the wet soil and low evapotranspiration. The annual loss through evapotranspiration in an Oak Ridge study area was estimated at 655 mm/year out of 1368 mm/year mean precipitation (Luxmoore and Huff, 1989).

Flow Processes and Water Chemistry

In forested watersheds, the cycling of nutrients generally occurs between plants, soil and atmospher. Rainfall interacts in the forest watersheds both as a source of nutrients and as the primary vehicle of nutrient movement. It is also the source of streamflow which is the primary route for elements to flow out of the ecosystem. Some proportion of rainwater is intercepted by the canopies, but the remainder reaches the forest floor directly or as throughfall. A small amount of precipitation may reach the streamflow directly through direct channel interception.

Some solutes, carried by rainfall and throughfall, infiltrate the soil and may reach streams relatively quickly, while others are leached into the groundwater. Portions of the soil water return to the atmosphere by evapotranspiration and leave solutes in the soil. Therefore, water quality changes as input water migrates through the watershed. The solute concentrations in each compartment of the flow generation processes differs according to the input sources and the routes of the water as it passes through diverse pathways in the soil matrix, cracks, and biologically induced channels (i.e. plant root cavities) (Aubertin, 1971; Hill and Parlange, 1972; Blake et al., 1973; Wilson and Luxmoore, 1988; Turton, 1989).

The concentrations of some elements decrease because of plant uptake and soil absorption, while the concentrations of other elements increase because of contact and exchange with the soil and the weathering of basic bedrock materials (Crabtree and Trudgill, 1985 and Dowd and Nutter, 1985).

Precipitation

Precipitation serves as a major contributor of nutrients to the ecosystem. The chemistry of precipitation originates from a variety of sources, including oceanic spray, terrestrial dust, gaseous pollutants, and volcanic emissions. The chemical concentration of precipitation (wetfall and dryfall) varies greatly across the southern United States and the earth. In order to measure precipitation chemistry at a particular location, precipitation samples collected on a storm basis must be obtained from an experimental area, such as a watershed (Likens et al., 1977 and Reid et al., 1981).

There is concern worldwide about precipitation chemistry and especially the biogeochemical effects of excess acidity in precipitation. The pH of natural rainfall which is in equilibrium with atmospheric carbon dioxide is considered to be 5.6 (Wooldridge and Larson, 1980). Nix and Thornton reported that mean annual rainfall pH for the south is considered to be acidic (pH < 5.0). In the Kiamici Mountains of southeastern Oklahoma, Kress et al. (1990) reported that the mean pH of bulk precipitation to be about 4.9. Excess acidity in precipitation can greatly depress the pH value of a solution as low as 3.0, even though only small amounts of strong mineral acids, such as H_2SO_4 are present. This can increase the amount of hydrogen ions, which, in turn, can potentially increase the effects on biological and chemical systems, particularly the leaching of cations from the vegetation canopy and soils. Furthermore, excess acidity in rainfall affects life on land and in water (Likens et al., 1977; Mclean, 1981). Although many researchers have identified negative effects of acid precipitation there may be some positive effects. For example, increasing nitrate concentrations in the precipitation may act as nitrogen fertilizer which could increase the productivity of the ecosystem (Likens et al., 1977; Lewis, 1981; Mclean, 1981).

Rainfall samples collected near the ocean generally reveal high sodium (Na) and chloride (Cl) concentrations together with less quantities of magnesium and sulfate. In a study conducted at Santee Forest, Richter and Ralston (1983) reported that the volume-weighted mean concentration of chloride and sodium were 1.06 and 0.42 mg/l, respectively. These values represent a higher ratio of chloride to sodium than the seawater ratio of 1.80. Samples from large industrial areas may have different ratios of these ions. Industrial samples are generally not similar to samples from the sea or any large bodies of water and show changing elemental concentrations due to other atmospheric influences. The chemicals in the atmosphere of industrial areas may react with water to form sulfuric and nitric acids due to the burning of fossil fuels. This alters the chemistry of the precipitation by contributing sulfur dioxides and nitrous oxides to the atmosphere. However, areas close to sources of pollution are not the only ones to show the presence of pollution (Likens, 1976; Likens et al., 1977; Reid et al., 1981). For example, Beasley et al., (1988) suggested that the aerosols from the Gulf of Mexico, are more likely the source of the high sodium inputs in the Ouachita Mountains.

Dry deposition of particulate matter is an important source of chemical inputs and is considered a part of bulk precipitation, the total of wet precipitation and dry deposition. Likens (1977) noted that bulk precipitation collectors may be very inefficient in collecting particles of dry deposits smaller than 1 μm. Swank and Waide (1988) reported that dry deposits contributed 10 to 22 percent of the total cation inputs of bulk precipitation with Ca^{+2} and K^{+1} being the highest. Likens, (1977) also stated that gaseous forms of nitrogen and sulfur may be generated by biogenic activity and by the combustion of fossil fuels. These gases can travel long distances in the atmosphere.

The Hubbard Brook experiment (Likens, 1977) showed that higher concentrations of nitrogen and sulfur gases exist in the atmosphere than would be expected from that local environment, and that dry deposition is underestimated by bulk precipitation collectors. The same study also found that long-term averages of cations and anions in precipitation are approximately balanced and the sulfate and hydrogen ions are the most prevalent inorganic ions in bulk precipitation.

Investigators, including Likens et al.(1967 and 1977), have concluded that there is no significant difference in the content of Ca, Mg, Na, K, NH_4, or Cl in precipitation samples collected at different elevations from their experimental watersheds. Specifically Likens (1977) reported no significant difference (P < 5 percent) in the chemistry of precipitation samples collected at 610 m mean sea level (MSL) and those at 252 m MSL.

Throughfall

The plant biomass influences the quantity and quality of incoming precipitation in a number of ways and to varying degrees. Dissolved substances in throughfall come from two different sources:

1) Outside the forested ecosystem: nutrients are contained in the incident precipitation and nutrient-impacted aerosols are washed off by the incident precipitation.

2) Within the ecosystem: nutrients with a normal gaseous phase which react with SO_2 or NH_3 are removed from plant tissues by incident precipitation and other nutrients which have been leached from plant tissues or associated with microflora (Likens et al., 1977).

Leaf interception can affect the chemistry of incoming water by altering acidity and increasing or decreasing chemical constituents through leaf-wash and ion exchange reactions. The vegetation canopy in a forested ecosystem is an effective collector of dust and minute particles of matter from the atmosphere. As the leaves age on a tree, they release organic and inorganic compounds which can be dissolved in intercepted rainfall. Therefore, as precipitation comes in contact with the vegetation, its chemistry is altered significantly.

Dissolved substances increase in the throughfall as compared to rainfall with the exception of the hydrogen ion, which can be held within the canopy by cation exchange reactions. In the forest ecosystem, the vegetation canopy is an important factor in the buffering of hydrogen ions in precipitation. In Oklahoma, Kress et al. (1990) reported that 50 percent of hydrogen ions in bulk precipitation were reduced by the forest canopy, while base cations (Ca, Mg, K, and Na) increased from 32 μeq/l to 87 μeq/l.

Likens et al. (1977) reported that during the growing season, all mean annual cation concentrations in throughfall were enriched greatly over precipitation concentrations. For example, potassium (K^+) increased from 0.07 to 6.37 mg/l, magnesium (Mg^{+2}) from 0.03 to 0.45 mg/l, and calcium (Ca^{+2}) from .16 to 1.59 mg/l in the experiment conducted at Hubbard Brook. Nitrate-N showed a decline as water passed through the canopy in a study by Beasley (1988) in Arkansas. Price and Watters (1988) found that volume-weighted mean seasonal concentrations (mg/l) of many elements in throughfall were greater than in incident precipitation. For example, K increased from 0.23 to 1.64, Mg from 0.08 to 0.21, Ca from 0.32 to 0.53, Na from 0.35 to 0.42, and NO_3-N from 0.25 to 0.33.

A number of investigators have suggested that throughfall studies require great numbers of samples in order to give an accurate measures of throughfall chemistry due to the wide variability in throughfall chemistry (Wilm, 1946 and Kimmins, 1973). They also reported that a large number of collectors is needed to obtain accurate estimates and the variation in the distribution of different chemicals may require a different number of collectors to insure accuracy. Thus, researchers such as Wilm (1946) and Kimmins (1973) have designed various throughfall sampling schemes and used various methods to assign the location of collectors and obtain highly precise and accurate results. Czarowski and Olszewski (1970) noted that the relative spacing of collectors had no effect on the standard deviations of throughfall chemistry. Kimmins (1973) reported that the use of data on an annual basis (Kg/ha) decreases variability and allows the use of a smaller number of collectors.

Soil and Subsurface Flow

Baldwin et al. (1938) and Buol et al. (1980) characterized soil formation as dependent upon a set of independent variables: climate, organisms, topography, rock type or parent material, and time. They suggested that soil forming processes may be divided into the following: 1) rock weathering which includes mechanical and chemical factors, and 2) biochemical alteration. It is the effect of these processes in the short and long term and the interaction between soil water and the soil system near the surface which influences soil water chemistry.

Subsurface flow chemistry is difficult to measure and evaluate, due to the soil horizon interactions and the complex processes which occur in the soil body. These processes include decomposition, ion exchange or substitutions involving di- and trivalent cations, leaching, and mineralization, which result in the formation of many different ion pairs and complex compounds (Flint and Skinner, 1974; Likens and Bormann, 1974; Likens et al., 1977).

Rainfall and throughfall pass soluble and insoluble nutrients through the canopy to the forest floor. Infiltrated water helps to transfer considerable amounts of nutrients from the decomposing litter layer downward to the mineral soil horizons (Dunne et al., 1975; Likens et al., 1977; Peterson and Rolfe, 1982). The release of elements from organic matter to the soil is primarily caused by microbial decomposition of the leaf litter layer. Removal of the elements from the leaf-litter layer is accomplished in several ways, such as leaching, plant uptake, and microbial uptake (Gosz et al., 1973).

Water that infiltrates into the soil moves laterally by subsurface flow above impeding horizons, and then reappears on the soil surface or joins streamflow downslope. The contributing area and flow rate greatly increases if the layer of high permeability is underlain by an impeding layer (Weyman, 1973; Pilgrim et al., 1978; Ahuja, 1986; Ahuja et al., 1983). The transportation of solutes with this flow influences the chemistry of streamflow. Turton (1989) found significant differences in the elemental concentration of certain ions between layers of the soil in a small sloping watershed in southeastern Oklahoma. Therefore, shallow subsurface flow may be an important pathway for the transfer of soluble chemicals in the runoff from soil horizons, when soil permeability is very high.

The quantity of subsurface flow may increase or decrease concentration of ions in streamflow. Gilliam (1983) found that the concentration of sodium, potassium, calcium, chloride and nitrate decreased with increasing streamflow volumes due to the dilution process.

As the upper layers of soil are exposed to roots of plants, animal activities, activities of both soil microflora and microfauna, and accelerated chemical weathering, mineral grains are altered. Foster (1985) reported that the forest floor layers have greater ion releases compared to other soil horizons due to the greater microbial activity. He also found that organic and mineral acids increased weathering of primary minerals in surface mineral horizons.

Soil water is the solvent medium for nutrients. Only small amounts of nutrients are removed with water infiltration in mature forested ecosystems (Likens and Bormann, 1974 and Likens et al., 1977). Some relationships between soil properties and chemical transfer have been reported. Flint and Skinner (1974), Press and Siever (1978), and Barbour et al., (1986) reported that soil horizons are an important source of nutrients and minerals in forested ecosystems. These nutrients are available as a result of pedogenesis of parent material, which contains different compounds and minerals.

Burwell et al., (1976) and Owens et al., (1983) reported that shallow subsurface flow was the main pathway for soluble nitrogen (N) transported to runoff from claypan soils of the midwestern United States. Similar results reported by Hubbard and Sheridan (1983) indicate 99% of the total N in runoff resulted from subsurface flow. The chemical transfer of ions is increased by an increase in rainfall intensity, slope, and soil permeability. A study by Ahuja (1986) indicates that chemical elements may be transferred from the soil to runoff from various depths. Chemicals may be transferred directly to runoff, with restricted infiltration. Turton (1989) reported that all chemical elements in soil water solution declined in concentration as water passed through the A horizon, except that H^+ and NO_3-N increased slightly. He also found that concentrations of some of these elements in subsurface flow were greater than those in the soil solution. For example, mean concentrations of Ca^{+2} and K^+ in the subsurface flow from A horizon were 2.4 mg/l and 2.37 mg/l, while mean concentrations of the same two cations in the soil solution of A horizon were 1.39 mg/l and 1.24 mg/l, respectively.

Streamflow

Streamflow is a combination of surface and/or subsurface flow processes which are produced by precipitation. Surface pathways for runoff include overland flow and channel interception and flow, while subsurface pathways include interflow and baseflow. The relative importance of each is determined by the intensity, duration, volume of the precipitation, infiltration capacity and permeability of the soil, and by the underlying geology (Dunne and Leopold, 1978).

The rate of flow of water from various soil depths as subsurface flow to streams is a function of antecedent moisture content, precipitation rate, and the duration of precipitation.

Streamflow may be composed of a mixture of "old" and "new" water (Pilgrim et al., 1979; Sklash and Farvolden, 1979; Pearce et al., 1986; Sklash et al., 1986; Shanley and Peters, 1988). They suggested that the old water which was stored in the soil prior to rainfall has been shown to form a large proportion of stormflow at the beginning of a runoff event, while the new water will eventually dominate streamflow later in the runoff process. The chemistry of old and new water have been found to differ and therefore affects streamwater chemistry.

Variability in stream chemistry is of primary interest because streamwater reflects the flow path and residence time in the path. Cheng (1988) found that the new water chemistry had lower electrical conductivity than the old water. He indicated that the new water had shorter contact time with soil minerals, and therefore had a lower mineral content compared to old water which had a longer resident time in the soil which increased mineral content. The new water increased as stormflow size increased due to the short flow routes and rapid release of new water through macropores (Cheng, 1988).

Cheng (1988) also reported that these two main types of water were found to exist in watershed ecosystems. The first type, the "new" water, is relatively dilute water newly added to the ecosystem in the form of rainfall. The second type, the "old" water may be derived from older, saline groundwater. The two types of water may be present in the streamwater in varying proportions.

The variability of streamwater chemistry can be quantified on a day-to-day or season-to-season basis. (Johnson et al., 1969 and Likens et al., 1977). Vitousek (1977) suggested that the majority of nutrients carried out of the watershed by streamflow are nutrients which the forested ecosystem is unable to absorb. Others (Likens et al., 1977; Vitousek and Melillo, 1979) reported that the degree of nutrient movement out of an undisturbed forested ecosystem through streamflow depended upon seasonal climate, biological activity, and the type of processes contributing to streamflow during a particular storm event. Therefore, in undisturbed forested ecosystems, if the subsurface flow occurs rapidly, nitrate may move rapidly out of the organic layer, thus contributing more nitrate to streamwater.

Turton (1989) reported that the nitrate concentrations in streamwater increase markedly with increasing streamflow. He found that the second largest storm (winter storm) of his study period contributed 72 percent of the total streamflow NO_3-N load. Likens et al. (1977) reported that nitrate concentration in streamflow averaged 0.40 mg/l during summer, increased in the autumn during a reduction in biological activity and averaged 0.76 mg/l, and reached a maximum concentration of 2.47 mg/l in early spring. This increase in nitrate concentration is attributed to increased nitrification during the winter (Likens et al., 1977; Vitousek and Melillo, 1979; Brozka et al., 1981; Reid et al., 1981; Swank and Caskey, 1982).

The measured streamwater concentration of most dissolved substances varies within a narrow range, even though discharge of water may fluctuate during an annual cycle (Likens et al., 1976 and 1977; Johnson et al., 1969). This is particularly true for magnesium, sulfate, chloride, and calcium concentrations. Nitrate and potassium concentrations are increased with increased discharge during the wet seasons specially during cold weather when biological activity becomes minimal. Gilliam (1983) reported that average annual stream potassium and NO3-N were 0.31 and 0.01 respectively in a lower coastal plain watershed. He also suggested that potassium peak which was observed on October was due to the decrease in the biologic activity.

Some researchers reported that concentrations of various ions in streamwater are much less variable seasonally (Likens et al., 1977; Lewis, 1981). Potassium and nitrate have lower concentrations during the summer season in streamwater than the winter season (Likens et al., 1977; Johnson et al., 1969; Lewis, 1981).

The level of biotic activity within the ecosystem plays an important role in determining the behavior of potassium and nitrate in streamwater. Nitrate and potassium are quite sensitive indicators of biological activity; therefore, streamwater concentrations for these two nutrients are markedly reduced during periods of plant growth and increased during periods of plant dormancy (Hem, 1985; Likens et al., 1977; Reid et al., 1981).

Likens et al., (1977) reported that the annual variation on a mass basis (Kg/ha) of dissolved substances, sulfate and dissolved silica are the dominant substances exported in streamwater, whereas on an ionic basis, sulfate and calcium dominate. They also stated that the annual gross output of total dissolved substances (excluding dissolved organic carbon and silica) during the first year of an experiment (1963-1974) on the undisturbed Hubbard Brook watersheds was 109.6 kg/ha.

CHAPTER III

THE STUDY AREA

The Alum Creek Experimental Forest area consists of 483 acres of private land and 4,281 acres of the Ouachita National Forest in the Ouachita Mountains and is located approximately 35 kilometers north of Hot Springs, Arkansas (Figure 1). The Alum Creek Cooperative Watershed study is located within the Experimental Forest and is managed by Weyerhauser Company, the U.S. Forest Service, Oklahoma State University and the University of Arkansas. Two small study sites are located on one of the experimental watersheds, undisturbed watershed 11, and are being monitored by Oklahoma State University for rainfall, streamflow, and streamwater chemistry. Watershed 11 occupies an area of 4.93 hectares and has a northerly aspect.

Topography and Vegetation

The two study sites are located at an approximate elevation of 1100-1200 feet (335-366 m) above mean sea level. A field survey conducted in May, 1989 shows ridges and valleys in the lower part of the watershed, while the upper section has a relatively constant gradient. The

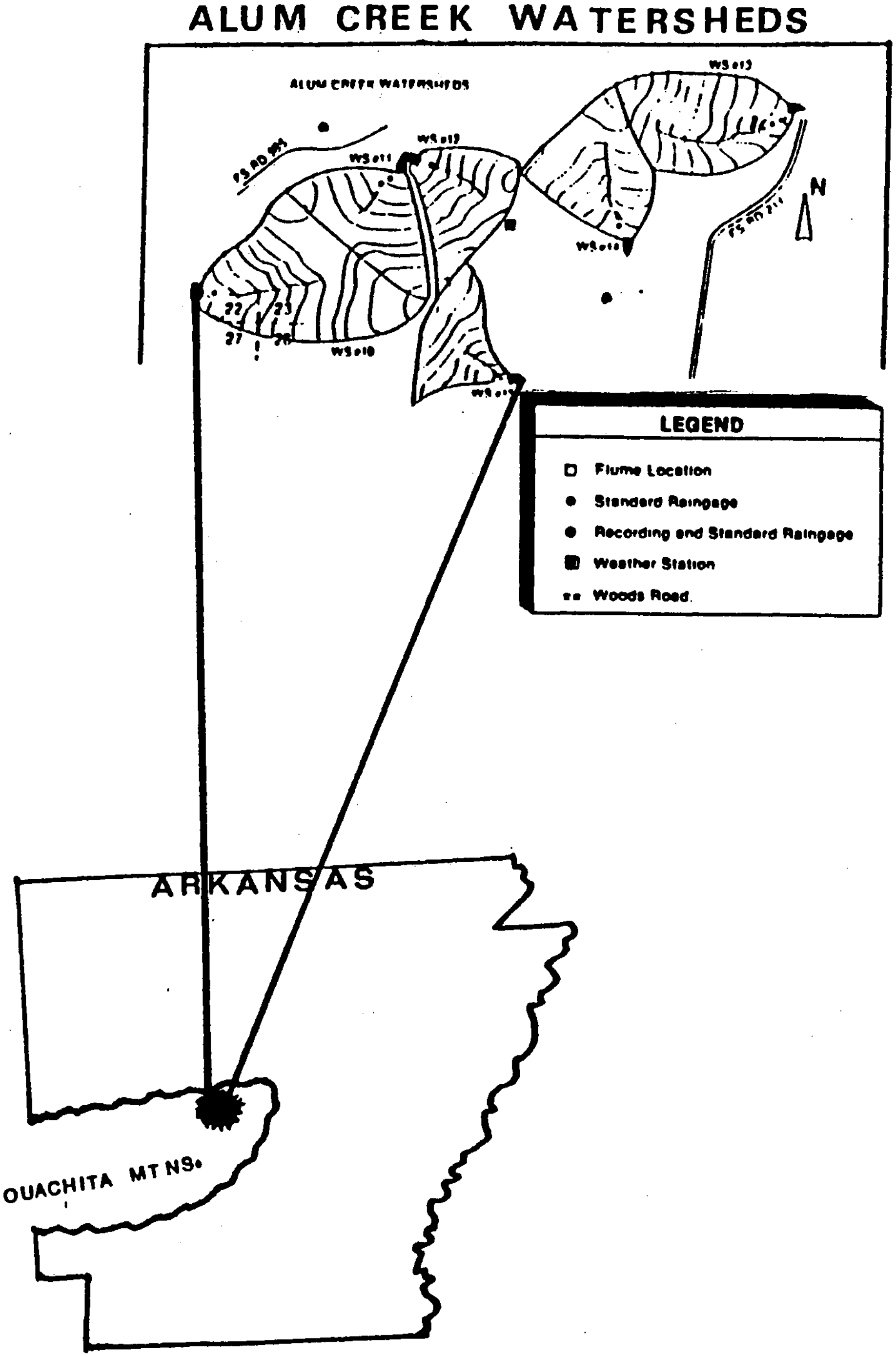


Figure 1. Location map of the Alum Creek Experimental Forest and the Alum Creek Cooperative Watershed (Modified from Miller et al., 1988).

watershed topography is characterized by moderate-to-steep slopes (12-30%) and cuts into stream channels with narrow valley bottoms (Figure 2).

The forest vegetation on the study area is mainly composed of shortleaf pine (*Pinus echinata*). Hardwood tree species such as elms (*Ulmus*), dogwood (*Cornus florida*), hickory (*Carya*), red maple (*Acer rubrum*), white oak (*Quercus alba*), red oak (*Quercus rubra*) and black gum (*Nyssa silvatica*) can also be found. The understory and the low ground vegetation consists of various herbaceous species poison ivy (*Rhus radicans*) and blueberry (*Vaccinium*). The soil surface is protected by accumulated organic materials and a litter layer and is sparsely covered by low vegetation (Lawson, 1975).

Climate

According to N.O.A.A. (1987), the climate may be described as temperate-humid with a mean annual temperature of 17 degrees Centigrade (^{o}C). In the summer, the temperature rises as high as 43^{o}C in July, and averages 26^{o}C. In the winter, the temperature falls as low as -22^{o}C in January, and averages 6^{o}C. Relative humidities average 85 and 55 percent at night and in the afternoon, respectively (Haley, 1979). The mean annual precipitation of the area under study is 128.9 centimeters. Of the total annual precipitation, about 33 percent occurs between April

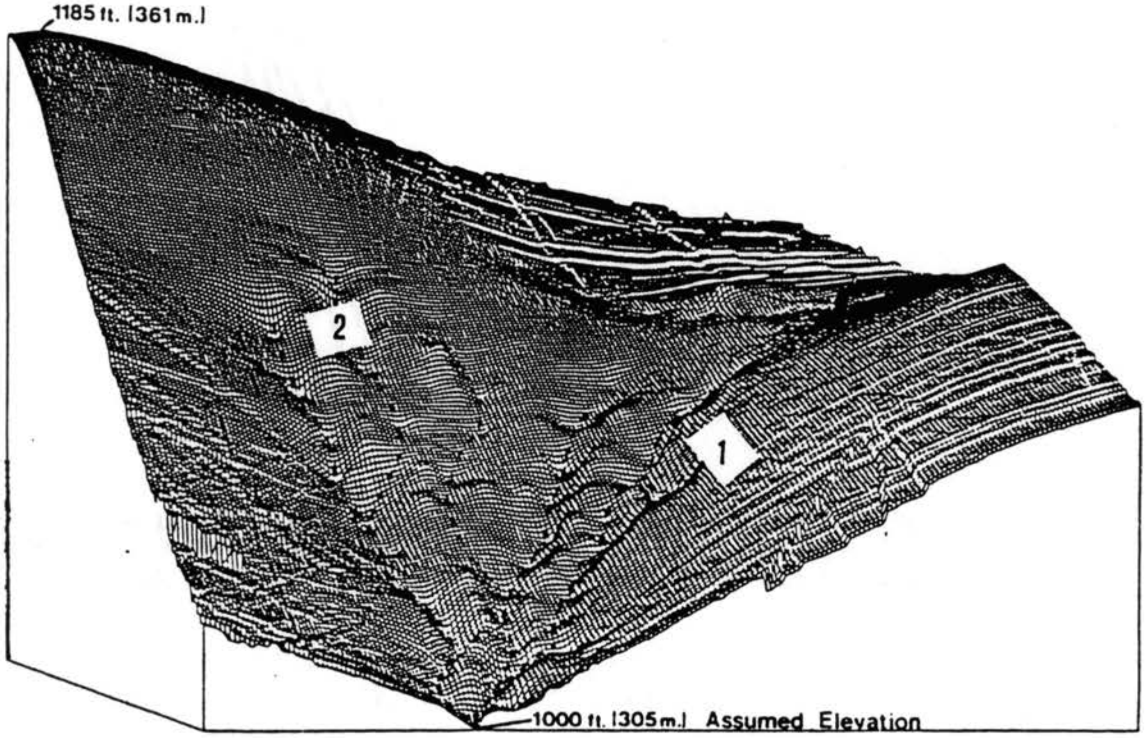


Figure 2. Watershed Number 11 showing topographic map and location of sampling sites (Modified from Williams, 1990)

and June. Showers of high intensity occur during these months mainly as a result of convective thunderstorm activity. Most of the annual precipitation is a result of rainfall with only 1 to 2 percent falling as snow (Lawson, 1975). Evaporation is high in the summer and low during the rainy season.

Geology and Soils

The Ouachita Mountains consist of rounded ridge tops, smooth slopes, and broad basins. The study site is composed of Pennsylvanian Jackfork Sandstone and Mississippian Stanley Shale. The Jackfork unit forms selected remnants on the ridge of the Alum Creek Watershed, while the Stanley shale provides the parent material. Williams (1990) provides a thorough description of the geology of the area.

The soils are generally classified as being within the Sandlick series (Dewitt and Steinbrenner, 1981). This series consists of shallow, well-drained soils, with textures varying from clay to clay loams derived from shale bedrock and sandstone colluvium. These soils typically have a thin litter layer, stony fine sandy loam A horizons, and yellow-red clayey B horizons. The United States Department of Agriculture (USDA) and Soil Conservation Service (SCS) classified the soils on the study sites as Carnasaw-Townley-Pirum soil association. The soils lying in the lower valleys and on the tops of hills are well-drained and moderately permeable. The soils have a predominantly clay loam and clay subsoils.

There are four distinct soil layers on the study sites, which will be referred to as horizons, identified for the conduct of this study. These horizons are not necessarily the same as the soil horizons described for the purposes of the soil survey:

1. The litter horizon (L) which extends from the surface to approximately 6 cm (range from 3-10). This layer consists of leaves, humus material, pine needles, and twigs.
2. The organic horizon (A) is a dark organic mineral soil. Highly permeable and well-drained, it extends to an average of 17 cm (range from 10-30). This layer is composed of a grayish light brown, stony fine sandy loam, with gravel and larger stones and a thick fine root mass.
3. The B horizon is highly variable in depth and less permeable than the litter and A and contains a higher clay content. This layer which also can be called the mineral layer, extends to a depth of 83 cm (range from 20-150).
4. The C horizon is composed of residual shale parent material and sandstone remnants. This layer extends to an average depth of 186 cm (Figure 3).

Responding to the changes in catchment topography, these four horizons' depths are inconsistent and highly

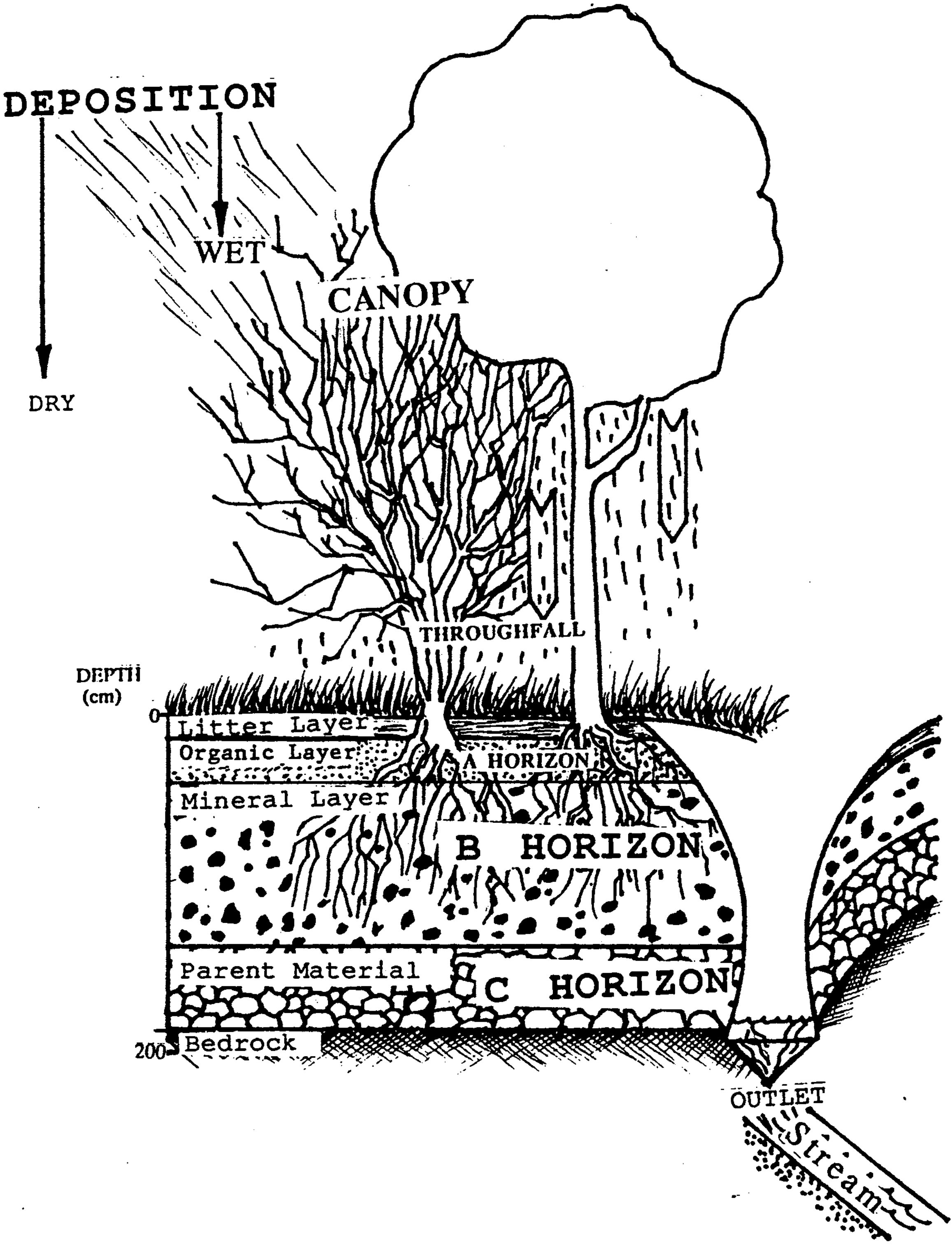


Figure 3. A diagrammatic representation of the soil profile showing the source of water.

variable between sites and within the hillslope study segments.

The A and B horizons of watershed number 11 were studied for soil chemical properties (Beasley et al., 1988). They reported that these soil horizons were acidic ($pH < 5$), Cation Exchange Capacity (CEC) was high in the A1 (42.38 meq/100g) and averaged 13.5 meq/100g in the E and B horizons. Adsorbed sulfate (SO_4) averaged 0.044 meq/100g in the A1 and E horizons but was greater (0.28 meq/100g) in the B horizon.

Hydrology

The streamflow on experimental watershed 11 occurs in ephemeral channels (flows in direct response to rainfall) and generally responds quickly to high intensity convective storms. Streamflow occurs most frequently during the rainy season between April and June. There is little evidence of overland flow on the slopes of watershed 11 and streamflow is generally produced by subsurface flow, which is thought to be the major influence controlling streamflow.

Streamflow and precipitation on this watershed have been continuously monitored since 1978 (Turton et al., 1988). In addition, the study sites have been monitored for stream flow, peakflow, erosion and sedimentation (Miller et al., 1988). This watershed was monitored for water chemistry, streamflow, and precipitation throughout this study.

CHAPTER IV

MATERIALS AND METHODS

Two sites were established on undisturbed watershed #11 of the Arkansas Cooperative Watershed study. The sites were chosen to represent the variations in degree of slope, slope shape, and vegetation on the watershed (Figure 4).

Each study site consisted of one subsurface flow collection system, six throughfall collectors, and one bulk precipitation collector. The watershed outlet water quantity and quality monitoring station was established in 1978 and is described herein.

Precipitation Measurement

The experimental watersheds have been continuously monitored for precipitation by the United States Forest Service since 1978. One of a network of recording weighing-bucket rain gauges is located adjacent to the study sites. This gauge monitors the precipitation depth and timing. A standard 8-inch rain gauge is located near the weighing bucket gauge for the official measurement of precipitation depth.

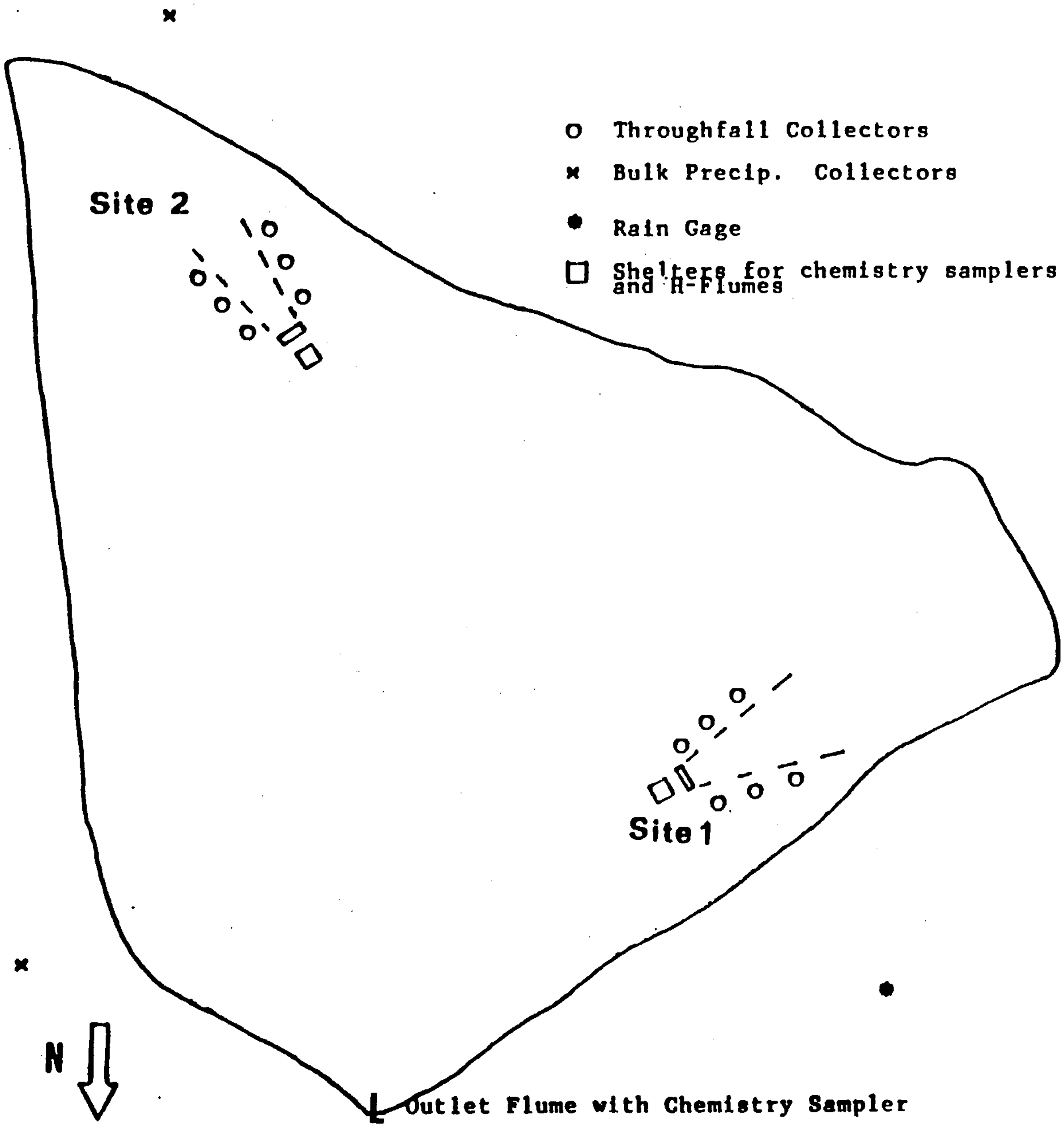


Figure 4. Location map for water chemistry sampling (Modified from Williams, 1990).

Precipitation And Throughfall Sampling

Bulk precipitation and throughfall are the input sources of water and chemical elements to the forested watershed system and also provide the driving force for the environmental fate of these elements in the watershed. Periodic bulk precipitation consisting of wetfall (rain and snow) and dry deposition (dust and debris) which accumulates between precipitation events, provide input into the watershed system (Likens, et al., 1977; Lewis and Grant, 1978 and Turton, 1989).

Two locations were selected for collecting wet precipitation samples for chemical analysis (Figure 4). Both collectors were located in open areas, one at the watershed outlet, and the other at the top of the watershed.

Since a large percentage of wet precipitation reaches the watershed as throughfall, throughfall collector locations were established and throughfall collected for chemical analysis (Figure 4). The actual placement of the twelve throughfall collectors was designed to minimize spatial variation, thereby providing better data collection of throughfall quantity and chemistry. Six of these throughfall collectors were placed at each study site under the short-leaf pine and hardwood forest canopy.

The collectors used for both bulk precipitation and throughfall (Figure 5) were designed similarly to those used by Turton (1989). These collectors consisted of a 10-inch

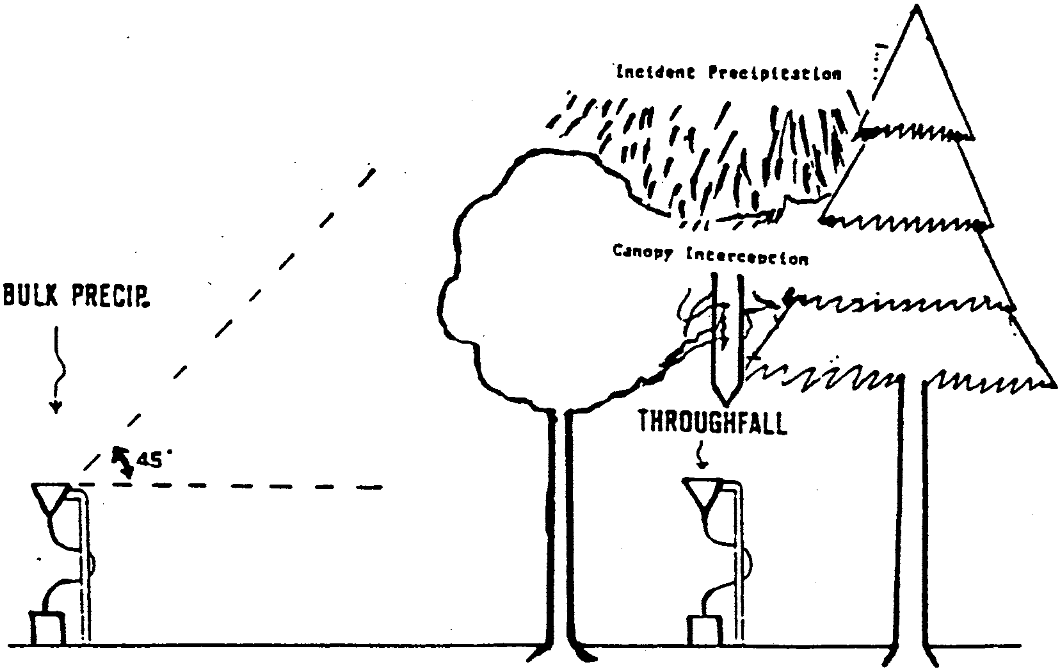


Figure 5. Illustration of the Bulk precipitation and Throughfall collectors.

diameter circular polyethylene funnel which drained through a 8/20 centimeter (cm) inside diameter plastic tubing into a five gallon polyethylene collection bucket. Glass wool was placed inside the funnel outlet to serve as a filter, keeping insect and organic debris from falling into the buckets. However, no protection was used to keep birds and other animals from the funnels.

Subsamples of 0.5 and 0.25 liters (L) were collected in polyethylene bottles from the precipitation and throughfall buckets, as soon as possible after the storm events, frozen and subsequently transported to Oklahoma State University for chemical analysis.

Subsurface Flow Sampling Methods

The subsurface flow collection systems were installed at the two study sites using modifications of the methods described by Atkinson (1978) and Turton (1989) (Figure 6). Basic study site characteristics are provided in Table I. The collection systems were strategically placed to provide data relating chemical changes over time with water migration after storms.

Each subsurface flow collection system consisted of a 6.7 meter long trench, excavated to bedrock (approximately 2 meter). Four subsurface flow layers or soil horizons were identified and isolated for the collection of subsurface flow. The identification of soil layers and the location of horizon boundaries was based on the physical evidence of

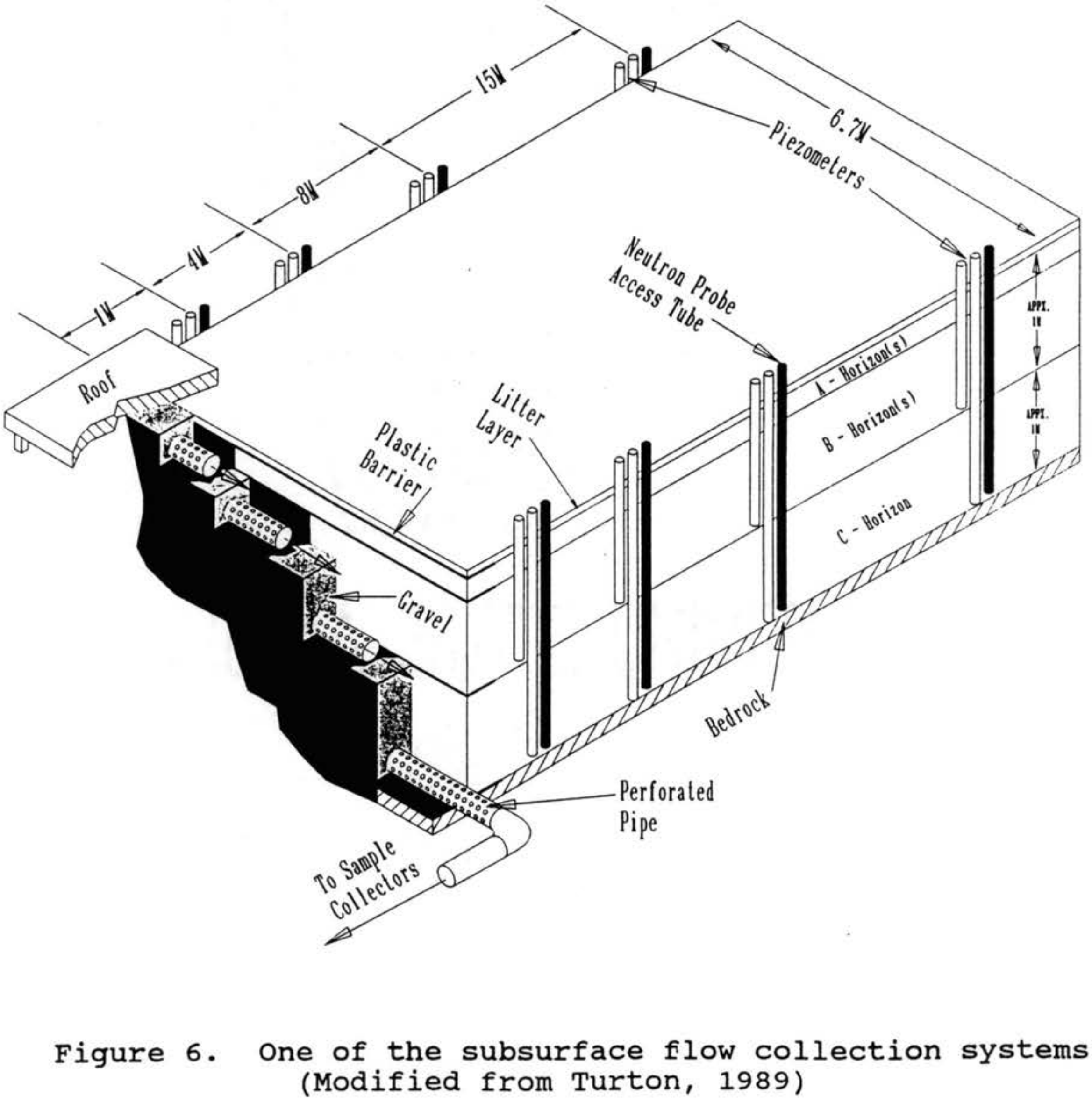


Figure 6. One of the subsurface flow collection systems (Modified from Turton, 1989)

TABLE I

STUDY SITE CHARACTERISTICS

Site	Hillslope Length (m)	Hillslope Site Area (m^2)	Mean Slope (%)
Lower	51	223	16
Upper	140	845	14
Total		1068	

TABLE II

HILLSLOPE SOIL PROFILE DEPTHS AND DESCRIPTION

Horizon	Range Depth (cm)	Average Depth (cm)	Soil Type
Litter	3-10	6	organic horizon
A	10-30	17	stony fine sandy loam
B	20-150	83	clay loam
C	80-310	186	clay

breaks in the hydrologic properties of the soil. Horizon depths from the surface and thickness varied between the two sites according to site conditions such as slope and parent material (Table II). Topographic measurements, performed by a crew of professional surveyors during drilling of onsite monitoring wells, provided a range of soil depths and descriptions for the four soil horizons at each site. Impermeable plastic sheet barriers were used to separate and isolate the soil horizons. A perforated pipe was placed at the base of the C horizon and parallel to the soil face and covered with cleaned quartz gravel to prevent soil from sloughing from the trench face and to promote normal flow at the disturbed interface. This procedure was repeated for the B, A and litter layers. The filled trenches and buried diversion pipes were finally covered with a roof to prevent the infiltration of precipitation directly into the flow collection system.

Lateral flow entering the perforated pipes from the soil horizons was routed to a shelter and into 15.24 cm (6 in) H-flumes (Figure 7). Modified FW-1 water level chart recorders were used for a timed recording of the stage in each H-flume. Automatic sequential samplers (ISCO model 1980) were used at each site to take discrete samples of subsurface flow from the four soil horizons during each storm event. Pumping sampler intakes were located just

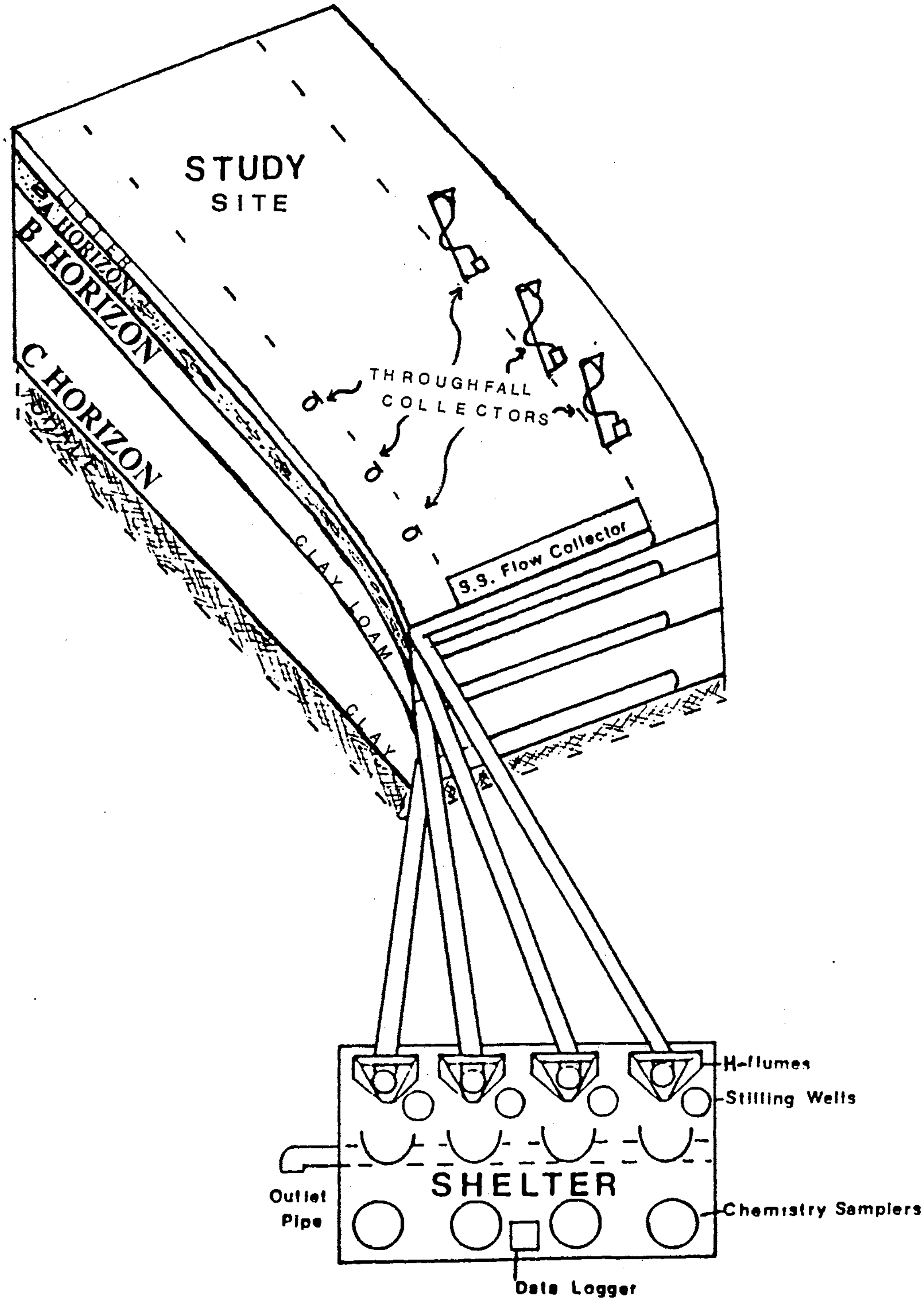


Figure 7. Example of one of the Study Sites, showing location of the througfall and subsurface flow collectors.

below the H-flume outflows. Once subsurface flow was routed through the measurement and sampling system, it was returned to the watershed 11 stream channel.

Pumping samplers were set to operate as soon as water began to flow from the H-flumes and into small cups where the water was intercepted by intake tubing of ISCO pumping samplers. The ISCO is an automatic pumping sampler which can be activated at discrete times. Sampling intervals between 10-30 minutes were used for the Litter (L), A, B, and C horizons. The use of this sampling system allowed the chemical characteristics of the subsurface to be measured and compared to the input from precipitation, throughfall and streamflow at the watershed outlet.

Streamflow Sampling

Streamflow discharge from watershed 11 was determined at the watershed outlet using a 3-foot H-flume. A FW-1 water level chart recorder was used to record the variation of the height of water with time. During storm events, discrete samples of streamwater were collected at the flume using an ISCO automatic pumping sampler. The sampler intake was placed in the concrete approach section of the flume. Grab samples of 500 ml and 250 ml were also collected periodically to verify the results of the automated sampling system.

Water Quality Sampling and Analyses

Storage and Analysis

All water samples were collected from pumping samplers within 6 hours after the storm events. The samples were subsequently frozen in a freezer located near the sampling sites. Frozen samples were then transferred to Oklahoma State University, where they were stored until they could be analyzed.

All bulk precipitation, throughfall, subsurface water, and streamwater samples were analyzed for pH, alkalinity, ammonium, and conductivity. The concentration of cations, including calcium, magnesium, sodium and potassium were determined. The concentration of anions, including nitrate-N (NO3-N), chloride, and sulfate were also determined. The procedures used for the chemical analyses were as outlined by the Environmental Protection Agency's methods for chemical analysis of water and wastes (EPA, 1985) and Standard Methods for the Examination of Water and Wastewater (APHA, 1980).

Quality Assurance

The quality assurance was preformed according to procedures outlined in Standard Methods for the Examination of Water and Wastewater (APHA, 1980) and Methods for Chemical Analysis of Water and Wastes (EPA, 1985). The procedures included the analysis of one duplicate sample for every ten samples. One spiked sample of known concentration was run for every 25 samples to test the percent recovery of the methods. Reagent blanks were also analyzed. In addition, quality control was maintained for every 10 samples by analyzing samples of known concentrations provided by the U.S. Environmental Protection Agency. Standard curves were also used for every ten samples for calibrating and validating the results of the analyses.

pH

A research grade combination electrode and pH meter was calibrated using pH 7.0 and 4.0 buffer solutions. The performance of the combination electrode was checked before taking sample readings against a poorly buffered pH 4.00 ± 0.02 quality control standard. The samples were then measured with this electrode. All pH readings were recorded to the nearest 0.01 pH units.

Conductivity

A conductivity meter equipped with a platinum glass electrode was used to measure the conductivity of each sample. A correction factor was used to convert conductivity readings to equivalent conductivities at $25^{o}C$ with a standard solution of known conductivity. Furthermore, an EPA standard solution of known conductivity was used to validate the meter. All measurements were recorded to the nearest 0.1 microsiemens.

Cations

Samples were analyzed for cations using the procedure outlined in Methods for Chemical Analyses of Water and Wastes (EPA, 1985). Cations analyzed included calcium (Ca^{+2}), magnesium (Mg^{+2}), potassium (K^{+1}), and sodium (Na^{+1}) using the varian Spectra AA-40 atomic adsorption spectrophotometer. Flame emission techniques were used for the measurement of sodium and potassium, while a hollow cathode lamp was used for calcium and magnesium. The EPA quality control standards for calcium, magnesium, potassium, and sodium were 2.00, 0.50, 0.50 and 2.00 mg/l, respectively.

Anions

Analyses for the inorganic anions were conducted according to procedures outlined in the Standard Methods for the Examination of Water and Wastewater, (EPA, 1985) EPA method 429, EPA method 300 and ASTM method D4327. The concentrations of nitrate-nitrogen (NO_3-N), chloride (Cl^-), and sulfate (SO_4^{-2}) were determined. The analyses were performed using a Dionex 2000i ion chromatograph.

Other Analyses

The analyses discussed above were performed on all samples. When the volume of samples were great enough dissolved organic carbon was measured. These measurements were performed by reading the absorbance of a filtered (45 um) water sample at a wavelength of 330 nm. For calibration, a standard curve of tannic acid standards was developed. The absorbance of the water samples was converted to "total dissolved organic carbon (TDOC) as tannic acid in mg/l". This method does not provide a quantitatively reliable measurement of TDOC. The TDOC results obtained are only intended to be used to help explain the influence of organic ions, which are often present in significant quantities, on the cation-anion balance.

Data Analysis

Of the storm events monitored during the period of study extending from May 1989 to June 1990, four rain events were selected for study. These storms produced adequate subsurface flow for sampling, significant streamflow and they covered a wide range of conditions. These storms were classified seasonally into three general periods; summer, winter, and spring. The Fall season was not included because no storms occurred which were large enough to produce measurable subsurface flow and sampling. On the other hand, the Spring season had several storms with measurable subsurface flow. Two storms were selected to represent this season. The two spring storms (4/20/90 and 5/01/90) were analyzed and it was found that these two storms were similar in water chemistry character. Therefore, the data from 5/01/90 storm were selected to represent the spring season.

Precipitation and Throughfall

Measurements of the precipitation depths were available for all storms from the rain gages which were located immediately adjacent to the study sites.

Although collected rainfall and throughfall samples were chemically representative, the quantative measurements of throughfall were not reliable. Canopy interception allows a fraction of the incoming rainfall to reach the forest floor as throughfall. This interception loss is influenced by seasonal factors, such as the density of the canopy. Lawson (1967) reported that throughfall varies on an average from 80% to 95% of precipitation based on a study done in the study area. Thus, following Lawson's recommendation, the throughfall depth in this study was calculated using the following assumptions:

1) During the spring and summer, canopy conditions allowed 87.5 % of the precipitation to pass through.
2) During the winter (the dormant season), the lack of canopy allowed 95 % of the precipitation to pass through.

Subsurface Flow Contribution

The total area of the hillslope study sites was measured and found to be 1,068 m^2. This area represents 2 percent of the total watershed area, 49,300 m^2.

Subsurface flows were totaled and associated precipitation and throughfall volumes were tabulated for the three seasons as represented by their storms. Data for both lower and upper sites were included in these calculations. The following will be compared:

a) Subsurface flow volume measured at both lower and upper sites with total precipitation.
b) Lower and upper site subsurface flow in terms of seasonal variation.

c) Subsurface mean area-weighted flow volumes, measured at the lower and upper sites with streamflow volumes measured at the watershed outlet.

d) The contribution of flow from each horizon, from the lower and upper sites, to the total subsurface flow.

Chemistry

Chemical Composition of Water

All chemical concentrations were volume weighted average values. Precipitation was considered the only input source of waterborne nutrients. The precipitation and throughfall concentrations were weighted against their respective depths. Calculations were performed on soil horizon flows to identify the concentration in μeq/l for the major ions. The concentration of nutrients in the subsurface flow were weighted against the volume of water measured at each horizon. The concentrations of nutrients in the streamflow was also volume weighted.

Chemical Loading by Source

The combination of chemical concentrations with volumes of water measured at each source allows calculation of chemical loads in equivalents per hectare (Eq/ha) or grams per hectare (g/ha). These load calculations were performed by multiplying the weighted concentration of each constitute by the volume of water from respective sources of water discussed above and divided by the source area in hectares.

CHAPTER V

RESULTS

The results have been divided into two major sections, the first describes the hydrologic processes which affect water quality, and the second, reports the chemical composition of storm water. Hydrologic processes are subdivided into water budget and the role of subsurface flow contributions. The chemical composition of water is divided into precipitation, throughfall, subsurface and streamflow chemistry.

Hydrologic Processes

Hydrologic Budgets

The storm data recorded by a rain gauge and stream outlet gauge were used to determine the storm water balance for the watershed (Table III) and to illustrate the variability in seasonal hydrologic cycles.

The hydrologic response for the three seasonal storms illustrates that soil moisture varied a good deal between storms. Of the 10.5 centimeters (cm) of precipitation input during the winter storm, 79 percent or 8.3 cm, became streamflow (Table III). Streamflow was 79 percent of

TABLE III

WATER BUDGET FOR WATERSHED NUMBER 11 BY STORM

Storm Date	Season	Prcp. cm	Streamflow cm	Hydro. Respones %
7-17-89	Summer	4.7	1.2	26
3-06-90	Winter	10.5	8.3	79
5-01-90	Spring	17.4	7.0	40
Total		32.6	16.6	
Mean		10.9	5.5	51

precipitation during the winter storm but only 26 percent for the summer storm. Although soil moisture measurements were not taken, it is logical that water not released as streamflow was either stored in the soil or became deep seepage. It is also logical that the low levels of streamflow and large amounts of soil moisture storage during the summer storm are due to the high levels of summer evapotranspiration.

Subsurface Flow Contribution

Subsurface flow was the dominant source of streamflow from the undisturbed watershed used in this study. Table IV shows the subsurface flow from the lower and upper sites as a percentage of precipitation. During the summer storm, about 16 percent of precipitation emerged as subsurface flow from the two sites. The winter storm produced the highest percentage of subsurface flow, 42 and 97 percent of precipitation from the lower and upper sites respectively. During the spring storm, 18 and 40 percent of the precipitation emerged as subsurface flow.

The amount of subsurface flow as a percent of precipitation from the upper site was found to be higher than the lower site, especially during the winter and spring storms. The greatest amount of subsurface flow as a percent of precipitation occurred in winter at the upper site. Conversely, the lowest percentage of subsurface flow

TABLE IV

THE SUBSURFACE FLOW CONTRIBUTION PER SITE AS A PERCENT OF PRECIPITATION OR STREAMFLOW

Storm	Season	Prcp.	Strm.	Flow					
				L-Site		U-Site		MAWF*	
Date		cm	cm	cm	%**	cm	%**	cm	%***
7-17-89	Summer	4.7	1.2	0.8	16	0.8	17	0.8	65
3-06-90	Winter	10.5	8.3	4.4	42	10.2	97	9.0	108
5-01-90	Spring	17.4	7.0	3.1	18	7.0	40	6.2	89
Total		32.6	16.6	8.3	25	18.1	55	16.0	97

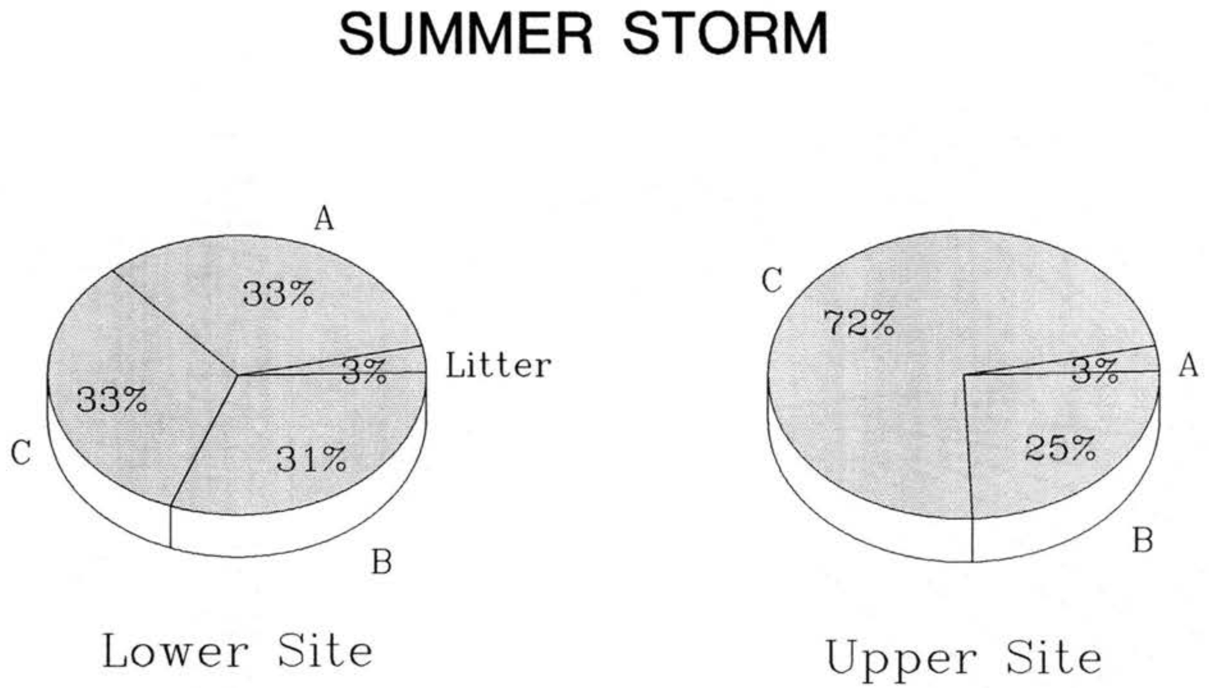
* MAWF = Mean Area Weighted Flow
MAWF = [Vol.L-site*Area + Vol.U-site*Area]/Total Area
** % of precipitation = [cm flow/cm Prcp.]*100
*** % of streamflow = [cm MAWF/cm Strm.]*100

resulting from precipitation occurred during the summer at the lower site (Table IV).

The streamflow data (Table IV) indicates that winter streamflow measured at the outlet is comparable to the mean area weighted flow (MAWF) calculated for both lower and upper sites. The summer season showed the lowest MAWF of subsurface flow of 65 percent of streamflow. The spring value of 89 percent is between the winter and summer values. The total mean area weighted flow of 108 percent during the winter season supports the idea that the subsurface is the dominant source of streamflow when soil are wet.

The striking difference in MAWF between the three seasons is probably related to changes in the forest canopy, temperature differences, growing versus dormant seasons, and changes in soil moisture storage. That is, the lowest MAWF occurred in the summer time, when interception is highest evapotranspiration is greatest, and therefore the soils are dry and the ability of the soil to store additional water is great. The opposite is true during the winter time when the greatest MAWF was observed.

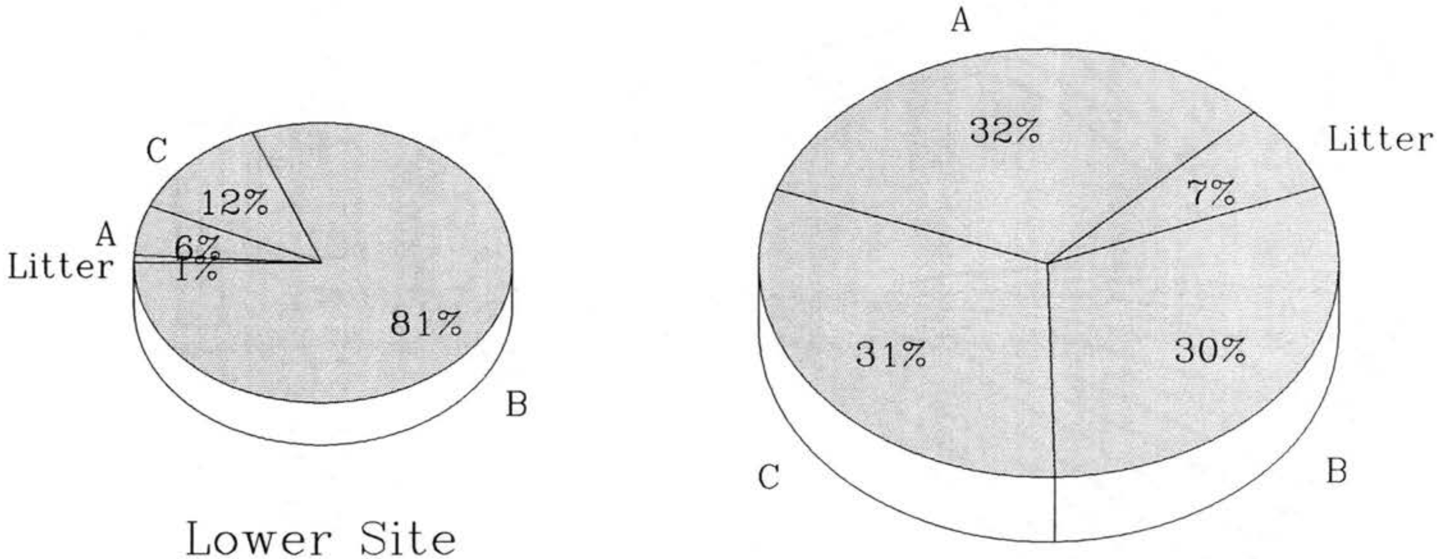
The contribution of subsurface flow by horizon, to the total subsurface flow (TSF) for each site was determined (Figures 8-10, appendix A) . During the summer storm, the lower site layers A, B and C contributed roughly equal proportions to streamflow (31-33 percent), while the L layer contributed only 3 percent. For the upper site, the major contribution to subsurface flow was from the C horizon



SUMMER STORM

Figure 8. The contribution per layer to the subsurface flow. Size of pies is proportional to TSF.

WINTER STORM



Lower Site

Upper Site

Figure 9. The contribution per layer to the subsurface flow. Size of pies is proportional to TSF.

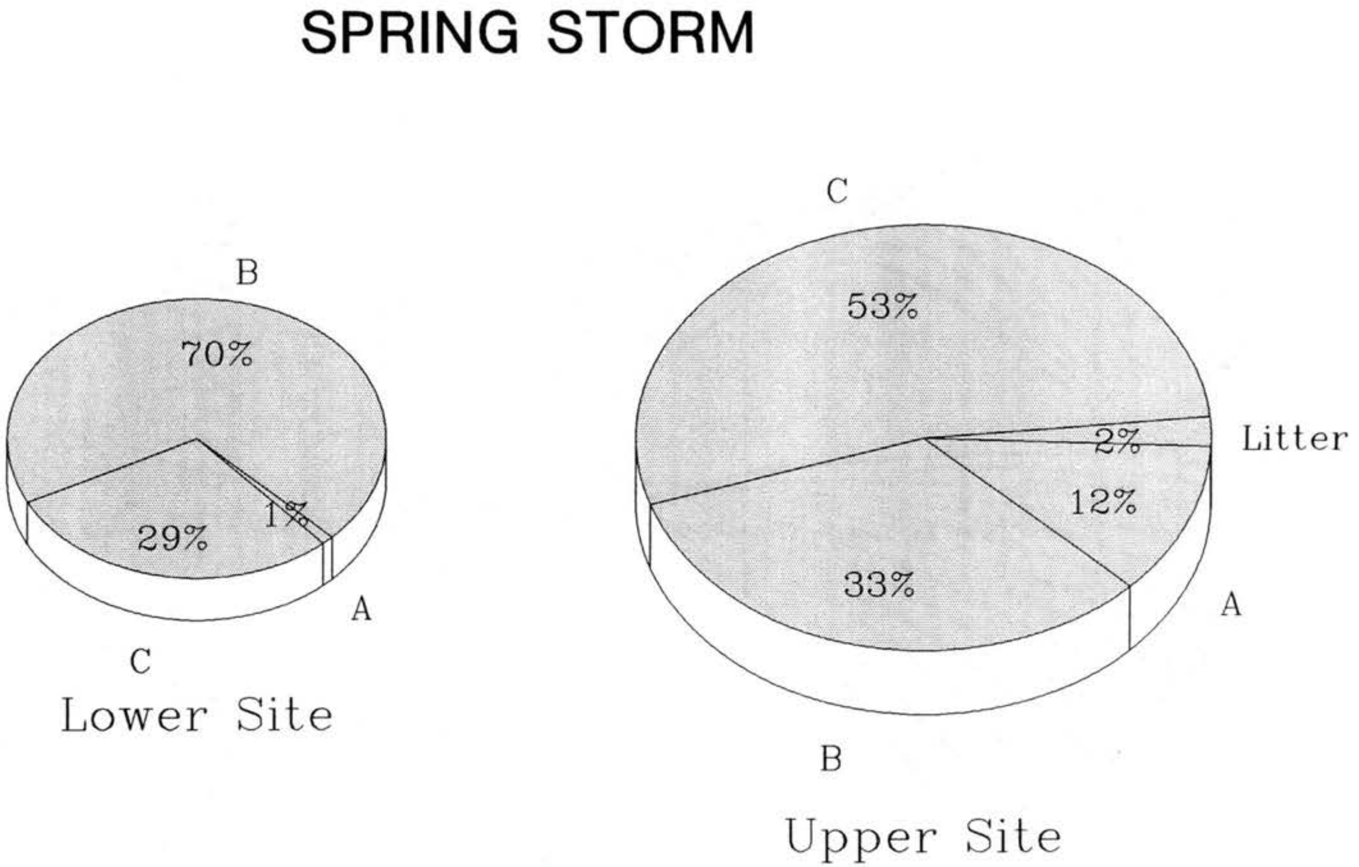


Figure 10. The contribution per layer to the subsurface flow.
Size of pies is proportional to TSF.

(72 percent) with no contribution from the L horizon. During the winter storm (Figure 9), the B horizon made the highest contribution to the total flow at the lower site (81 percent), while the L horizon made the lowest contribution from both the lower and upper sites. At the upper site, the contribution to total flow from the A, B, C horizons are similar (30-32 percent). The spring storm (Figure 10) also showed a similar tendency. The B horizon yielded the highest flow volume on the lower site, while the C-horizon yielded the highest flow volume on upper site as observed during the summer storm.

The total subsurface flow per horizon for each seasonal storm was calculated (Table V). During the growing season storms (spring and summer), the organic horizons (litter and A) produced the smallest quantity of subsurface flow for a given quantity of precipitation. For the same spring and summer storms, the C horizon produced the largest quantity of subsurface flow. During wet periods (winter and spring storms), the B horizon produced the greatest quantity of subsurface flow (Table V). The litter layer yielded the smallest quantity of subsurface flow, while the C and A horizons resulted about equal quantities of subsurface flow. The litter horizon contribution to the total subsurface flow was the lowest for both lower and upper sites in all seasonal storms. Note that the subsurface flow values from each layer in the upper site were greater than the values

TABLE V

VOLUME CONTRIBUTION BY SITE AND HORIZON TO THE TOTAL FLOW FOR THE THREE SEASONAL STORMS

Storm Date	Season	ThF	Site	Soil Horizon			
				L	A	B	C
		cm		cm			
7-17-89	Summer	4.1	Lower	0.02	0.25	0.24	0.25
			Upper	0.00	0.02	0.20	0.59
			Total Per Horizon	0.02	0.27	0.44	0.84
			Average % of Total Flow	1	17	28	54
3-6-90	Winter	10.0	Lower	0.04	0.25	3.54	0.54
			Upper	0.68	3.27	3.11	3.17
			Total Per Horizon	0.72	3.52	6.65	3.71
			Average % of Total Flow	5	24	46	25
5-01-90	Spring	17.4	Lower	0.00	0.03	2.19	0.89
			Upper	0.16	0.82	2.30	3.75
			Total Per Horizon	0.16	0.85	4.49	4.64
			Average % of Total Flow	2	8	44	46

from the same layer in the lower site, especially during the wet periods (Table V).

Chemical Composition of Water

Selected chemical constituents of water flowing between the terrestrial components of the forested ecosystem is presented. Water is introduced into the ecosystem through precipitation and its chemistry is altered as it moves through the canopy and subsequently through the soil horizons to the stream. Each of the sources of water is characterized on a seasonal storm basis and the total volume-weighted mean concentrations are used to compare the changes in ionic composition by source as water moves through the ecosystem.

Precipitation Chemistry

Precipitation is considered the major input source of nutrients into the undisturbed and unfertilized forest ecosystem. The volume-weighted mean concentrations by seasonal storms and total weighted means of major cations, anions, and specific conductance and pH are presented in Table VI. The total weighted mean of specific conductance for the study period was 18 micromhos per centimeter (μs/cm) and ranged from 14 μS/cm during the spring season to about 21 μS/cm during the winter (Table VI). The volume-weighted pH of precipitation at the Alum Creek Watershed Number 11, for these storms, averaged 4.8 and ranged from a low of 4.6

TABLE VI

VOLUME-WEIGHTED MEAN CONCENTRATION OF MAJOR CATIONS AND ANIONS IN PRECIPITATION

Constituent	Seasonal Storm Summer	Winter	Spring	Total Mean	% of sum Cation or Anion
pH	4.9	4.6	4.9	4.8	
Cond (μS)	18	21	14	18	
	μeq/L				
Ca	16	9	10	12	19
Mg	13	8	3	8	13
K	2	3	4	3	5
Na	20	11	12	14	24
H	24	27	20	24	39
SO4	35	39	33	36	61
NO3-N	12	6	4	7	13
Cl	14	14	18	15	26

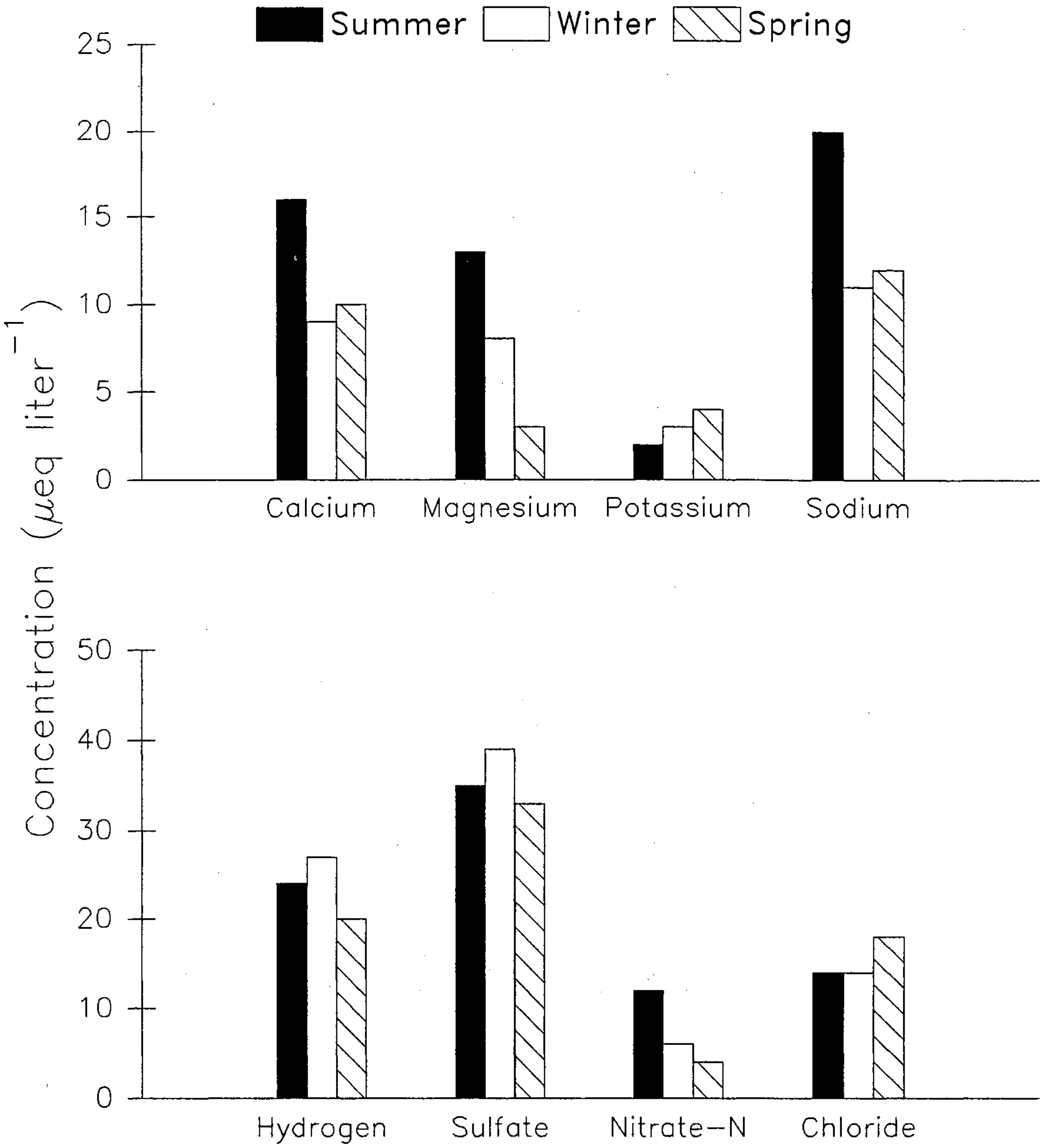


Figure 11. Seasonal volume–weighted concentration of major ions in precipitation.

during the winter storm to a high of 4.9 for both summer and spring storms. Most ions showed a considerable degree of variation from season to season, except for potassium and chloride (Figure 11). On a charge equivalent basis, the chemical concentration of the precipitation was dominated by hydrogen ions, which accounted for about 39 percent or 24 μeq/l of the total cationic strength, followed by sodium at 14 μeq/l. Calcium and magnesium, also important cations, represent 20 and 13 percent, respectively.

Sulfate and hydrogen ion were the most abundant dissolved inorganic ions in rainwater at watershed number 11 during all seasonal storms (Figure 11). Dissolved anions were dominated by sulfate, which comprised approximately 61 percent of total anionic constituents. The remaining 39 percent of the measured anions were chloride, 26 percent, and nitrate-N, 13 percent. Therefore, rainwater at this watershed represented by total weighted mean pH of 4.8 (Table VI) may be characterized as a dilute solution of sulfuric acid.

Throughfall Chemistry

The chemical composition of water from precipitation is altered as water passes through the canopy in form of throughfall. The volume-weighted mean pH of throughfall was higher than the pH of precipitation by 0.7 units during the winter storm and by 0.1 and 0.2 units during spring and summer storms. Throughfall specific conductance remained almost unchanged from precipitation and ranged from 13 μs/cm during the wet season (spring) to about 23 μs/cm during the winter storm (Table VII).

The volume-weighted mean concentration of most constituents was greater in throughfall than rainfall and showed great variability among seasonal storms (Table VII and Figure 12). However, seasonal ionic concentrations of base cations were greater during the summer storm, except for potassium which was greater during the spring storm (Figure 12). Seasonal differences were most apparent in throughfall and such distinctions were best illustrated by the contrast between potassium and sulfate (Figure 12); the potassium was enriched as it passed through the forest canopy especially during summer and spring while sulfate remained almost unchanged seasonally.

The composition of throughfall was enriched during the summer and spring storms for all ions in relation to the ion concentration in precipitation (Table VIII), except for hydrogen-ion and nitrate-N which were reduced by the canopy during all seasonal storms. Magnesium and calcium concentrations were 70 percent greater during the summer storm while the potassium concentration in throughfall was 85 percent higher than in precipitation. The greatest hydrogen-ion concentration reduction was 63 percent during summer storm while hydrogen-ion retention by the canopy of only one percent occurred during the spring.

TABLE VII

VOLUME-WEIGHTED MEAN CONCENTRATION OF MAJOR CATIONS AND ANIONS IN THROUGHFALL

Constituent	Seasonal Storm Summer	Winter	Spring	Total Mean	% of sum Cation or Anion
pH	5.1	5.3	5.0	5.1	
Cond (μS)	18	23	13	18	
	μeq/L				
Ca	58	7	12	26	24
Mg	63	9	10	27	26
K	10	7	27	15	14
Na	44	11	15	23	22
H	9	19	18	15	14
SO4	38	35	40	38	63
NO3-N	2	4	1	2	3
Cl	28	12	21	20	34

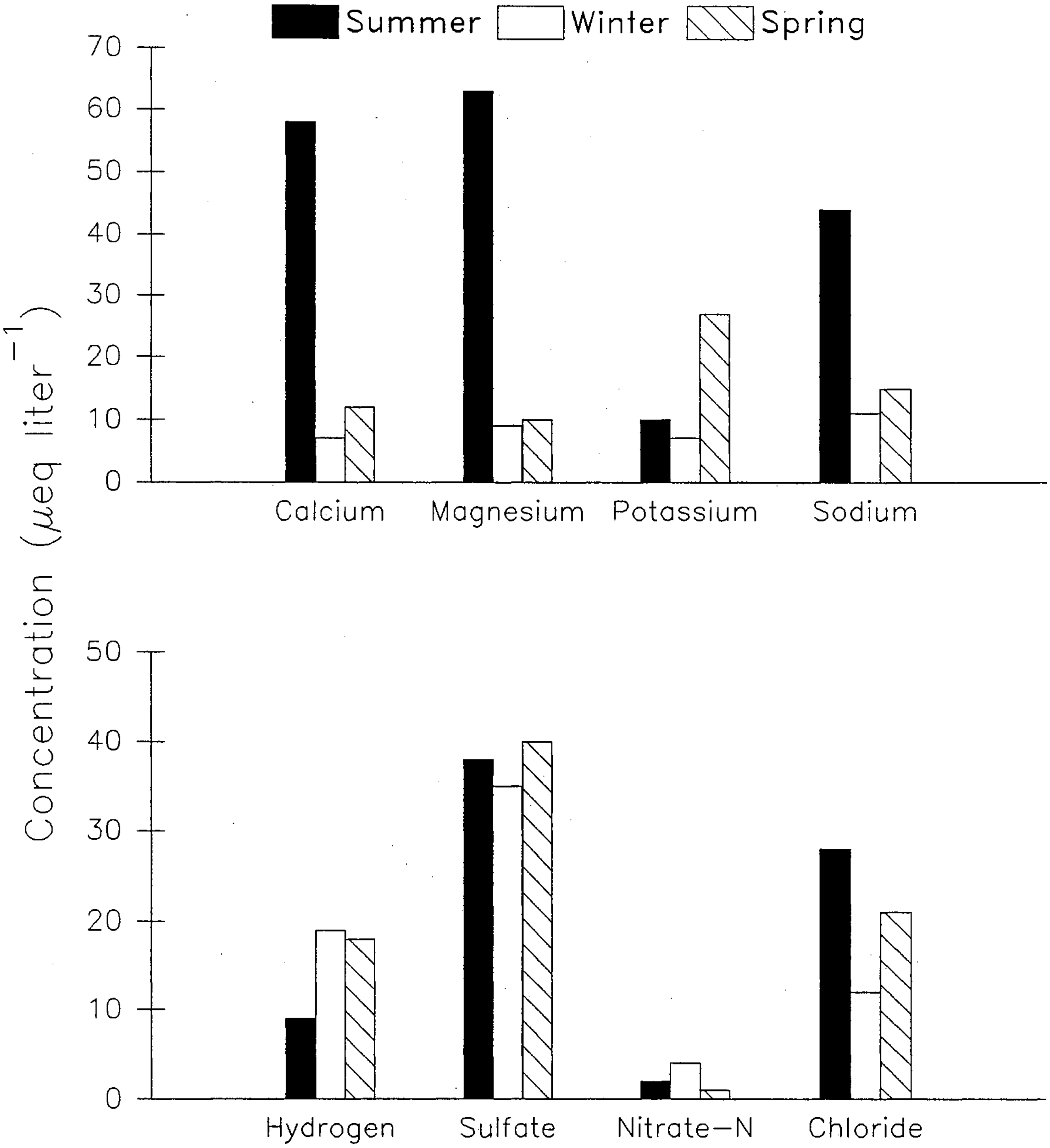


Figure 12. Seasonal volume−weighted concentration of major ions in throughfall.

TABLE VIII

THE INCREASE OF CHEMICAL CONCENTRATION BY CANOPY IN THE CONSTITUENT OF THROUGHFALL OVER PRECIPITATION

Constituent	Summer Storm	Spring Storm
	Increase over precipitation	
	μeq/L	
Ca	42	2
Mg	50	7
K	8	23
Na	24	3
H	−16	−2
SO4	3	7
NO3−N	−10	−5
Cl	14	3

Throughfall Nitrate-N concentration was reduced compared to precipitation by 83 and 75 percent during summer and spring, respectively. However, element concentrations of throughfall remained nearly unchanged during the winter storm for most ions, except hydrogen and nitrate-N, which were reduced 30 and 33 percent, respectively.

Total seasonal weighted mean concentrations of constituents in throughfall (Table VII) showed that magnesium and calcium were the predominant cations and sulfate was the most abundant anion in throughfall for storms examined during study period.

Subsurface Flow Chemistry

Litter-Layer Flow Chemistry

The major input of water into the litter layer is throughfall. A highly permeable organic layer, permeable soil surface, together with abundant macropores, allows water to quickly pass through the litter and A soil horizon. The pH of throughfall was reduced as it passed through the litter horizon. Reductions were only 0.2 units during both summer and spring seasonal storms, while the pH was reduced by 0.5 units during the winter storm (Table IX). The reduction of the pH was associated with an increase in conductivity of 7 μs/cm during the summer storm and 8 μs/cm during the spring storm. The winter storm showed a decrease in conductivity of 2 μs/cm (Table IX).

TABLE IX

VOLUME-WEIGHTED MEAN CONCENTRATION OF MAJOR CATIONS AND ANIONS IN LITTER LAYER

	Seasonal Storm			Total	% of sum
Constituent	Summer	Winter	Spring	Mean	Cation or Anion
pH	4.9	4.8	4.8	4.8	
Cond (μS)	25	21	21	22	
	μeq/L				
Ca	137	125	53	105	52
Mg	55	33	42	43	21
K	17	18	13	16	8
Na	33	15	32	27	14
H	5	11	17	11	5
SO4	42	43	52	46	79
NO3-N	0	1	0	0	0
Cl	12	12	13	12	21

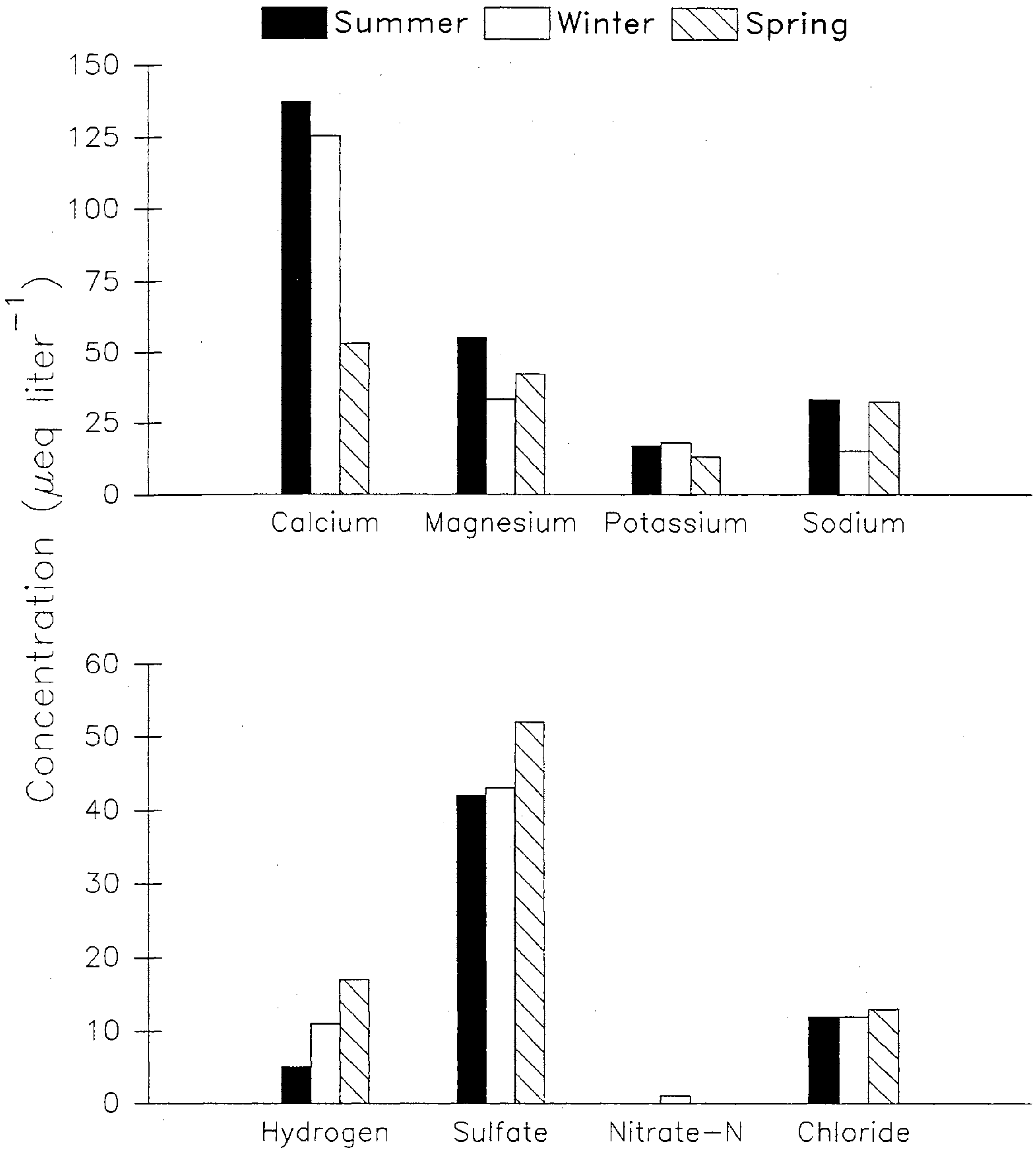


Figure 13. Seasonal volume−weighted concentration of major ions in litter layer.

On the basis of volume-weighted concentration data (Figure 13), calcium and sulfate dominated the litter-layer flow chemistry during the three seasonal storms. Calcium was the dominant cation from season to season. Calcium accounted for the largest proportion, about 55 and 62 percent of the total cations in litter flow, during summer and winter storms, respectively. Calcium concentrations were three to four times greater than magnesium, the next most abundant cation in litter-layer flow. The spring storm showed that the calcium and magnesium both were important and accounted for 34 percent and 27 percent of the total cations. Sulfate was by far the most abundant anion. Sulfate accounted for nearly 77 to 80 percent of the total anionic constituents for the three seasonal storms (Figure 13).

Total volume-weighted mean values for the study period showed that calcium and sulfate were the predominant ions in the litter-layer flow (Table IX).

A-Horizon Flow Chemistry

The volume-weighted mean pH and specific conductance of flow from the organic and mineral A horizon, remained unchanged from the litter-layer flow during the three seasonal storms, except for the summer storm conductivity, which decreased by 2 μs/cm (Table X).

The results of volume-weighted mean concentrations of dissolved constituents from the A-horizon flow showed that

TABLE X

VOLUME-WEIGHTED MEAN CONCENTRATION OF MAJOR CATIONS AND ANIONS IN A-HORIZON

Constituent	Seasonal Storm Summer	 Winter	 Spring	Total Mean	% of sum Cation or Anion
pH	4.9	4.8	4.8	4.8	
Cond (μS)	23	21	21	22	
	μeq/L				
Ca	131	101	101	111	43
Mg	45	37	41	41	22
K	19	16	15	17	9
Na	37	36	31	35	19
H	10	12	17	13	7
SO4	44	54	66	55	64
NO3-N	3	0	0	1	1
Cl	33	27	31	30	35

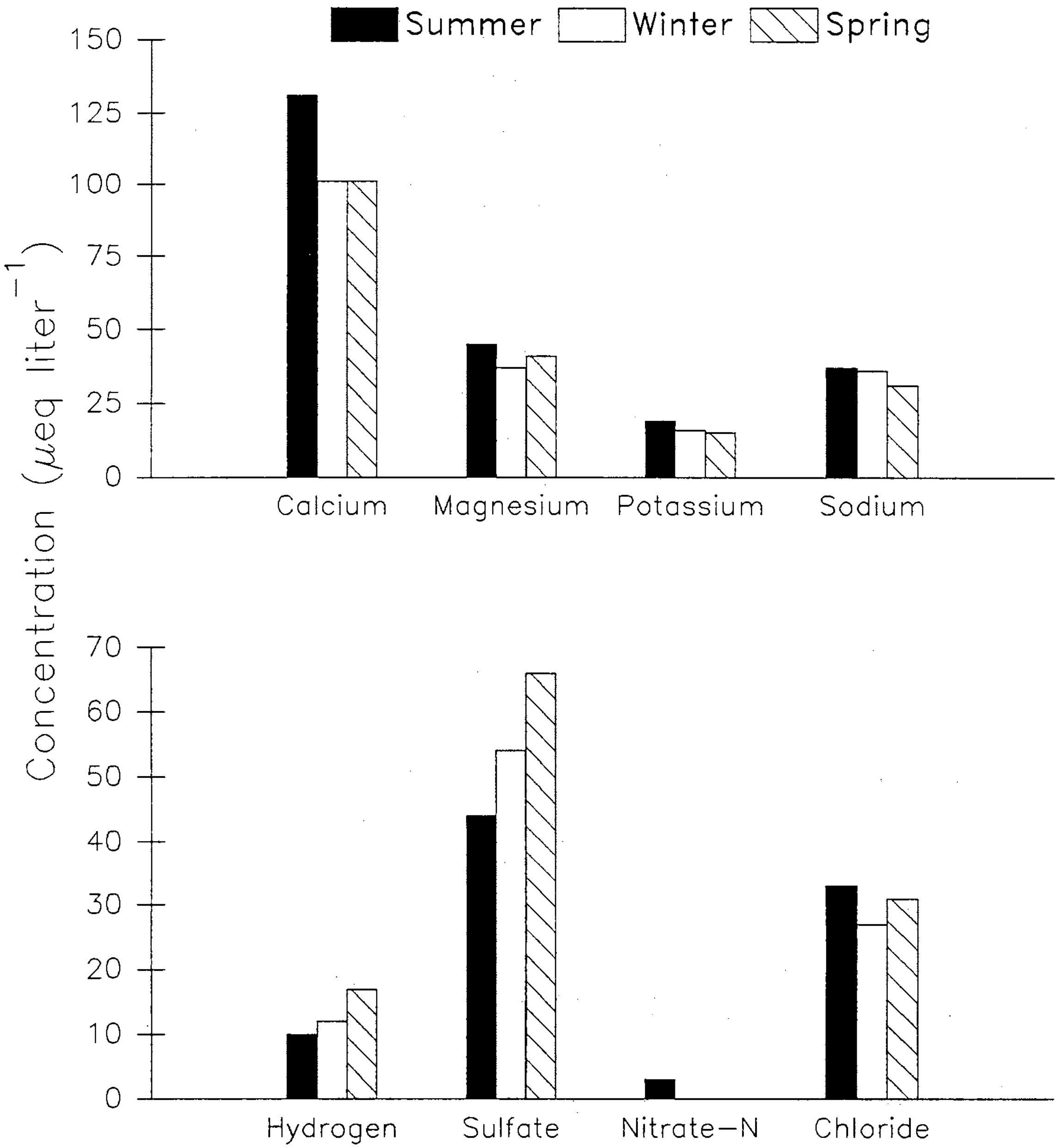


Figure 14. Seasonal volume−weighted concentration of major ions in A−Horizon.

the chemical composition of water was dominated by calcium and sulfate (Figure 14). Calcium comprised 57 percent of the total cations in the A-horizon flow during the summer storm and was slightly lower, 50 percent, during both winter and spring, followed by about 20 percent magnesium and about 17 percent sodium. Sulfate accounted for about 55 percent of the total anionic constituents during the summer storm and approximately 63 and 68 percent of total anionic constituents for the winter and spring storms, respectively. The remaining anions were mostly chloride. Total volume-weighted mean concentrations (Table X) for the study period showed that calcium and sulfate were two times more abundant than the next most abundant cation and anion, magnesium and chloride, in A-horizon water.

B-Horizon Flow Chemistry

Subsurface flow from the B-Horizon within each storm was slightly higher in pH (2 to 3 units) than from the A-horizon, while the conductivity remained relatively constant from the A to the B horizon (Table XI). The pH values of B-Horizon subsurface flow among the three seasonal storms were about the same, whereas summer storm conductivity was slightly higher than both winter and spring storms (Table XI). The volume-weighted mean concentrations of calcium (Figure 15) showed that calcium was retained in the B-Horizon compared to the litter and A horizons; this retention of calcium was associated with increases in

TABLE XI

VOLUME-WEIGHTED MEAN CONCENTRATION OF MAJOR CATIONS AND ANIONS IN B-HORIZON

Constituent	Seasonal Storm Summer	Winter	Spring	Total Mean	% of sum Cation or Anion
pH	5.1	5.0	5.1	5.1	
Cond (μS)	23	21	20	21	
	μeq/L				
Ca	51	48	44	48	29
Mg	64	38	48	50	31
K	11	17	12	13	8
Na	58	27	32	39	24
H	12	14	13	13	8
SO4	60	51	67	59	69
NO3-N	0	0	0	0	0
Cl	34	20	25	26	31

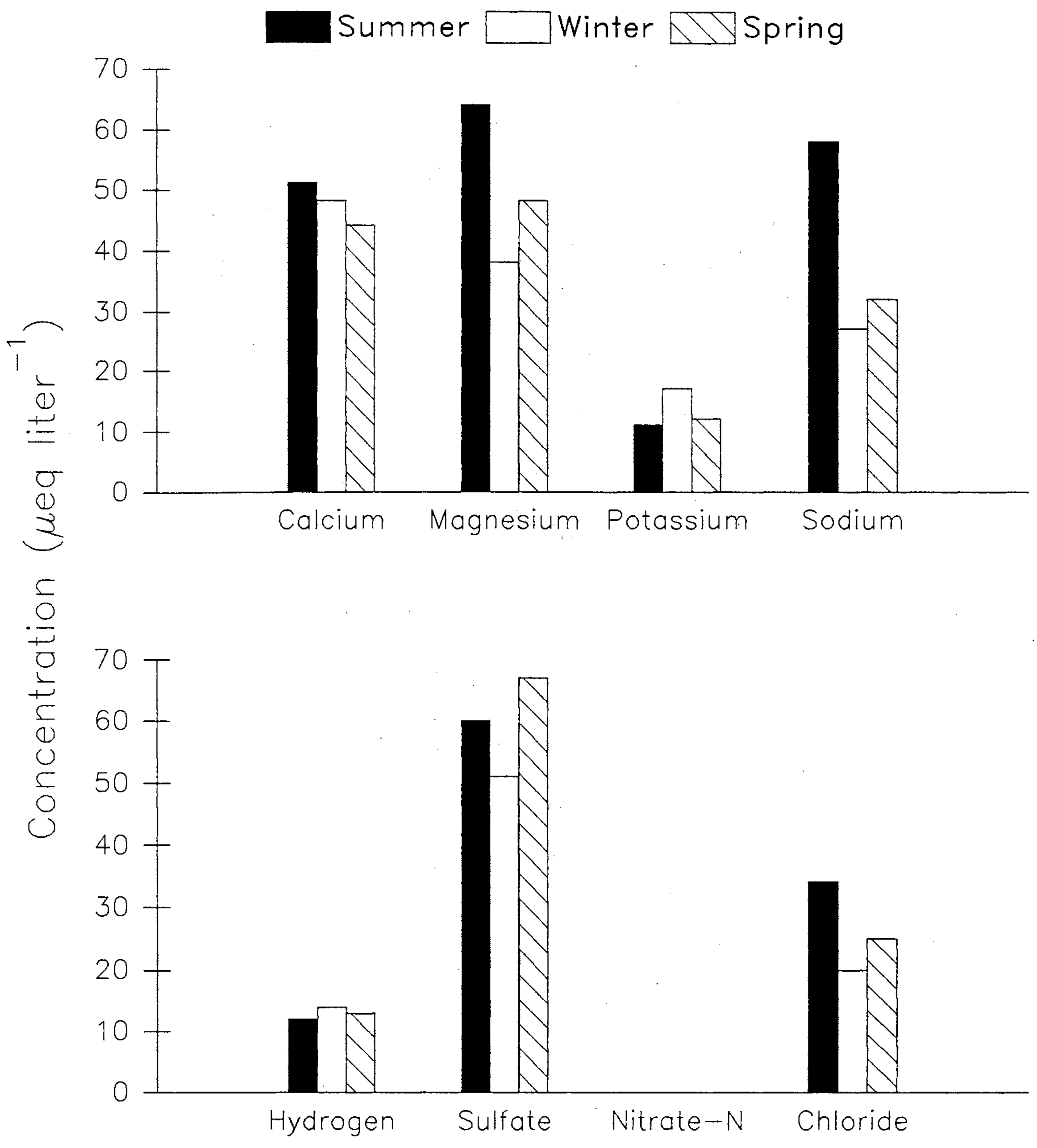


Figure 15. Seasonal volume−weighted concentration of major ions in B−Horizon.

outputs of magnesium and sodium in the B-Horizon flow compared to A-Horizon flow. The water migrated from the organic litter and A horizons to the mineral B-Horizon was associated with qualitative and quantitative chemical changes of cations and anions, especially during summer and spring storms. Magnesium, the dominant cation during summer and spring storms, accounted for about 32 percent of the total cations, but sodium and calcium were also relatively abundant. Compared to the winter storm, which followed the similar pattern that existed in the A-Horizon, calcium was the dominant cation in the B-Horizon followed by magnesium (Figure 15). Sulfate was by far the most abundant anion in the B-Horizon during the summer, winter and spring storms.

Total volume-weighted mean concentrations for the study period (Table XI) showed that magnesium and calcium were the most abundant cations followed by sodium. Sulfate was two times more abundant than the next most abundant anion, chloride, in B-horizon water.

C-Horizon Flow Chemistry

The volume-weighted mean pH of subsurface flow from C-horizon (parent material) showed a marked increase in pH compared to the B-Horizon flow for all storms. These increases in pH were 0.8 units during the summer storm, slight increase in pH (0.3 and 0.2 units) during the winter and spring storms. The increase in pH values were associated with a decline in conductivity during the summer

TABLE XII

VOLUME-WEIGHTED MEAN CONCENTRATION OF MAJOR CATIONS AND ANIONS IN C-HORIZON

Constituent	Seasonal Storm Summer	Winter	Spring	Total Mean	% of sum Cation or Anion
pH	5.9	5.3	5.3	5.5	
Cond (μS)	19	21	18	19	
	μeq/L				
Ca	57	28	45	43	26
Mg	67	52	60	60	36
K	12	13	10	12	7
Na	55	39	43	46	27
H	7	7	5	6	4
SO4	74	51	73	66	65
NO3-N	0	1	0	0	0
Cl	52	20	34	35	35

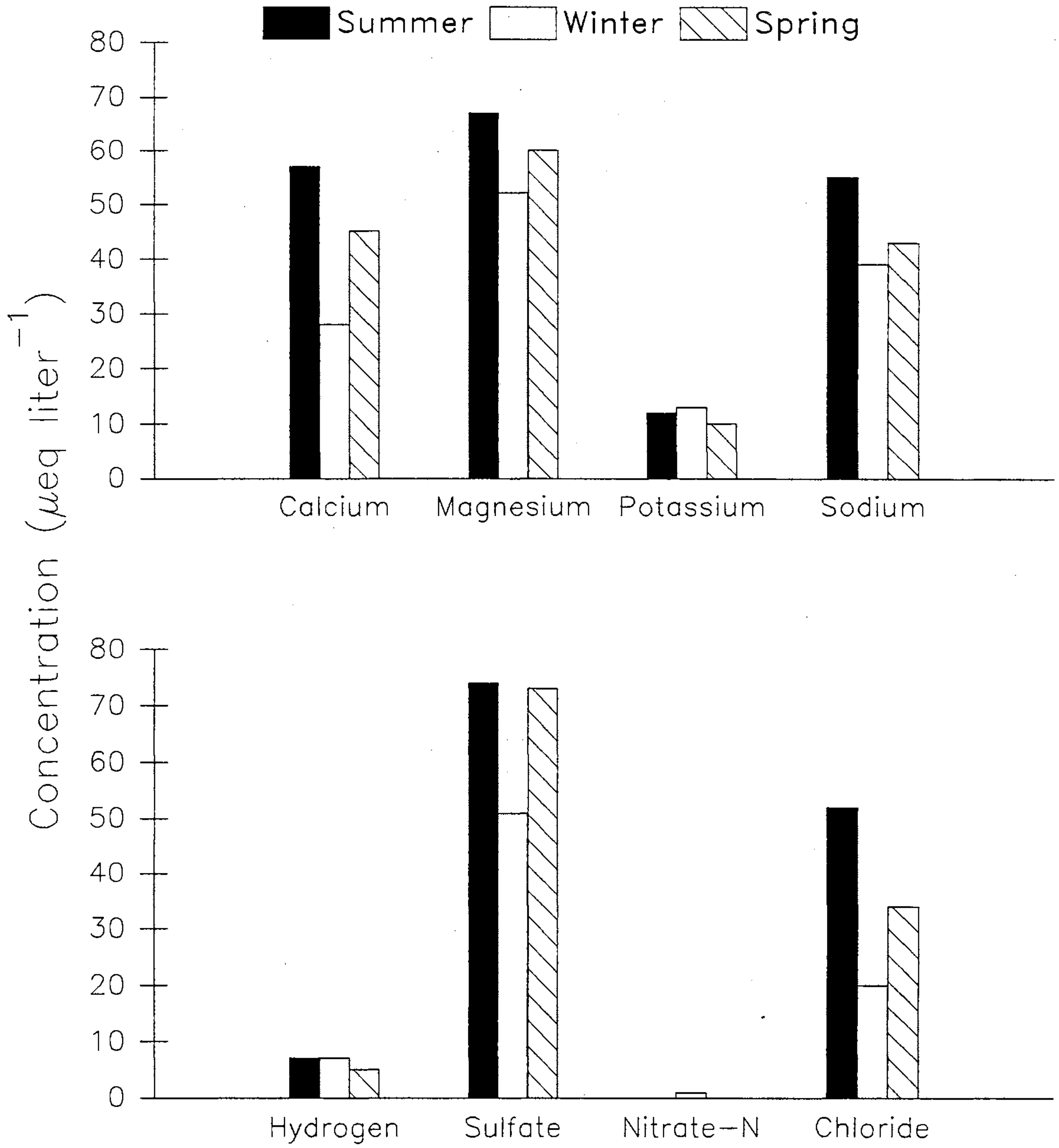


Figure 16. Seasonal volume−weighted concentration of major ions in C−Horizon.

and spring storms, while there was no difference in the conductivity of flow from the A and B horizons during the winter storm (Table XII).

On a charge equivalent basis (volume-weighted mean concentrations in μeq/l) magnesium was the predominant cation in the chemical composition of C-horizon flow during the three seasonal storms (Figure 16). However, calcium and sodium concentrations were nearly as great as magnesium concentrations, especially during the summer and spring storms (Figure 16). Dissolved anionic equivalents from subsurface flow from the C horizon showed that sulfates and chloride ions were higher in concentration than from the B-horizon during the summer and spring storms. For the winter storm, sulfate and chloride ion concentrations remained unchanged from the B-Horizon to the C horizon. Sulfate continued to be the dominant anion within each storm and among the seasonal storms in the chemical composition of C-horizon water (Figure 16).

Total volume-weighted mean concentrations of C horizon flow for the study period (Table XII) showed that magnesium was the predominant cation, which suggests that geochemical weathering in the parent material horizon contributed to increases in the concentration of magnesium in the subsurface flow from the C-horizon.

Streamwater Chemistry

The volume-weighted mean pH of streamwater at the study site averaged 5.5 ± 0.1 for the study period (Table XIII). This pH value reflects the combined effect of hydrochemical changes as precipitation passed through the canopy and soil horizons on its way to becoming streamwater. Mean values of specific conductance showed a similar pattern with high values during summer and winter and low values during spring (Table XIII).

Total volume-weighted mean concentrations for the study period showed that magnesium and sulfate were the dominant ions in the chemical composition of streamwater. Magnesium contributed about 42 percent of the total cations, while sulfate contributed about 69 percent of the total anionic constituents (Table XIII).

The volume-weighted mean concentration of streamwater chemistry for the three seasonal storms showed that magnesium and calcium were consistently the major cations and sulfate the major anion (Figure 17). During the summer storm, magnesium ion was by far the most abundant cation and comprised 45 percent of the total cation equivalents. During winter and spring storms magnesium was likewise the dominant cation in the streamwater chemistry, and accounted for nearly 38 and 36 percent of the total cations, respectively. Calcium was also relatively abundant at 32 and 34 percent. Dissolved anionic equivalents were

TABLE XIII

VOLUME-WEIGHTED MEAN CONCENTRATION OF MAJOR CATIONS AND ANIONS IN STREAMFLOW

Constituent	Seasonal Storm Summer	 Winter	 Spring	Total Mean	% of sum Cation or Anion
pH	5.4	5.5	5.6	5.5	
Cond (μS)	19	19	14	17	
	μeq/L				
Ca	61	53	54	56	32
Mg	101	64	57	74	42
K	12	14	11	12	7
Na	29	31	33	31	17
H	4	5	3	4	2
SO4	32	48	47	42	69
NO3-N	0	0	0	0	0
Cl	15	21	20	19	31

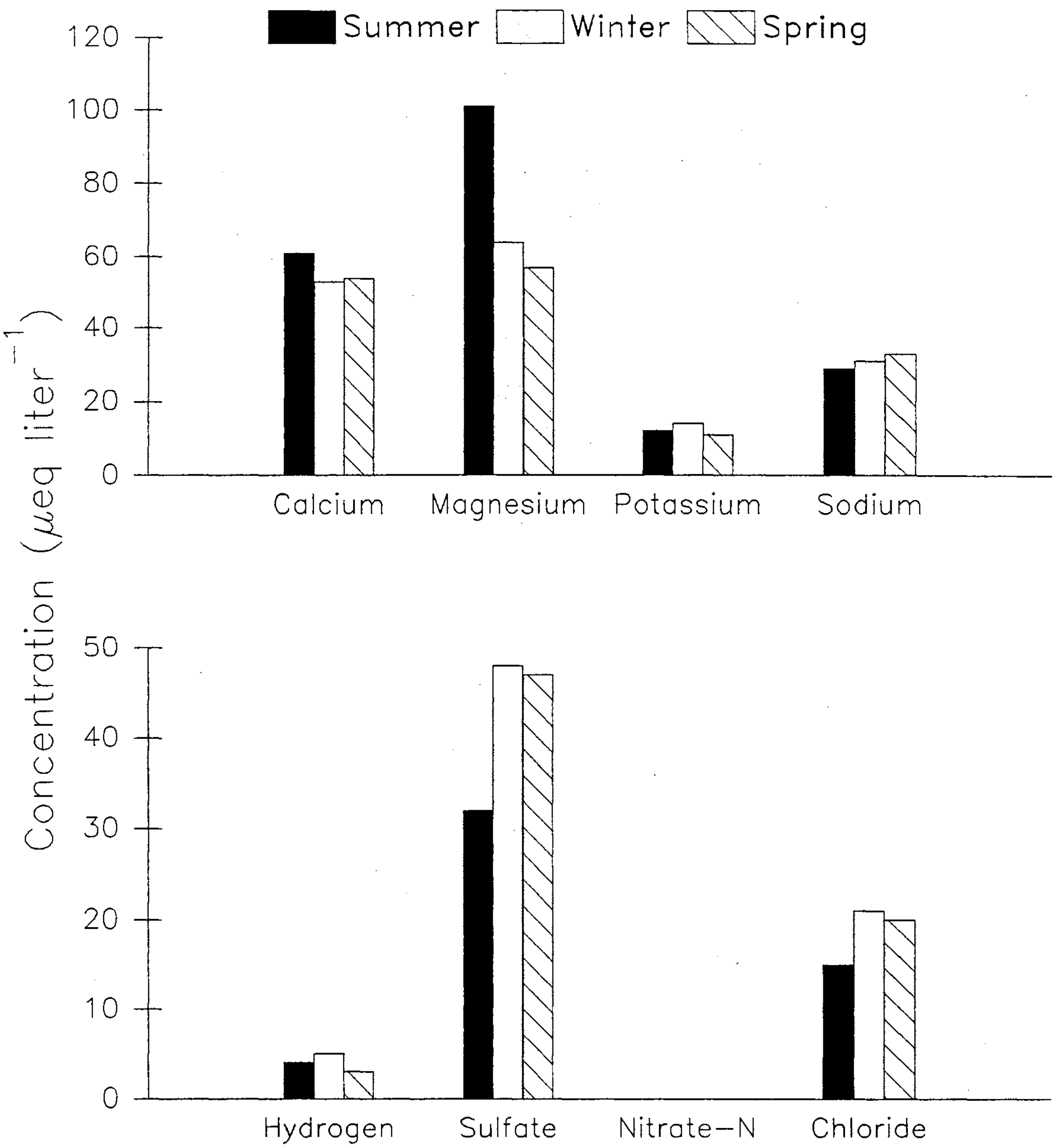


Figure 17. Seasonal volume−weighted concentration of major ions in streamflow.

dominated by sulfate, which was two times more abundant than chloride. No NO3-N was observed in the streamwater.

The total-weighted mean concentrations of potassium and magnesium are used to demonstrate the impact of the vegetation and the geochemical weathering factors on water chemistry as water migrated through the system (Figure 18). Increases in potassium concentrations took place as precipitation passed through the canopy and water interacted with the organic components in the litter and A horizon, then slightly but steady declined in concentration as water migrated downward. Magnesium showed steady increases in concentration as precipitation passed through the canopy and water migrated through the organic horizons (litter and A) into the mineral and the parent material horizons (B and C) where large increases in magnesium concentrations took place due to geochemical weathering.

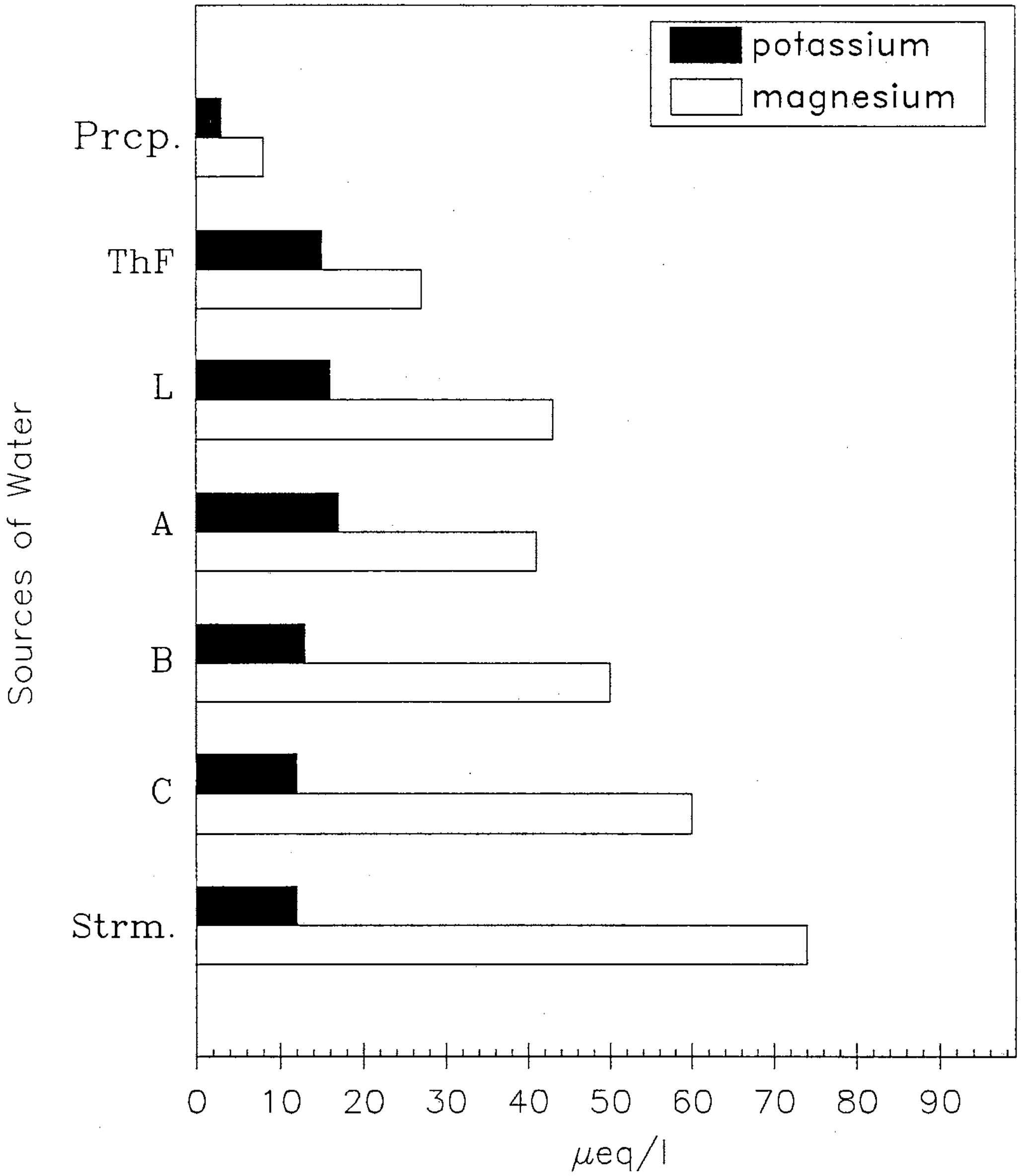


Figure 18. Total seasonal weighted-mean concentrations of potassium and magnesium.

Chemical Loading by Source

Chemical loading per unit area (Eq/ha) for each constituent is derived by multiplying the volume of water measured from each source by the concentration of respective ions and dividing by the total source area. The chemical loading inputs and outputs from the ecosystem are presented in terms of total average seasonal loading by source and seasonal storm load variation. Assumptions concerning the average flow and rainfall are made and measured seasonal storm chemistry is assumed to be representative of seasons for these calculations and comparisons.

Total Average Seasonal Chemical Loading

The total average seasonal chemical constituent loading in the study area is presented by source in Figures 19 through 26 and Table XXIV, Appendix B. A total average measured load of 123 Eq/ha (3642 g/ha) was introduced into the watershed by precipitation during the study period. Out of this total average, 35.6 Eq/ha (773 g/ha) were base cations (hydrogen excluded) and 62.1 Eq/ha (2843 g/ha) were anions. Sodium and calcium were the dominant cations introduced into the ecosystem by precipitation. The total percentages of base cations introduced into the watershed were: sodium 41 percent, calcium 30 percent, potassium 19 percent, and magnesium 10 percent. Hydrogen, measured as pH amounted to 25.2 Eq/ha (25.4 g/ha) or 1 percent of the

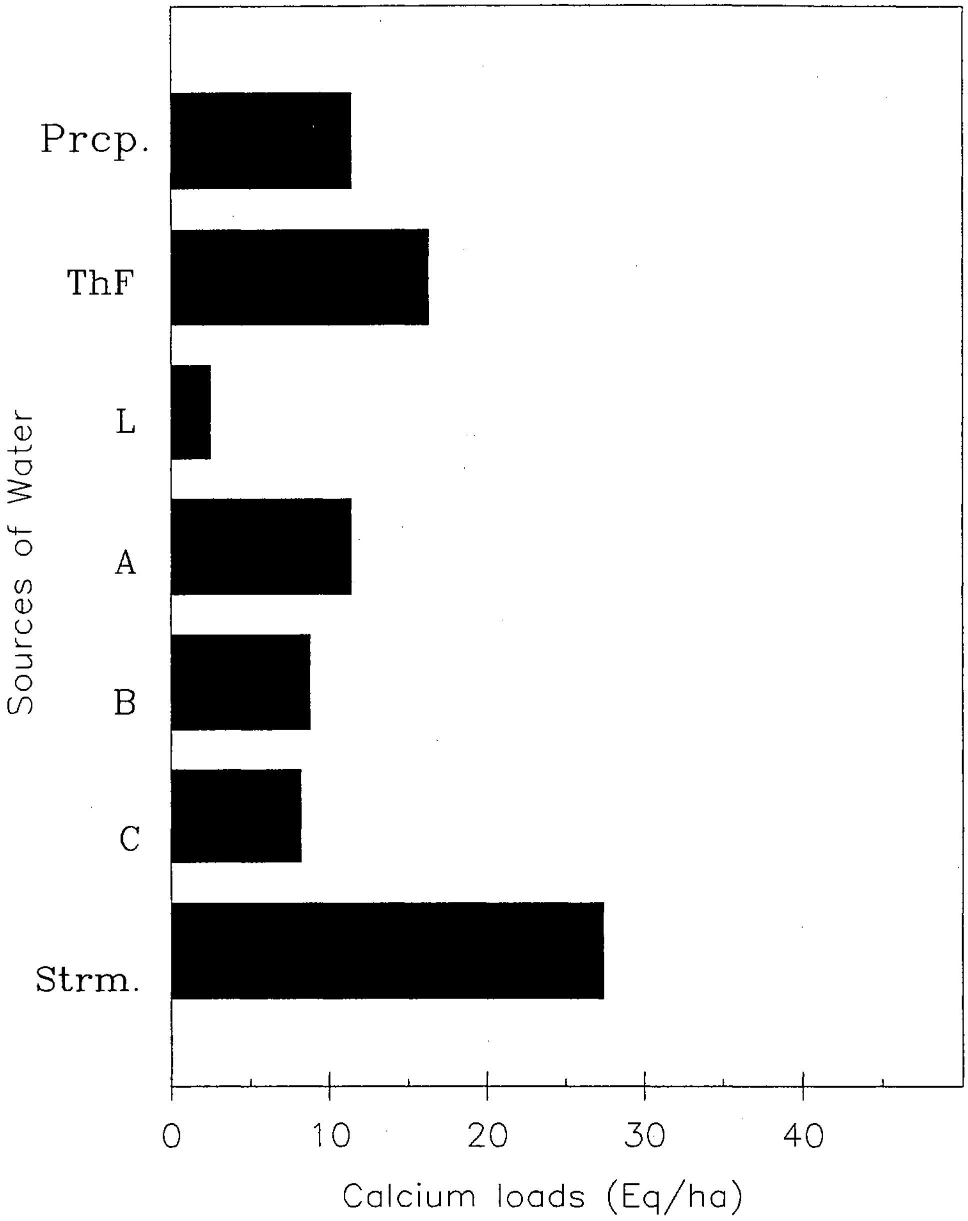


Figure 19. Total seasonal average loads of calcium.

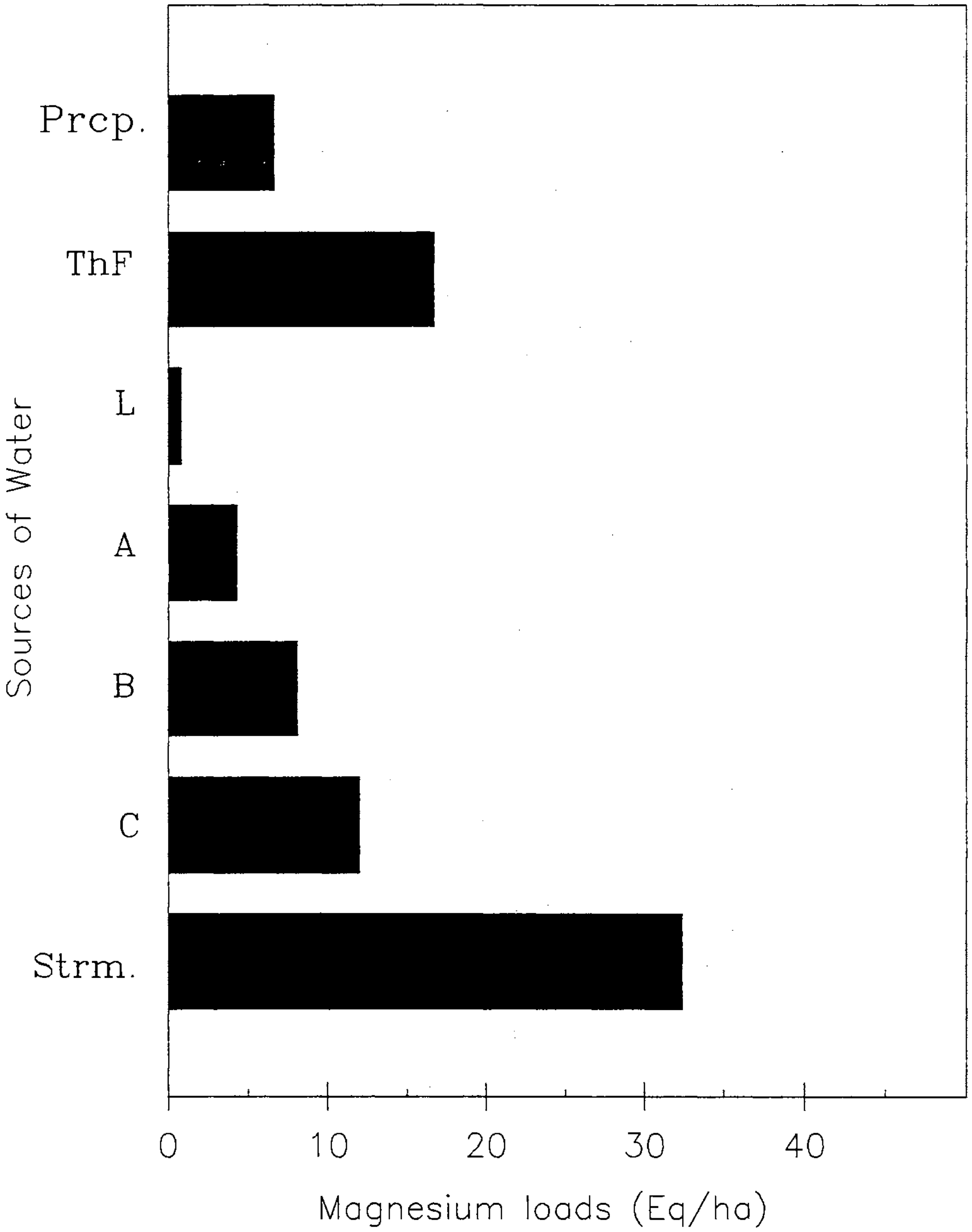


Figure 20. Total seasonal average loads of magnesium.

etotal average. Sulfate was the dominant anion introduced into the ecosystem; it represented 31 percent of the total ion load and 62 percent of the total anion load.

Total seasonal average loads of throughfall increased by 20 Eq/ha (601 g/ha) over precipitation through ion exchange and chemical weathering processes which occurred in the canopy. All cation loads increased due to canopy effects except hydrogen ion. Sulfate and chloride loading from throughfall remained about the same compared to the loading introduced by precipitation, while nitrate-N was accumulated in the canopy. Hydrogen was neutralized by the canopy while nitrate was retained by vegetation. Approximately 34 percent of the total average seasonal load of hydrogen and 62 percent of the total average seasonal load of nitrate was removed from precipitation by the canopy. Potassium exhibited the highest increase in load 370 percent over precipitation while other increases included: Magnesium (153 percent), calcium (42 percent), and sodium 23 percent.

In general, total seasonal average subsurface flow loads, of all cations and anions except nitrate-N showed increased output with depth as more water migrated from the upper soil horizons to the lower horizons.

The total seasonal average load produced at the subsurface outlet of the organic litter layer was about 96 percent less than the total average load input calculated from throughfall. In the litter layer flow, all anion and

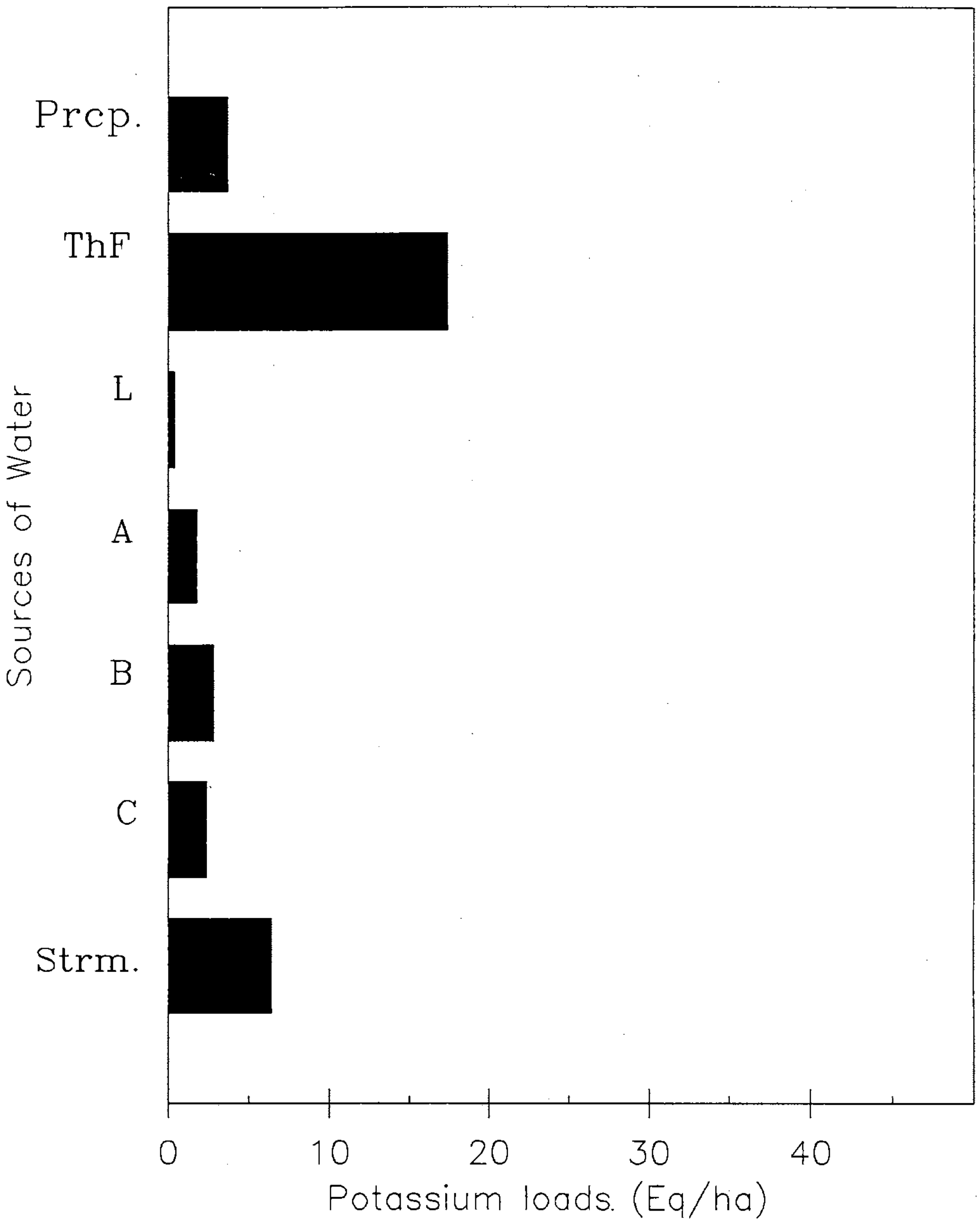


Figure 21. Total seasonal average loads of potassium.

cation loads were lower in quantity when compared to the respective quantity in the throughfall. The total seasonal average load measured from the litter layer flow was also relatively small compared to the other sources (Figure 19 to 26). The total seasonal average load of cations from the litter layer was 94 percent less than that measured from throughfall. The total seasonal average load of the hydrogen ion produced by the organic layer flow was 98 percent less than in precipitation. The total seasonal average load of anions in the litter layer flow was also less than input by 97 percent. Potassium and sodium loads were the lowest among the base cation loads measured in the litter layer flow. Sulfate showed the highest decrease in load among the anions. Out of the total average ion load of 5.7 Eq/ha from the litter layer flow, 4.1 Eq/ha (72 percent) were base cations (hydrogen ion excluded). Of the remaining 28 percent, 23 percent were anions and 5 percent was hydrogen.

In the A horizon flow, the total seasonal average ion load was greater than from the litter layer and each of the individual ions also showed varied increases. Total seasonal average load was five times greater from the A-horizon flow than litter layer flow. Total seasonal average load of base cations was about 419 percent greater from the A than from the litter. Similarly, anion loading was 630 percent greater from the A than from the litter. Calcium contributed the highest load of 11.4 Eq/ha to the change in

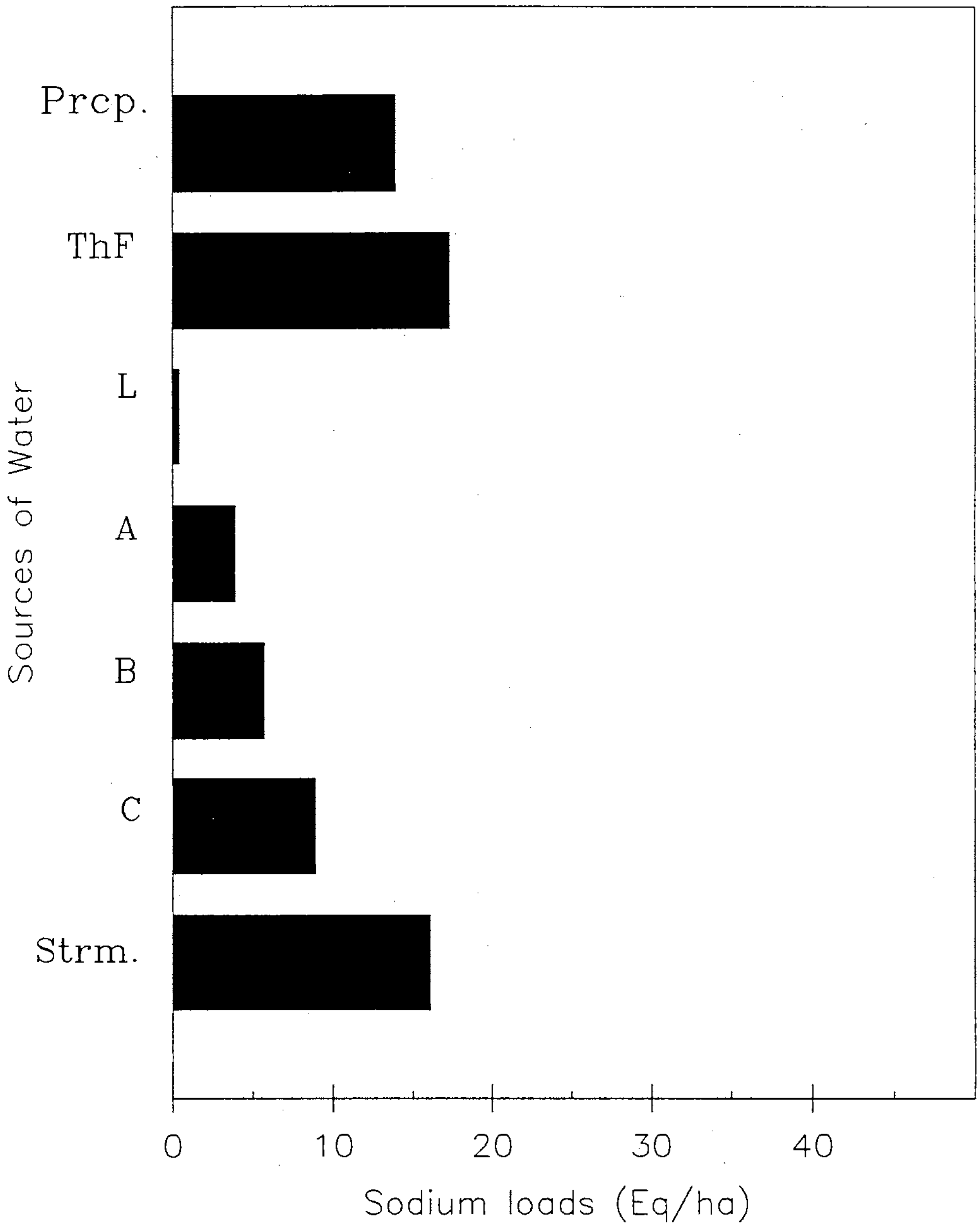


Figure 22. Total seasonal average loads of sodium.

cation loads. Sulfate total seasonal average load was 5.3 Eq/ha greater from the A-horizon than from the litter layer and accounted for the greatest load of the major anions. Nitrate-N concentrations of the A horizon flow were negligible and therefore the contribution to the total average load of nitrate-N from this horizon was negligible.

The total seasonal average load of ions from the B horizon was 43.4 Eq/ha, which exceeded the output measured from the A horizon by 11.1 Eq/ha. Of the 43.3 Eq/ha total, 25.4 Eq/ha were base cations and 15.3 Eq/ha were anions. The total average load of cations from the B horizon was 4.0 Eq/ha greater than the A horizon output. Calcium was the only cation load that less in the B-horizon flow compared to the A-Horizon flow. Anion loads showed greater increases in B-horizon flow (5.8 Eq/ha) as compared to cations. Nitrate-N did not contribute to the ion load from B-horizon flow.

The total average load of all ions from the C-Horizon was 52.5 Eq/ha. This exceeds the total seasonal average load from the B-horizon by 9.1 Eq/ha. The increase comes from an increase of 6 Eq/ha base cations and 4.5 Eq/ha anions. Sulfate and chloride were the only anions which contributed to the increased loads. Surprisingly, nitrate-N was observed in C horizon flow resulting in a very small load of 0.1 Eq/ha. This may indicate the influence of active macropores in the soil which fed the C-horizon. Among the cations, magnesium load in the C-horizon flow was about 4.0 Eq/ha greater than in the B-horizon flow and

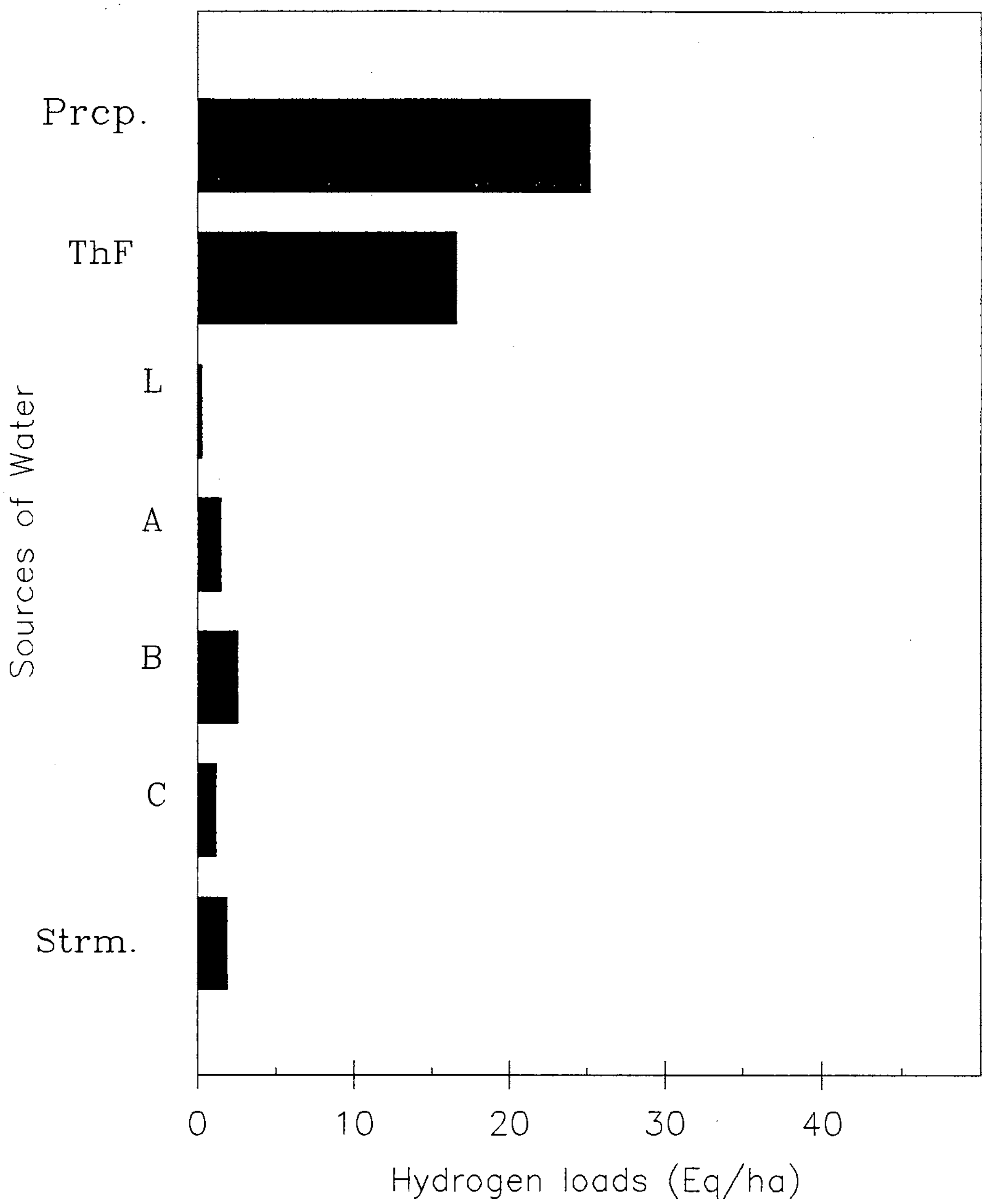


Figure 23. Total seasonal average loads of hydrogen.

dominated C-horizon flow at 12.0 Eq/ha. Calcium and potassium loads were slightly less in the C-horizon as compared to the B horizon loads.

The total seasonal average load of base cations expressed as in Eq/ha exported by streamwater, exceeded precipitation imports (Table XXIV, Appendix B). Streamwater exported 82.3 Eq/ha of base cations while precipitation delivered 35.6 Eq/ha of base cations. Magnesium net loss was the highest among the base cations, 25.8 Eq/ha, compared to calcium net loss of 16 Eq/ha (Figure 19 and 20). The watershed canopy and soil accumulated nitrate-N, sulfate and chloride (Figure 24, 25 and 26). Streamwater output of the major anions was 30 Eq/ha, while precipitation input was 2.1 Eq/ha. Even though the sulfate load exported in streamwater, was larger than loads of the other anions, the accumulation of sulfate by the watershed accounted for 48 percent of the imported load (38.4 Eq/ha) by precipitation.

The enrichment of rainfall as it passed through the canopy caused the throughfall load of calcium to exceed the load introduced by precipitation (Figure 19). The organic layer acted as an accumulator or sink of calcium as well as all other ions. The total load of calcium measured from the litter layer flow was 2.5 Eq/ha. This amount (2.5 Eq/ha) from the litter flow represented 15 percent of the calcium input by throughfall. The total load of calcium from the A-horizon flow was about 4.5 times greater than the amount measured from the litter layer. The B-horizon acts as an

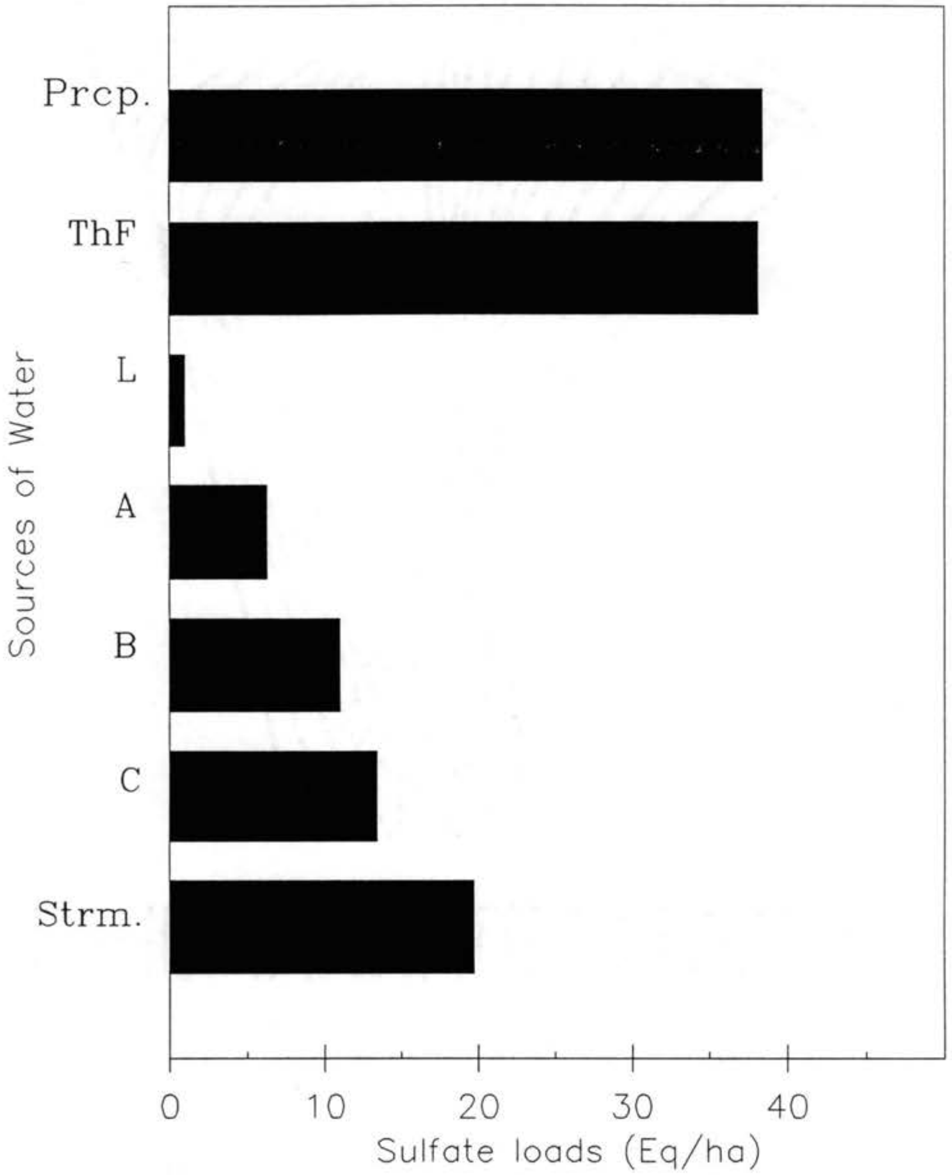


Figure 24. Total seasonal average loads of sulfate.

exchange column for calcium and reduced this cation by 23 percent. The total average load measured from the C-horizon was 7 percent less than from the B horizon. The largest total average load of calcium measured from the streamwater, which exported 27.4 Eq/ha. This represents an increase of 19.2 Eq/ha over the C horizon load (Table XXIV, appendix B).

The total seasonal average load of magnesium in subsurface flow from soil horizons steadily increased as water migrated downward through the soil (Figure 20). Precipitation delivered a 6.6 Eq/ha magnesium to the watershed. This load increased to 16.7 Eq/ha as water passed through the forest canopy. The total average load of magnesium was small, only 0.8 Eq/ha from the litter layer. Magnesium loads consistently increased with depth through the soil horizons to the streamwater. The total average load of magnesium measured from the A-horizon flow was 4.3 Eq/ha. This was five times greater than the load measured from the litter layer. There was a consistent increase in the total average load of magnesium, which ranged from 30 to 47 percent as the water passed through the soil horizons. The total average load of magnesium from streamwater was 32.4 Eq/ha, which was a 63 percent greater than the load in C-horizon flow.

Nearly 4 Eq/ha of potassium was introduced by precipitation. This was increased to 17.4 Eq/ha in the throughfall, which represents a 370 percent increase over the precipitation (Figure 21). Again, the litter layer

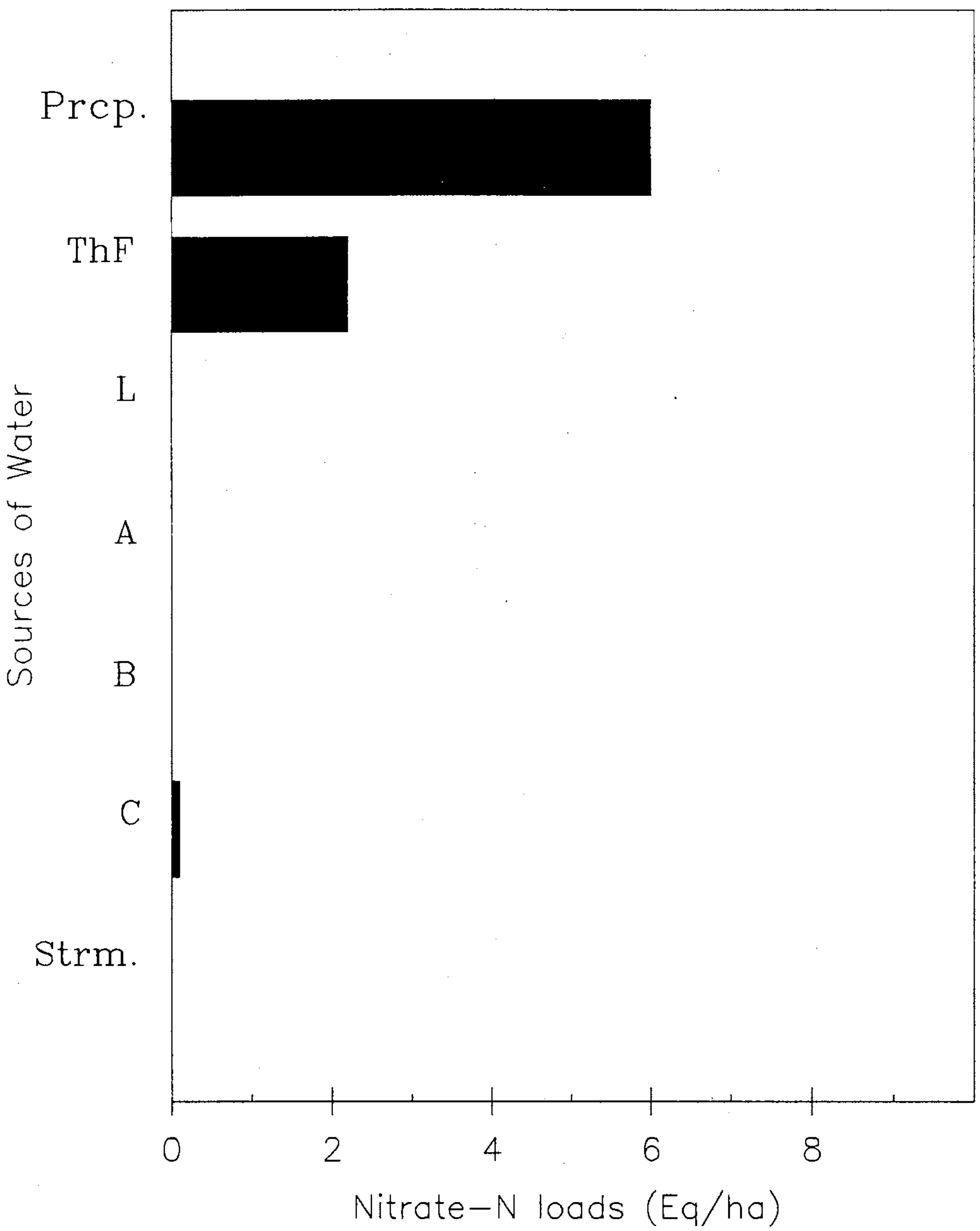


Figure 25. Total seasonal average loads of nitrate—nitrogen.

acted as an accumulator of potassium. The total load of potassium measured from the litter layer flow was 0.4 Eq/ha. This amount from the litter flow represented two percent of the potassium input by throughfall. The remaining 98 percent of the potassium ion removed by the organic matter or leached to the A-horizon. The watershed exported potassium, thereby exhibiting a similar pattern to the other cations, that is a net loss of potassium from the watershed.

The total seasonal average load of sodium was the greatest among the cations introduced into the watershed by precipitation. Sodium exhibited the same pattern of average total seasonal load as magnesium. (Table XIV) suggested that the three storms probably originated from the same sources rich in sodium and provided 13.9 Eq/ha of load to the watershed. This input was increased by 3.4 Eq/ha as the water passed through the canopy. The litter layer removed 98 percent of sodium load in a pattern similar to the other cations. There was a steady increase in load of sodium from the litter layer flow to stream flow. Total average load of sodium measured from A horizon flow was ten times greater than the load calculated from the litter layer flow. A 32 percent larger load was released as water moved from A to B horizon and an extra 36 percent of sodium load was released in the C horizon flow. The watershed exported 16.1 Eq/ha of sodium. This net loss of sodium from the watershed followed the similar pattern to the other cations, especially magnesium.

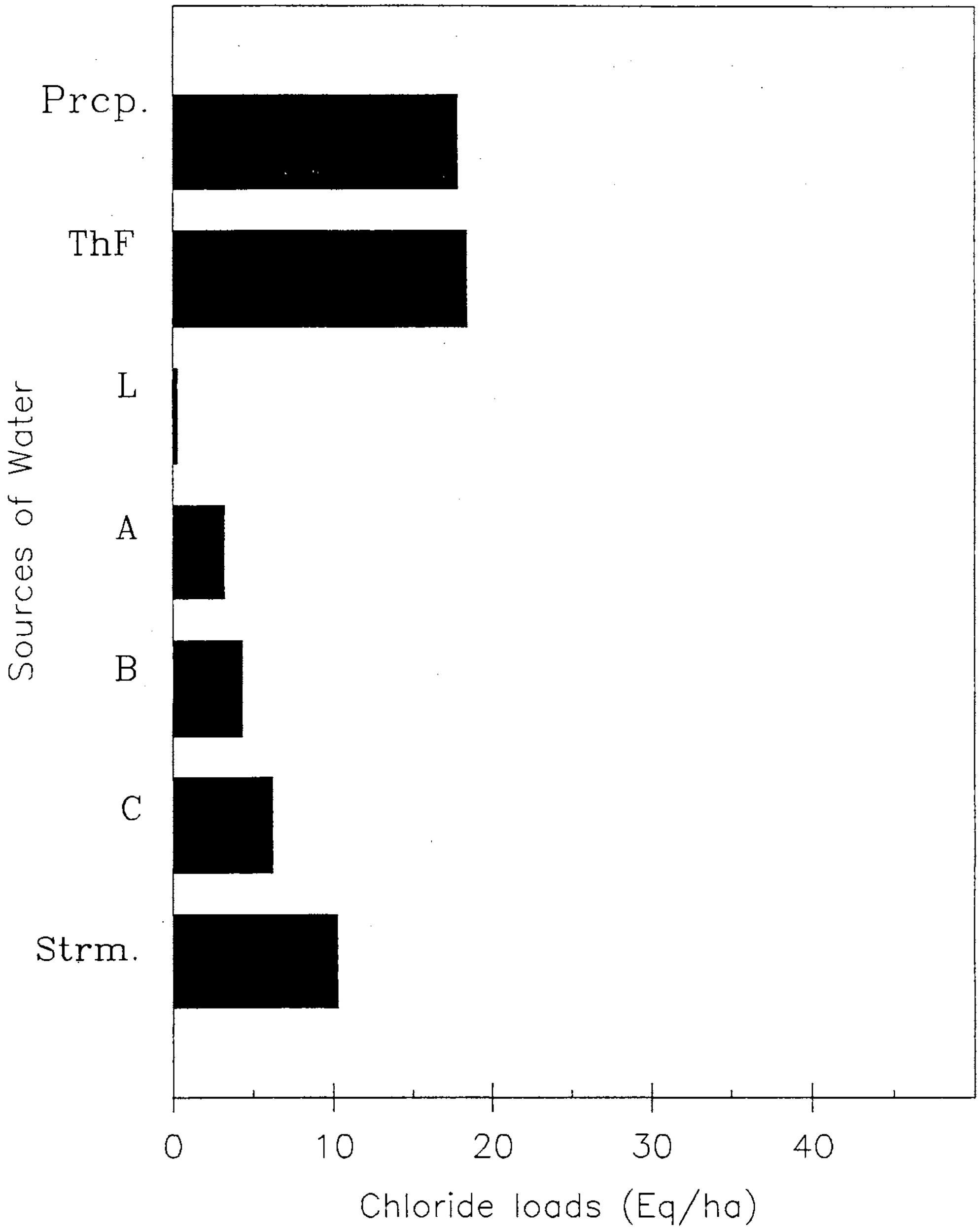


Figure 26. Total seasonal average loads of chloride.

A 25.2 Eq/ha of hydrogen total seasonal average load was introduced by precipitation (Figure 23). The forest canopy removed 34 percent of precipitation load and an additional 64 percent removed by the litter layer.

Figures 24-26 show the distribution of three anions measured in the watershed. The three anions measured were sulfate, nitrate-N and chloride. Precipitation and throughfall total average loads show that sulfate and chloride anions simply passed through the canopy, while 63 percent of nitrate-N was retained by the canopy vegetation. These anions, as well as the major cations exhibited low variation in total seasonal average loads from the litter layer. Figures 24 and 26 show that sulfate and chloride exhibited a similar pattern of increasing loads as water migrated through the soil horizons. Ion exchange and geochemical weathering may have resulted in increasing loads with depth. However, the total seasonal average load of sulfate and chloride exported by stream were about half compared to the input by precipitation.

Nitrate-N was conserved within the forest ecosystem (Figure 25). The total seasonal average load introduced into the watershed of nitrate-N was 6.0 Eq/ha. About 63 percent of nitrate-N was retained by the canopy and the remaining 37 percent of nitrate-N load was removed by the organic litter layer. No nitrate-N was observed in the soil horizons and streamflow, except the C-horizon were a very small load of 0.1 Eq/ha was recorded.

Seasonal Storm Load Variation

The climate of the study area is seasonal and can be divided into summer, winter, spring and fall. Since no significant storms occurred in the fall during this study, the comparisons of the seasonal loads were based on the results of the three seasonal storms.

Tables XIV and XV and Figures 27 through 31 show the seasonal storm loads of constituents in precipitation and throughfall, soil horizon flows and the output from the watershed ecosystem represented by streamflow loads. Graphs presented are for a selected set of ions that show the variations from season to season. Three different seasonal patterns of variation in loads were observed (Table XIV). In general, the load of base cations lost via streamflow was consistently higher than the input in precipitation across seasons, except that in the summer storm, the calcium inputs and outputs were equal. In contrast, anion outputs were consistently lower than the inputs for all seasons. The load of base cations exported in the streamflow was highest in winter, followed by spring and summer.

Among the three storms, the spring storm precipitation introduced the largest load of calcium into the watershed (348 g/ha), while the smallest load was introduced in the summer (150 g/ha). The calcium load in throughfall was greater than in precipitation during the summer and the spring storms. During the summer storm, the calcium load in throughfall was 217 percent greater than in precipitation, while a five percent enrichment occurred during the spring storm. Calcium load in throughfall was smaller than in precipitation by 26 percent only in the winter storm.

The load of calcium in litter layer flow was small in the spring and summer storms primarily because of the small amounts of flow produced (Figure 27). In the winter, the litter layer flow was greater than during spring and summer storms. Consequently, the calcium load in litter layer flow in the winter was larger than litter layer loads in the spring and summer storms and nearly equaled the load of calcium delivered to the litter layer in winter throughfall.

Calcium load from the A, B and C horizons were increasingly larger with depth for both the summer and spring storms. Loads from subsurface flow from all horizons in the spring were larger than respective loads in the summer, primarily due to greater flow volumes. Loads of calcium in subsurface flow in the winter did not follow the spring and summer pattern. Despite increasing flow volumes with depth, decreasing calcium concentration in the flow from the A to the B and to the C horizons caused loads to decrease with depth.

The addition of calcium load by geochemical weathering was greater in the winter and spring than in summer season. The winter storm exported the greatest load of calcium from the watershed (787 g/ha), while the smallest load was exported in summer (150 g/ha).

TABLE XIV

INPUT AND OUTPUT OF CHEMICAL LOADS BY SOURCE FOR THE MAJOR CATIONS AND ANIONS

Seasonal Storm	Source of Water	Ca	Mg	K	Na	H	SO4	NO3-N	Cl
		(values in grams per hectare)							
Summer									
	Prcp Load	149.8	73.8	36.5	214.9	11.2	785.7	348.9	231.9
	ThF Load	475.2	313.1	159.9	413.6	3.7	746.4	50.7	405.9
	TSSC Load	101.0	62.6	38.9	99.7	0.7	260.4	3.3	130.3
	Strm Load	150.4	151.0	57.7	82.0	0.5	189.7	0.5	65.8
Winter									
	Prcp Load	190.1	102.5	123.2	266.6	29.2	1989.7	370.0	547.9
	ThF Load	140.4	109.5	274.0	253.2	19.1	1803.5	276.0	419.9
	TSSC Load	1124.0	453.6	549.0	670.3	10.4	2237.9	16.4	691.9
	Strm Load	786.9	576.3	405.6	528.1	3.4	1142.6	1.2	551.8
Spring									
	Prcp Load	348.1	63.3	271.7	479.3	35.8	2753.8	387.8	1114.7
	ThF Load	365.5	184.7	1604.5	524.2	27.4	2942.4	84.8	1131.6
	TSSC Load	631.0	401.9	274.9	535.3	6.0	2077.9	11.1	660.7
	Strm Load	710.8	455.1	282.5	498.4	1.9	1508.4	1.6	477.4

* TSSC Load= Total Subsurface Chemical Load

TABLE XV

CHEMICAL LOAD OF MAJOR CATIONS AND ANIONS IN SOIL HORIZONS

Seasonal Storm	Source of Water	Ca	Mg	K	Na	H	SO4	NO3-N	Cl
		(values in grams per hectare)							
Summer									
	Litter	1.8	0.4	0.4	0.5	0.0	1.3	0.0	0.3
	A-Horizon	18.8	3.9	5.3	6.1	0.1	15.3	1.3	8.5
	B-Horizon	21.3	16.2	8.9	27.7	0.2	59.9	0.3	25.4
	C-HOrizon	59.1	42.1	24.3	65.4	0.3	183.9	1.7	96.1
	TSSC Load	101.0	62.6	38.9	99.7	0.7	260.4	3.3	130.3
Winter									
	Litter	136.7	21.9	38.4	18.8	0.6	113.8	2.4	24.0
	A-Horizon	533.4	118.5	164.9	218.2	3.3	685.0	2.3	256.3
	B-Horizon	307.8	147.8	212.7	198.6	4.6	791.5	1.9	228.4
	C-HOrizon	146.9	165.4	133.0	234.7	1.9	647.6	9.8	183.2
	TSSC Load	1124.0	453.6	549.0	670.3	10.4	2237.9	16.4	691.9
Spring									
	Litter	13.7	6.6	6.6	9.5	0.2	32.2	0.1	5.9
	A-Horizon	132.3	32.6	38.4	46.6	1.1	207.0	0.8	71.6
	B-Horizon	200.4	132.6	106.6	167.2	3.1	733.6	0.4	200.6
	C-HOrizon	284.6	230.1	123.4	312.0	1.5	1105.1	9.8	382.6
	TSSC Load	631.0	401.9	274.9	535.3	6.0	2077.9	11.1	660.7

* TSSC Load= Total Subsurface Chemical Load

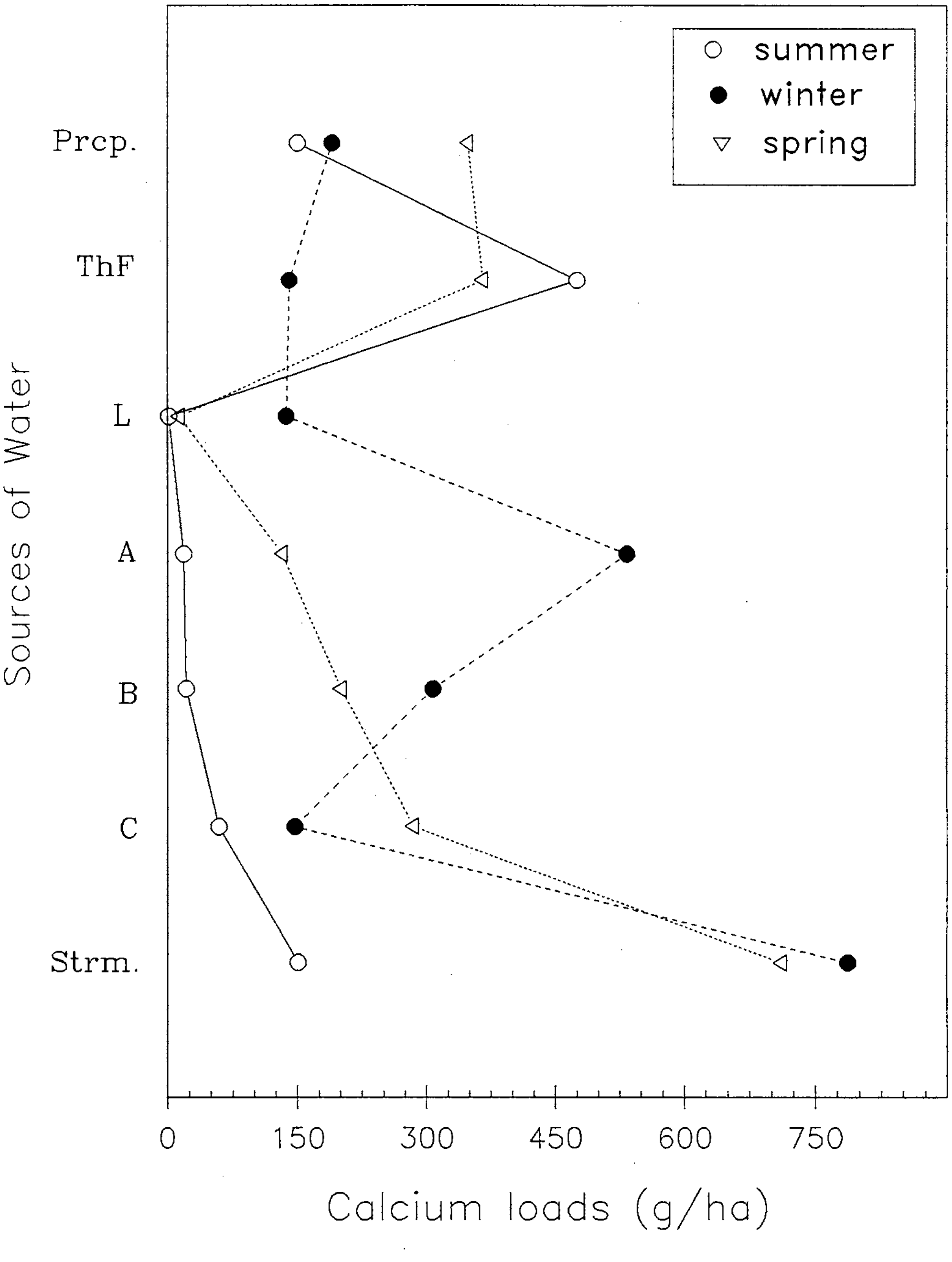


Figure 27. Calcium loads per source of water for each seasonal storm.

The seasonal storm load of magnesium introduced by precipitation varied seasonally. The largest load of magnesium delivered into the watershed was by the winter storm (102 g/ha), while the smallest load was introduced in the spring storm (63 g/ha). The magnesium load in throughfall was greater than in precipitation during all three seasonal storms . During the summer storm, the magnesium load in throughfall was 324 percent greater than in precipitation, which also represented the highest enrichment among the three seasonal storms. Magnesium enrichment of throughfall was 192 percent in the spring storm.

The magnesium load in the litter layer flow was smaller than in throughfall for all three seasonal storms. In the litter layer, the load of magnesium was small in the spring and summer storms once more because of the small amounts of flow produced (Figure 28). A greater flow from the litter layer during the winter storm produced larger magnesium load than the litter layer loads in the spring and summer storms.

Magnesium loads from A, B and C horizons were increasingly larger with soil horizon depths as water migrated during the seasonal storms. Loads from subsurface flow from all horizons in the winter were larger than respective loads in the summer and spring, except for the C horizon in which the spring storm produced greater magnesium load than the winter storm. The greatest addition by geochemical weathering to magnesium load in the C-horizon

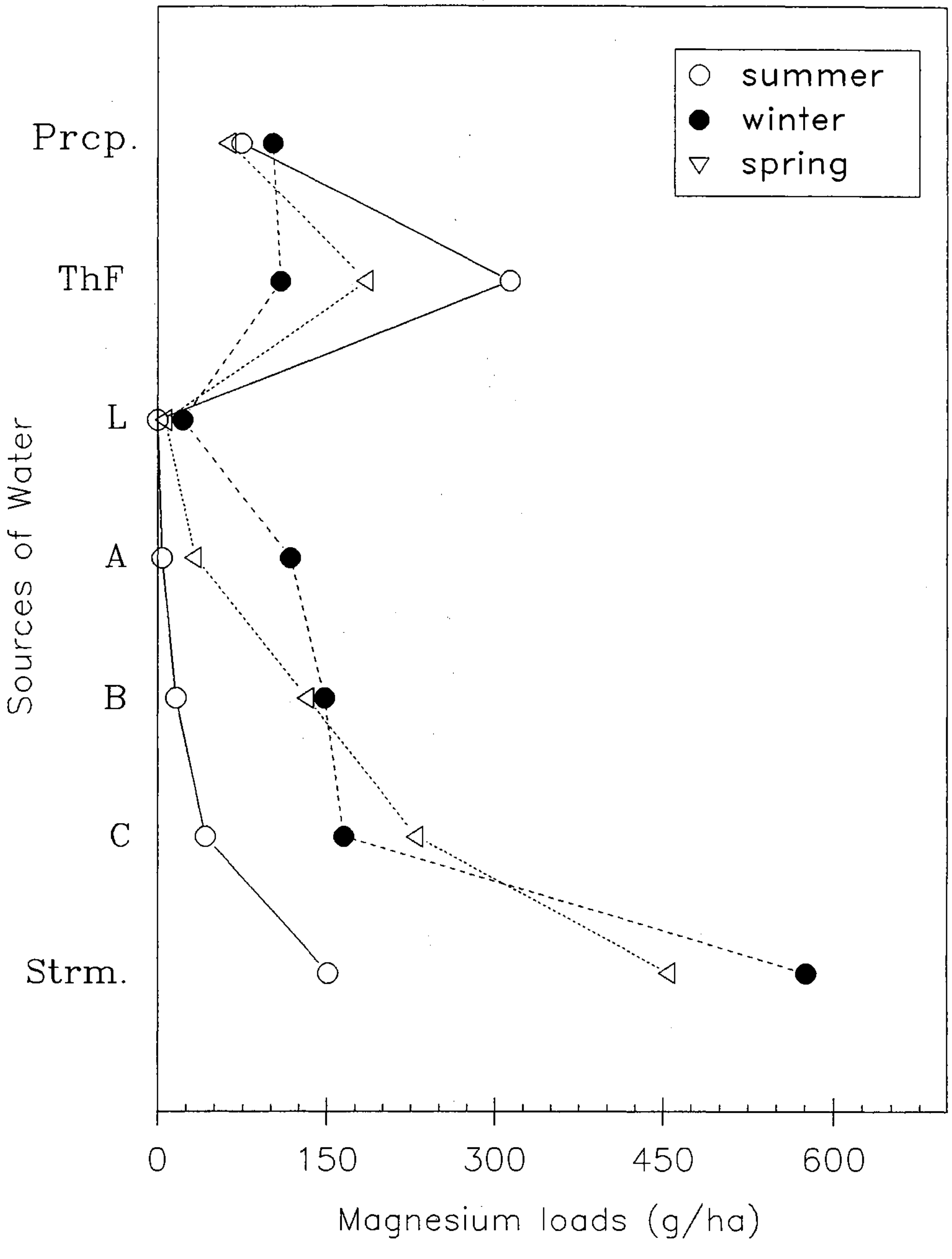


Figure 28. Magnesium loads per source of water for each seasonal storm.

occurred during the winter storm. The magnesium load exported by streamwater was the highest in the winter storm compared to other seasonal storms.

The seasonal variation of potassium loads in the watershed is shown in Figure 29. The potassium loading introduced into the watershed by precipitation was the largest during the spring (272 g/ha), while the smallest load was introduced in the summer storm (36 g/ha). The potassium load in throughfall was greater than in precipitation for all three seasonal storms. The greatest potassium enrichment occurred in throughfall during the spring storm. A striking increase in load of potassium, from 272 g/ha in precipitation to 1604 g/ha in the throughfall, was observed during that storm.

The loads of potassium from litter layer flow were smaller than in throughfall for the three storms. Litter layer flow delivered the smallest seasonal potassium load during the summer storm compared to spring and winter storms (Table XV).

Potassium loads from the A, B and C horizons were gradually increased with depth for both the summer and spring storms. Subsurface flow from all horizons produced larger loads during the spring than respective loads in the summer. Loads of potassium in subsurface flow in the winter followed the spring and summer pattern and produced larger loads from all horizons compared to both the summer and spring storms. However, decreasing potassium concentrations

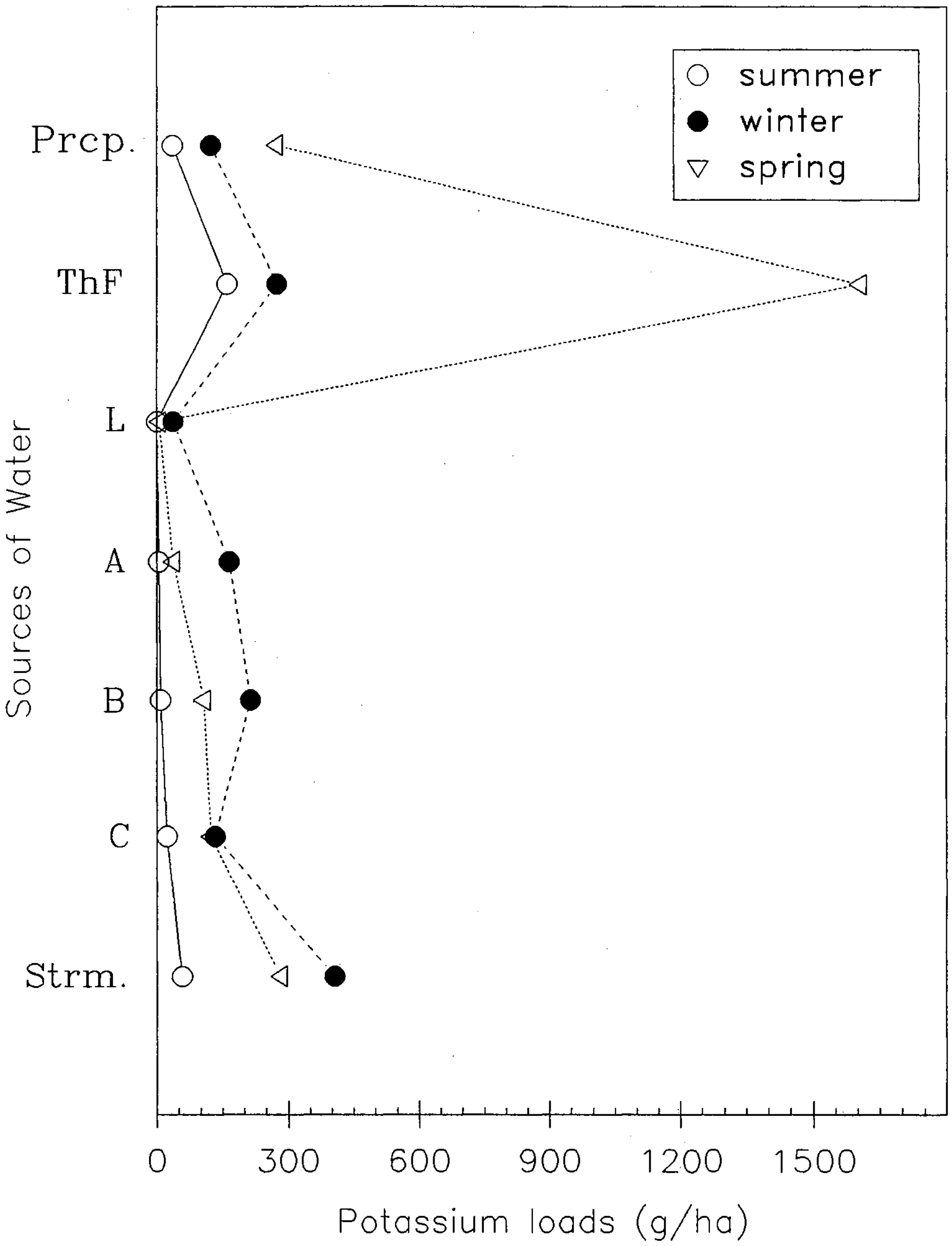


Figure 29. Potassium loads per source of water for each seasonal storm.

in the flow from the B to the C horizon caused loads to decrease in the C horizon. Geochemical weathering in the C-horizon was greatest during the winter storm. This resulted in higher releases of potassium to streamflow.

The variation of selected anions within the watershed is shown in Figures 30 and 31. Among the three seasonal storms, the spring storm precipitation delivered the largest load of sulfate into the watershed (2754 g/ha), while the smallest load was introduced in the summer storm (786 g/ha). The spring storm was the only storm when the sulfate load in throughfall was larger than in precipitation (Table XIV). The sulfate load in throughfall was slightly smaller than in precipitation during the summer and winter storms.

The load of sulfate in litter layer flow was smaller than in throughfall for all three storms. The sulfate load in litter layer flow in the winter was larger than litter layer loads in the spring and summer storms (Figure 30).

Sulfate loads from the A, B and C horizons were similar to those of calcium, with increasingly larger loading with depth for both the spring and summer storms. Greater subsurface flow volumes during the spring storm from all horizons produced larger sulfate loads than were produced by the summer storm. Loads of sulfate in subsurface flow in the winter did not follow the spring and summer pattern. Despite similar sulfate concentrations in the B and C horizons, sulfate load in B horizon flow was smaller than in the C horizon. Geochemical weathering of sulfate was not

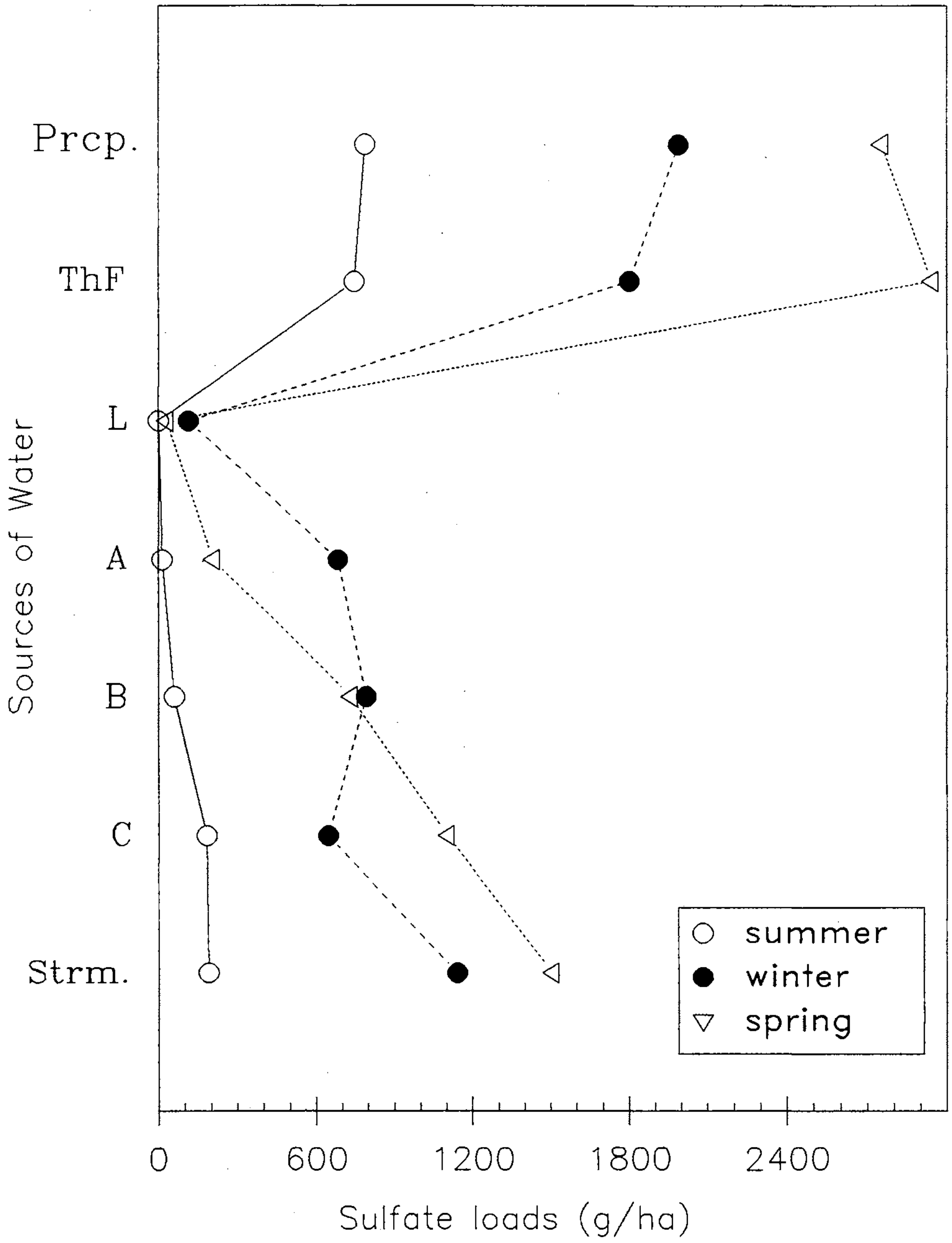


Figure 30. Sulfate loads per source of water for each seasonal storm.

enough to exceed the input load by precipitation. The load of sulfate exported in the streamwater during the spring storm was the largest, followed by winter and summer storms.

Figure 31 shows the storm load variation in nitrate-N. The input of nitrate-N into the watershed by precipitation was greatest during the spring, followed by winter and summer. The retention by the canopy of nitrate-N during the spring and summer storms was about 78 percent and 86 percent, respectively, while the retention was 26 percent in winter. There was nearly a total reduction in the load of nitrate-N from the precipitation and throughfall to streamflow. Nitrate-N was retained by the soil horizons. The exception was the C-horizon where the nitrate-N load about 8-9 g/ha occurred in the winter and spring, and 1 g/ha in the summer.

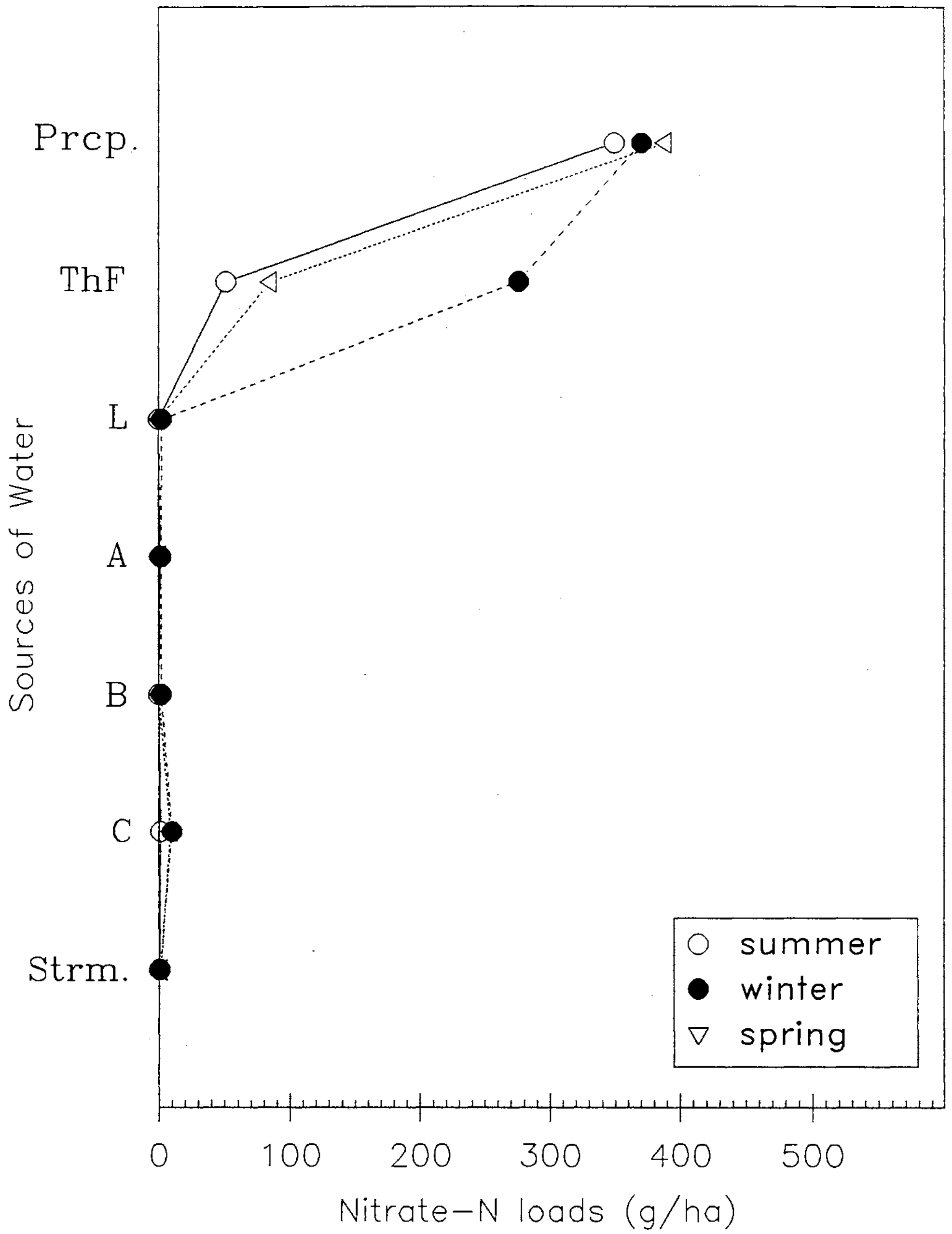


Figure 31. Nitrate–N loads per source of water for each seasonal storm.

Cation - Anion Balance

A comparison of the total meq/l of cations to the total meq/l of anions was made for the seven sources of water for each seasonal storm (Tables XVI, XVII and XVIII). The total meq/l of cations exceeded the total meq/l of anions in all sources except precipitation and in winter-season throughfall for all storms. The ionic balance for precipitation was good with total cationic strength exceeding anionic strength by only 1 to 5 percent among storms. A general increase in cation and anion concentrations occurred from the precipitation and throughfall inputs to the subsurface flow from the four soil horizons and in the streamflow. Differences in ionic strength were greatest in subsurface flow from the L and A horizons for all storms, with cationic strength from 30 to 60 percent greater than the anionic strength.

Samples of rainfall, throughfall and sources of flow from the winter and spring storms were analyzed for dissolved organic carbon (DOC) (Tables XVI, XVII and XVIII). Results show a good correlation between DOC and ionic imbalance (Figure 32 and 33).

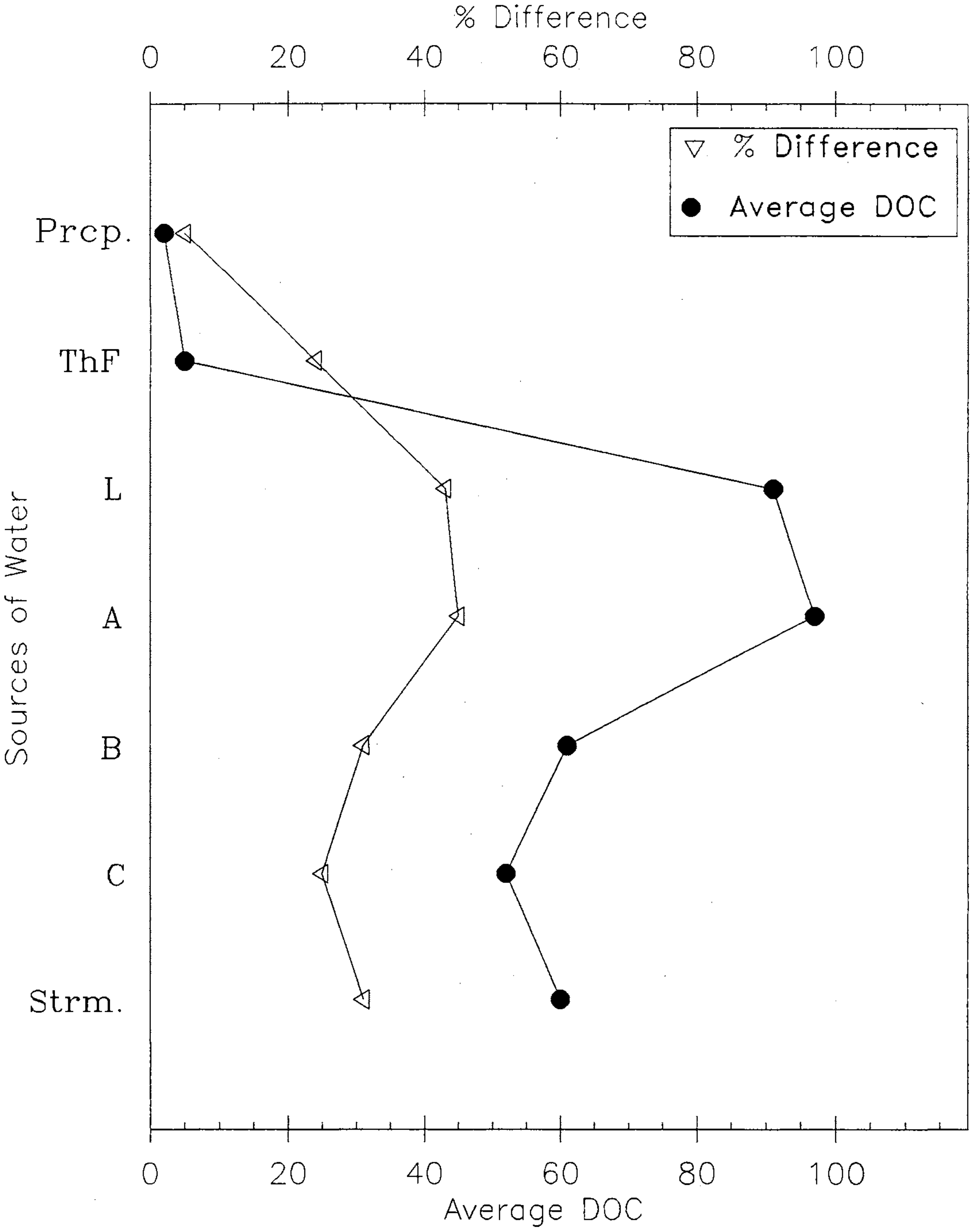


Figure 32. The relationship between average DOC (mg/l) and the % of cation–anion balance for winter storm.

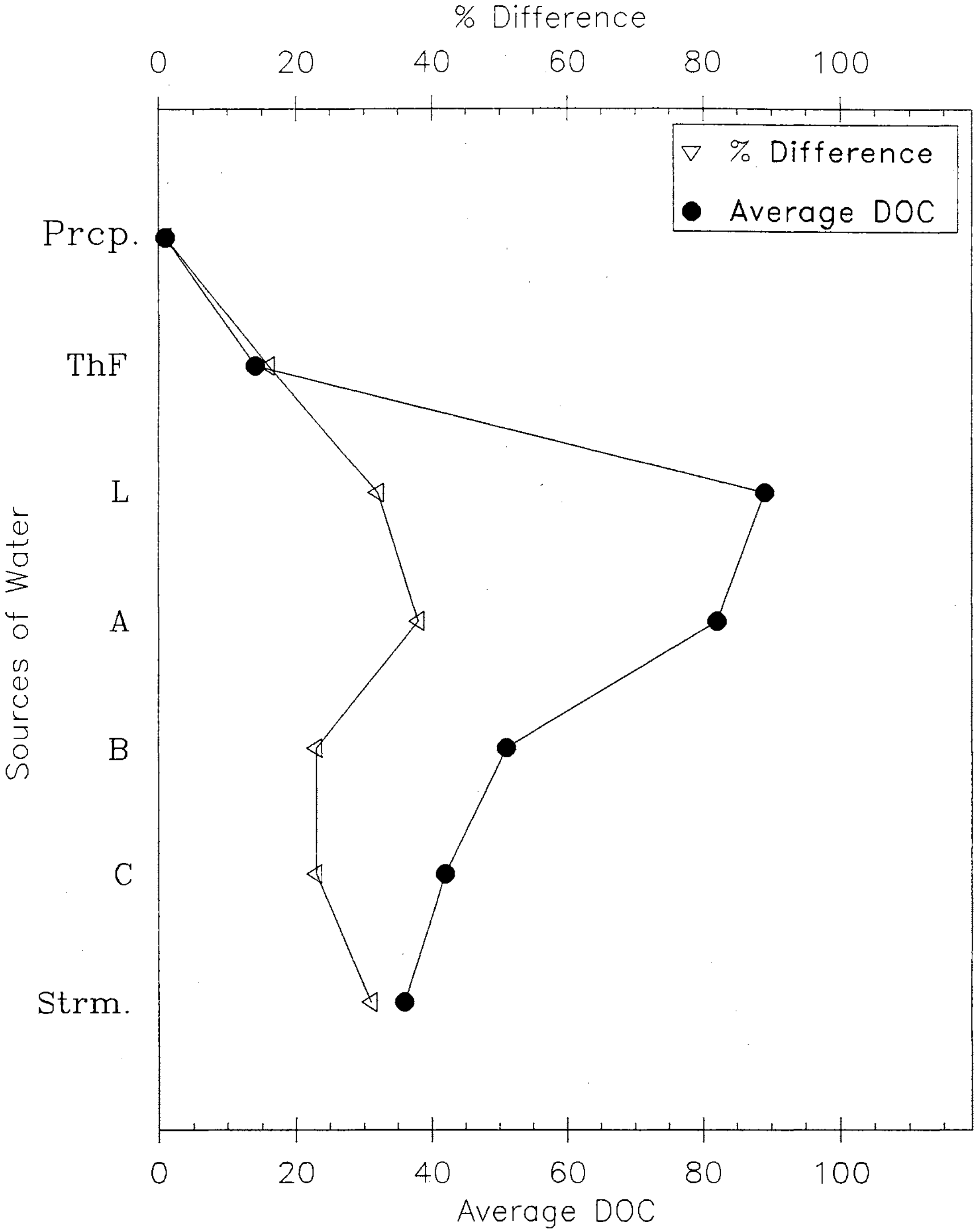


Figure 33. The relationship between average DOC (mg/l) and the % of cation–anion balance for spring storm.

TABLE XVI

CATION ANION BALANCE FOR SUMMER STORM

Source of Water	SUM CATION	SUM ANIONS meq/l	% DIFFERENCE	Average DOC (mg/l)
Prcp.	0.0	0.090	5	NA
ThF	0.1	0.100	6	13
L	0.3	0.080	62	NA
A	0.2	0.080	53	NA
B	0.2	0.100	33	NA
C	0.1	0.180	4	NA
Strm.	0.2	0.100	36	96

NA=not available

TABLE XVII

CATION ANION BALANCE FOR WINTER STORM

Source of Water	SUM CATION	SUM ANIONS	% DIFFERENCE	Average DOC (mg/l)
	meq/l			
Prcp.	0.062	0.068	5	2
ThF	0.038	0.062	24	5
L	0.159	0.064	43	91
A	0.189	0.071	45	97
B	0.162	0.085	31	61
C	0.158	0.095	25	52
Strm.	0.163	0.085	31	60

TABLE XVIII

CATION ANION BALANCE FOR SPRING STORM

Source of Water	SUM CATIONS	SUM ANIONS	% DIFFERENCE	Average DOC (mg/l)
	meq/l			
Prcp.	0.054	0.055	1	1
ThF	0.080	0.058	16	14
L	0.150	0.078	32	89
A	0.189	0.086	38	82
B	0.154	0.097	23	51
C	0.176	0.109	23	42
Strm.	0.157	0.083	31	36

CHAPTER VI

DISCUSSION

Hydrologic processes

Hydrologic Budgets

Rainfall is strongly seasonal. Over 50 percent of the total precipitation fell in the spring season, which extends from March 25 to June 30. The hydrologic behavior of a watershed is largely determined by the precipitation input, soil moisture storage, and evapotranspiration. As expected, high precipitation produced higher streamflow; however, this was dependent on the different seasons. Streamflow responded quickly to rainfall and the discharge from the watershed outlet was at a maximum during the winter storm period when soil moisture was at or above field capacity and evapotranspiration was minimal. During the summer storm period, when evapotranspiration was very high, streamflow discharge was low and it declined rapidly to baseflow levels soon after rain terminated (Table III). The hydrologic response data showed considerable seasonal differences in the streamflow discharge. The percent of precipitation which emerged as streamflow during the winter storm was 79 percent (Table III) compared to 26 percent for the summer storm. The remaining percent of precipitation was lost due to increases in evaporation, increased canopy interception, transpiration of trees and other vegetation during the stress periods of the summer, and losses to soil storage. An average of 51 percent of total precipitation was produced as streamflow (Table III). Therefore, the remaining 49 percent of the total precipitation was lost as evapotranspiration and soil storage during the period of the year 1989-1990. Johnson and Swank (1973) reported average annual streamflow from a catchment in North Carolina was 53 percent of precipitation, while at Walker Branch, 56.5 percent of precipitation was lost as streamflow during a 2 year period (Elwood and Henderson, 1975). The total mean average of 49 percent net gain is comparable to the study by Luxmoore and Huff (1989) who estimated an average net gain of 48 percent. A two year study by Elwood and Henderson (1975) resulted in net gain estimate of 43.5 percent, or 5.5 percent lower than this study.

The hydrologic budget is an important component of the chemical budget and our estimates of the chemical budget can be used to help quantify some aspects of the biogeochemical cycle for the watershed.

Subsurface Flow Contribution

The variation in total subsurface flow as a percentage of rainfall (Table IV) indicates that soil moisture storage influenced the amount of lateral flow. The small percentage of precipitation that emerged as subsurface flow during the summer storm is most likely due to the greater canopy interception, greater demand for water to supply soil storage and the high rates of summer evapotranspiration. During the winter storm, 42 percent of the 10.5 cm of the precipitation emerged as subsurface flow at the lower site and 97 percent emerged at the upper site. This high percentage of winter storm precipitation which was produced as subsurface flow occurred because of the absence of the leaves in the canopy, the trees had little interception capacity and the low temperature helped to reduce the soil losses. Beasley (1976) and Turton (1989) concluded that during periods of lower rainfall a smaller percentage of precipitation emerged from the site as subsurface flow because most of the water went to evapotranspiration and soil storage.

The upper site produced more flow than the lower site for all storms and seasons. This is because of the area difference with the upper site being more than three times the size of the lower site, and also probably due to the variability of soils and geology.

The 9.0 cm of mean area weighted flow (MAWF) calculated for both sites indicates that subsurface flow can accounts for the total streamflow produced during the winter storm (Table IV). These results also indicate that subsurface flow from the soil horizons was the major source of contribution to the total streamflow volume and that channel precipitation is probably a minor contributor to the total streamflow volume for this watershed.

The difference in total subsurface flow produced by the summer and spring storms and the total outlet streamflow (Table IV) could be caused by one or more of the following factors: First, and possibly most important, is that our sites do not represent the "total watershed" very well. The second possibility is that saturated overland flow, may have occurred in limited areas along the stream channel. Finally, macropores and root channels may have transferred precipitation and throughfall inputs directly to the stream. Mosley (1979) reported that root channels and macropores in the upper soil could contribute substantially to streamflow.

In the winter storm, total streamflow volume was less than the total subsurface flow volume (MAWF) produced by the two sites. This was probably due to the additional water movement from outside the topographic boundary of the subsurface flow sites or the expansion of the variable source area in the watershed.

The high percentage of flow contribution by the B-horizon during the wet period was due to the wet antecedent condition which already existed in the B-horizon prior to rainfall (Figures 8 and 10). Precipitation passed through the highly permeable organic horizons by vertical macropore triggered saturated subsurface flow in the B-horizon (Williams, 1990). For spring and summer, small and large storms preceded by dry period, the C-horizon contributed the highest percentage of subsurface flow to total flow (Figure 8 and 10). This was because of the saturated flow conditions that persisted in the C-horizon; therefore, small inputs of precipitation caused lateral movement of water to occur. These results also demonstrated the influence of intensity and duration of the precipitation and antecedent moisture conditions on controlling the discharge from the horizons. These outcomes are in total agreement with results reported from the same study area by Williams (1990) and from a similar study presented by Turton (1989).

Table V shows the values and the percentage of the total subsurface flow contributed from each horizon by seasonal storms. These results indicate that flow contribution is evident in all four horizons. The organic horizons (L and A) contributed the smallest percentage to the total flow during the growing season. This is expected as these horizons have higher hydraulic conductivities due to the high organic content and lower clay content. An noteworthy observation is that these same organic horizons produced the next highest percentage of subsurface flow during the winter storm. The majority of the percentage of subsurface flow was contributed by the A horizon on the upper site. This contribution and the subsurface flows production per unit area from the upper site, which is almost equal to the total input of precipitation, might be due to an underestimate of the contribution area of the upper site, or additional water flow from outside the topographic boundary of the upper site. Note that the winter storm is the only storm (Table V) in which subsurface flow exceeded total precipitation. This is most likely due to the wet conditions which may have extended the saturated zone upward into the organic horizons including the A horizon and produce saturated lateral flow . The existence of a perched water table in the B-horizon was confirmed by field observation of water levels (Williams, 1990). The existence of this saturated zone was supported by the vertical residual flow from previous storms, which provided for water flowing through the C-horizon flumes.

Overall, the B and C horizons were the major contributors of subsurface flow to the total subsurface flow. This is may be due to greater soil storage and thickness of lower soil horizons than the upper soil horizons. Williams (1990) measured saturated hydraulic conductivities of the B and C-horizons in the study area and found average values of $4.06 * 10^{-2}$ cm/sec and $6.45 * 10^{-5}$ cm/sec, respectively. Ahuja (1986) reported that in highly permeable soil on sloping sites, as was the case on our study sites, percolation into the lower horizons can occur rapidly and reduce the lateral flow contribution to subsurface flow from the upper horizons.

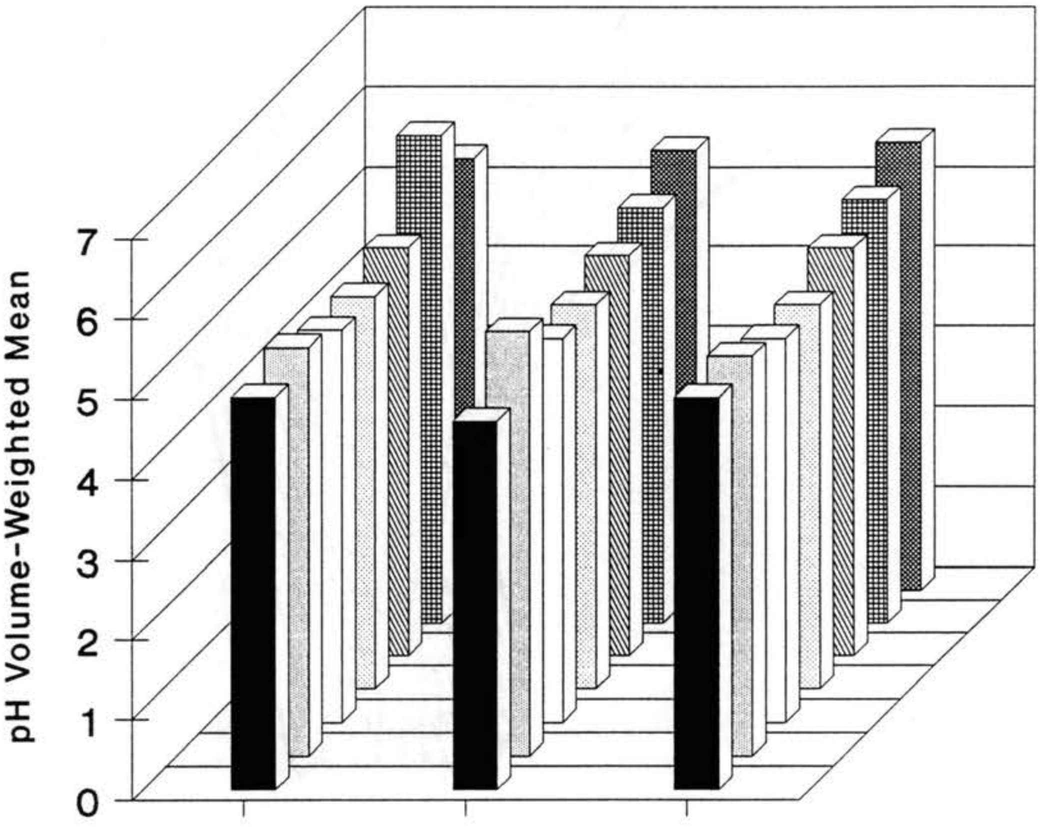
Chemical Composition of Water

The results of this study help explain the process of water flow through the soil horizons, which ultimately contributes to streamflow. Since it is difficult to identify the contribution of flow from each soil horizon, this study used the chemical composition of water to specify the source or sources of flow which contributed to streamflow. Streamwater quality is affected by seasonal and spatial variations in the quantity of precipitation, vegetative canopy structure in the watershed, chemical weathering, biological activities, and the hydro and geochemical changes in the soil horizons. The quantity of the input of dissolved constituents into the ecosystem through precipitation, is also vital in understanding the hydrochemical processes, which ultimately forms streamwater chemistry.

pH by Source and Season

Figure 34 summarizes the relationship between the sources of water and their pH during different seasons. The precipitation introduced into the watershed was slightly acidic with an average pH of 4.8, about 0.8 units more acidic than the pH of natural water (pH of 5.6). Granillo and Beasley (1985) and Nix and Thornton (1986) have found that the mean annual pH of precipitation for the mid-south region, including the study area, is less than five. Since the region used in this study is far from the industrial areas which produce atmospheric pollution, there are two possible explanations for the observed acidity due primarily to sulfate ions. First, all the storms are generated from the same source in the Gulf of Mexico. The other possible explanation is that the summer and spring storms are generated locally while the winter storm is generated from the south, crossing highly polluted industrial areas. This study is in agreement with earlier studies by Switzer et al. (1988) who observed a lower pH of 4.60-4.69 for the winter season when compared to the spring and summer seasons. This pattern of long distance transportation is similar to that observed by Beasley for the transport of sodium in the same watershed.

Throughfall pH was greater than precipitation pH. This was probably due to ion exchange in the forest canopy, which alters the existing chemicals in the vegetative canopy by replacing hydrogen ions with Ca^{2+}, Mg^{2+}, K^+ and Na^+. Kress et al. (1990) reported increased throughfall pH is in part due to cation exchange. The pH values of 5.0 to 5.1 observed in the throughfall is similar to the pH of 5.0-5.3 reported by Beasley et al. (1988). The summer storm had the highest neutralization of hydrogen ions by the forest canopy. This is in agreement with earlier studies by Eaton et al., 1973; Lovett et al., 1985. Eaton et al. also observed that 90% of the hydrogen ions introduced by precipitation into the forest canopy were neutralized within



		SUMMER	WINTER	SPRING
Strm.	▩	5.4	5.5	5.6
C	▦	6.1	5.2	5.3
B	▧	5.1	5	5.1
A	░	4.9	4.8	4.8
L	□	4.9	4.8	4.8
ThF	▒	5.1	5.3	5
Prcp.	■	4.9	4.6	4.9

Figure 34. pH volume-weighted mean of water samples by source and season.

the canopy. In the spring season, the reduction in hydrogen ions by the canopy was less than in the summer. This is due to the small leaves of the forest canopy. In the winter season a lack of ion exchange in the canopy resulted in a small reduction of hydrogen ions. This was simple due to a lack of leaves in the tree canopy in the winter as reported by other researchers (Switzer et al., 1988).

With the exception of the flow from the organic horizons (litter layer and A horizon), the pH of the flow from the other soil horizons increased slightly with depth. Apfelbeck (1987) recognized a similar trend. This increase in pH was probably due to the neutralization of hydrogen ions by the accumulated cations or by the adsorption of organic acids to the clay of the B-horizon. The total mean pH of flow from the organic horizons was lowered to 4.8, relative to throughfall, because of biological activity and decomposition of plants and leaves within the organic layer. The resulting activity produced organic acids. In turn, this contributed to lowered pH values. However, the total average pH values slightly increased with depth from the A-horizon to C-horizon presumably because the organic acid is neutralized and retained in the B-horizon. The streamflow pH was similar to the value of 5.5 observed within the C-horizon flow. This pH value is about the same as unpolluted precipitation, which is in equilibrium with atmospheric carbon dioxide (pH 5.6). This is the first chemical indication that supports the conclusion that the major contribution to the streamflow comes from the lower soil horizons (B and C horizons).

Precipitation Chemistry

Precipitation chemistry is affected by atmospheric pollution, seasonal weather conditions, the proximity of the area to the sea and other factors. Possible sources of cations and anions in precipitation include oceanic spray, terrestrial dust, gaseous pollutants, and volcanic emissions (Likens, 1977). The precipitation in this study was slightly acidic, providing the domination of hydrogen and sulfate ions. Hydrogen ions which dominated the precipitation were probably the result of anthropogenic emissions of SO_2 and NO_X which were hydrolyzed and oxidized to form strong acids in the atmosphere (Bolin, 1971; Likens and Bormann, 1974; and Likens et al., 1972).

The next most prevalent cations in precipitation were sodium, calcium and magnesium. The Gulf of Mexico is the most likely source of sodium into the watershed with other possible sources such as local land use and the weathering of shales in the Ouachita Mountains, as proposed by Nix and Thornton (1986).

The total average volume-weighted concentration of calcium in precipitation for the study period (Table VI) was similar to the study period average at Southern California which is reported by Schlesinger and Hasey (1980). Calcium was probably derived locally from the dust caused by forest roads and local human activities. Previous study by Martin and Harr in undisturbed watersheds in the Cascade Mountains of Oregon (1988) reported that calcium is derived locally from dust particles caused by agricultural activities while sodium was derived from ocean sprays from the Pacific Ocean. The total average volume-weighted magnesium concentration for the study period was 8 μeq/l (Table VI). This concentration is similar to an average concentration of 9 μeq/l reported by (Gilliam 1983). In this study, base cations such as calcium and magnesium may have come from dust particles, weathering of limestones, dolomites or carbonaceous shales. Likens anticipated that dust particles could be chemically altered to produced cations (1977).

Sulfate was the predominant anion in precipitation during the three seasonal storms (Table VI and Figure 11). The source of the sulfate is probably atmospheric pollution. This result is comparable to an earlier study by Nix and Thornton (1986) conducted in Polk County, Arkansas and similar to the result reported from Santee Experimental Forest (Gilliam 1983). Sulfate is the major source of rainfall acidity, contributing more than 60 percent of total acidity introduced into the watershed. This assessment agrees well with the findings of Richter et al. (1983) and Likens (1977).

Throughfall Chemistry

The chemical quality of precipitation is altered as it passes through the forest canopy. The changes in canopy structure in response to seasonal changes and climate conditions apparently has a pronounced effect on throughfall chemistry. The canopy leaves in the summer and spring increase the interception of atmospheric dry deposition while in the winter season, the absence of leaves in the canopy reduce the dust particles that could be collected on leaves and subsequently washed out as nutrients into the system. Precipitation and canopy condition may affect a great deal of the water quality reaching the forest floor, small amounts of precipitation resulted in high concentrations of nutrients. As described by Gilliam (1983), dilution may result in lower concentrations of ions in water at high precipitations. During the winter seasons, in the absence of leaves in the canopy, precipitation passed through the canopy and into the watershed soil almost unchanged. However, an increase in all cations except hydrogen and an increase in all anions except nitrate was observed for summer and spring storms as shown in Table VIII. Hydrogen ions are probably retained in the canopy due to cation exchange. During the summer, base cations such as calcium and magnesium were higher in the throughfall samples by more than 50 percent than in the precipitation samples. This increase of base cations in the throughfall was due to the removal of these ions from the canopy vegetation through ion exchange. This is in general agreement with the results presented by Lowrance (1981) showing increases in the base cations in throughfall due to washout and ion exchange. In the spring, the concentration of potassium was 575 percent greater in throughfall than in precipitation. This result is comparable to a 560 percent increase observed by Attiwill (1966) for a eucalyptus forest. Potassium probably comes from leaching of plant tissues due to susceptibility of leaf surface to cation exchange (Tukey, 1970).

All seasonal storms showed a decrease in nitrate-N as rainfall passed through the canopy. This is consistent with previous observations by Price and Watters (1988), Beasley (1988) and Lowrance (1981). The retention of nitrate-N by the vegetation of the forest canopy is probably due to direct uptake by foliage. In contrast, Switzer (1988) reported an increase in nitrate concentration in throughfall compared to precipitation in a canopy of loblolly pines. In addition, Henderson et al. (1977) observed an enrichment of nitrogen as it passed through different type of forest canopies. The retention measured during the summer in this study was more than 80 percent because of direct uptake by the high density of the canopy vegetation. In the spring, a reduction of about 63 percent occurred. The total average seasonal reduction of nitrate-N was 71 percent. This corresponds to the findings of Carlisle et al. (1966) and Peterson (1980).

The total average sulfate concentration was almost unchanged in the throughfall relative to the precipitation. That is, sulfate was less available for leaching or exchange by other ions. Nix and Thornton (1986) reported a similar trend of unchanged sulfate concentration in the throughfall at the same study area.

Subsurface Flow Chemistry

Water is the agent for transporting chemical constituents from the soil horizons to streamflow. It appears that the subsurface flow is a major source of streamflow based on our measurements of both. Subsurface water chemistry will help to identify the predominant sources of subsurface flow into the streamwater.

Litter Layer Chemistry

The increase of hydrogen ion (decreased pH) in the flow from the litter layer relative to throughfall was mainly caused by the production of naturally occurring organic acids by biological decomposition (Foster, 1985). Carbonic acids formed by the reaction of carbon dioxide with soil water may also contribute to the lower acidity (Likens, 1977). The biological activity produced hydrogen ions as a result of converting ammonium to nitrate. This may contribute to the acidity of the flow from this layer. Any increase in soil acidity will result in more cations losses due to the replacement of base cations by hydrogen ions.

Hydrochemical changes within the litter layer could be due to plant uptake, microbial activity and sorption-desorption mechanisms within the soil (Watters, 1988). The enrichment of the cations in flow from the litter layer was probably due to the decomposition of decaying plants and the formation of organic acid. This was reflected in the high concentration of calcium and magnesium which was measured in the flow from the litter layer. The highest concentration of cations such as calcium and magnesium occurred in the flow during the summer season, and were probably due to high microbial activity associated with high temperature compared to the winter and spring seasons. Kress (1990) observed a similar trend in calcium concentration within the litter horizon of an Oklahoma watershed. The concentration of litter leachate of 109 μeq/L of calcium obtained by Kress is comparable to the total average concentration of calcium (105 μeq/L) observed in this study.

Precipitation was the major source of sulfate to the forest floor. Sulfate is the dominant anion in the precipitation, throughfall and throughout the soil horizon flows and streamflow. In the litter layer, sulfate may play an important role in base cation loss due to the strong association with calcium and magnesium. The retention of sulfate by soil may decrease the leaching of calcium and magnesium.

Nitrate-N was conserved within the forest ecosystem. No nitrate-N was detected in the flow from the litter layer during the summer and spring storms, likely due to the high consumption of nitrate by organisms and plants. In winter, nitrate was observed at a low level (1 μeq/L), probably due to low temperature which reduced the activities and the uptake by plants (Likens, 1977). Turton (1989) reported that nitrate-N concentrations were the most variable of all of the constituents he measured.

A-Horizon Chemistry

The low pH observed in the flow from the A-horizon is the result of the same processes which increased the acidity in the litter layer. The high calcium concentrations in A-horizon flow can also be explained in the same way as the litter layer calcium concentrations. Increase hydrogen ion concentration can also result in the increased leaching of calcium. Increased sulfate mobility from the litter layer to the A-horizon may contribute to the leaching of calcium due to the strong association between these ions. The observed nitrate-N concentration in the A-horizon during the summer storm may be either due to the lower volume of flow and/or the increased nitrification as a result of higher microbial activity. The low concentrations of nitrate-N observed in the flow from the litter layer and A-horizon are probably due to the formation of organic acids (Foster, 1985).

B-Horizon Chemistry

The high clay content of the B-horizon was probably responsible for reducing the organic acid in flow from this horizon. In general, exchange sites on the clay in the B-horizon retained the organic acids with the associated cations. This retention of the organic acids leads to increased pH and reduced loss of base cations in the flow from the B horizon. The decline in the total mean concentration of calcium and potassium in the B-horizon was probably caused by both plant root uptake and the retention of these cations in the mineral soil. These ions will later be available to the plants. The result is similar to an earlier study by Turton (1989). Magnesium increases in this horizon were presumably due to geochemical weathering. In addition, the uptake of calcium which is required by plant roots, instead of magnesium and the mobility and the association of sulfate, the dominant anion, may result in higher magnesium migration.

Sodium concentration was increased from A-horizon to B-horizon flow due to geochemical weathering or replacement by potassium or calcium. Sodium could be exchanged for potassium and calcium which is required by the plants. Sulfate continued to be the dominant anion in B-horizon flow, with only a slight increase in concentration from the A to B-horizon. This increase may be due to geochemical weathering and the higher sulfate ion concentrations.

C-Horizon Chemistry

The higher pH observed in flow from the C-horizon (pH of 5.5) as compared to other flow sources was probably due to higher accumulated cations in this horizon. The concentration of calcium in the C-horizon flow reflects the effect of two sources, the biological activities which occur in the upper soil horizons and the geochemical weathering which occurs in the lower horizons. The first, biological activity, increases during the spring and is maximized during the summer season. This activity which occurs in the organic soil horizons (litter and A) may result in producing higher concentration of calcium in the upper horizons. This is transferred in the water in association with the organic acid to the lower horizons (B and C-horizons). The lower concentration of calcium in winter is probably due to the negligible contribution from biological activity. The second major source is the geochemical weathering which occurs year round due to the contact between the water and the soil. The domination by magnesium in the B-horizon flow continued in the C-horizon. The increased concentration of magnesium in the C-horizon was most likely due to the major geochemical weathering, which produced more magnesium in this horizon (Figure 16). This is probably because the soil is rich in magnesium and had less uptake by plants. Kress (1990) reported that magnesium was probably exchanged for calcium, especially in the lower soil horizons.

The primary anion in subsurface flow continued to be sulfate. A higher concentration of sulfate in the C-horizon flow compared to other horizons was probably due to geochemical weathering or exchange with other available anions such as carbonates. No nitrate was observed during the growing season in C horizon flow, although nitrate concentrations of 1 μeq/L were observed in the winter. The presence of nitrate in winter was probably due to the lower biological activity and less uptake of nitrate or flow through macropores which resulted in the direct transfer of water from the upper horizons to the C-horizon.

Streamwater Chemistry

The pH of water leaving the watershed as streamflow was slightly acidic and averaged 5.5. This is similar to the pH of unpolluted atmospheric precipitation of about 5.6 (Beasley, 1988). However, the water entering the ecosystem as precipitation was more acidic than streamflow with an average pH of 4.8. The vegetation, litter and mineral soil horizons had an overall buffering effect.

The large contribution of subsurface flow from the B and C horizons, affects the chemical concentrations in the streamwater during seasonal storms. Magnesium concentrations which dominated flow chemistry from the lower soil horizons (B and C) also dominated the streamwater and accounted for 42 percent of the total cations (Table XIII). This result agrees with the findings of a previous study in by Kress (1990). On a storm basis, streamwater chemistry was also dominated by magnesium during all seasonal storms, especially during the summer storms (Figure 17) where the concentration of magnesium was about twice that of calcium. During winter and spring magnesium and calcium were the major cations, which formed a magnesium-calcium type of streamwater chemistry. The increase of calcium concentration in streamflow during the winter and the spring seasons compared to the summer season was largely due to the greater volume of water flowing through the C horizon which increased the geochemical weathering additional to the decline of plant uptake. Gilliam (1983) reported that magnesium concentrations were highest during August and November and decreased from winter to mid-summer.

From the above observations, the chemical concentration of magnesium is an indicator of the flow sources that combine to produce streamwater. This leads to the conclusion that the lower soil horizons (B and C), which contributed the high percentage of flow to the stream also dominated the release of the chemicals in the subsurface flow and the streamwater chemistry. The domination of magnesium in the flow from the B and C horizons was likely due to the following:

1) Magnesium ions were released by geochemical weathering, especially in the C horizon.
2) The ion exchange process could have released magnesium in return for a more exchangeable

calcium required by the plants in the soil solution.

3) Plant uptake, biological activity and soil retention of calcium left more magnesium available in the water.

The dominant anion in all flow sources, including the streamflow, was sulfate. The concentration of sulfate decreased during the summer in the streamflow. During the winter and spring sulfate concentration was greater in the streamflow than in the precipitation. A small amount of sulfate may have accumulated in summer when there was high temperature and biological activity and less subsurface flow available. In winter and spring, with less biological activity, lower temperatures and greater subsurface flow, the concentration of sulfate in the streamflow increased. Nitrate was not observed in the streamflow because it was retained within the system. This retention of the nitrate-N was due to the biological activities and the root uptake (Bohn et al., 1985; Johnson et al., 1986).

Figure 18 shows the contrast between the influence of biological activity and geochemical weathering on the concentrations of potassium and magnesium. Both magnesium and potassium increased in the throughfall. Potassium concentrations remained nearly constant in soil horizons and streamflow due to plant uptake and soil retention. Similar results were reported by Wooldridge and Larson (1980) for undisturbed forests of western Olympic mountains. They found that potassium moved within the vegetation and was retained throughout the soil profile with only slight additions by geochemical weathering from the lower soil horizons. The concentration of magnesium continued to increase with depth due to the influence of geochemical weathering.

Chemical Load by Source

Total Average Seasonal Chemical Load

The purpose of monitoring the hydrological processes was to determine the subsurface flow volume contributed by each soil horizon and calculate the water budget for the experimental watershed. Rainfall, throughfall and flow volumes were then used to calculate the total average chemical load and seasonal storm chemical load for each source of flow. Total average chemical loads of the constituents allow us to evaluate the input and output chemical budgets for the watershed and to compare the load contribution by soil horizons to stream load.

Examination of the watershed-scale chemical load data indicates that first, the load of cations lost from the watershed in streamflow exceeded the cation load input by precipitation and second, the anion load input by precipitation was greater than the output by streamflow, that is anions were retained within the watershed ecosystem. Cation losses at the watershed level appear to be regulated by chemical and geochemical weathering, which contribute to higher base cation loads. Biological transformations, vegetative uptake and storage, fixation by plants and retention in the soil led to the retention of anions. Foster (1985) reported that plant uptake of nitrate and sulfate regulate cation losses from the soil through adsorption-desorption reactions. Similar trends were reported by Swank and Waide (1988).

The throughfall loads of all base cations were greater than precipitation loads due to canopy releases of cations. Sulfate and chloride loads were relatively unchanged while hydrogen and nitrate were retained in the forest canopy. Cation enrichment in throughfall could be caused by the chemical weathering, ion exchange and wash-out of dry deposition on the leaves. These findings were generally in agreement with results from Hubbard Brook reported by Likens et al. (1977) and from Coweeta as reported by Swank and Waide (1988). Beasley (1988) and Kress (1990) reported that rainfall is enriched upon passage through the canopy and cation and total ion loads are therefore greater in throughfall than in precipitation.

The litter layer appears to serve as accumulator of all constituents and produced the smallest load of all constituents for the following reasons:

1) The interflow volume output from the litter layer was smaller than the other layers because of it's high vertical rate of percolation. The large volume of water passing through the litter into lower horizons increased the load of nutrients obtained from the other horizons.

2) The vertical movement of water in higher volume transferred the available nutrients downward to the A-horizon with a resultant reduction in lateral movement.

3) Biological decomposition, which makes the constituent available for plant uptake. Nutrient were tied up with the roots making it less likely for the nutrient to be transferred out of this layer by the water.

The total average chemical constituent loads increased with soil depth because of the greater water volume which migrated vertically. Consequently, more constituents were carried through to the lower horizons and eventually showed up in the subsurface flow. The permeability of the soil decreases with depth as clay content increases. The C horizon is very restrictive to flow and the parent material below allows almost no vertical water movement. This results in more lateral flow from the lower horizons compared to upper horizons.

The total average streamflow load was primarily a result of the combined subsurface flow loads from the soil horizons, especially A, B, and C horizons. Base cation loads from these horizons generally exceeded anion loads and this was reflected in streamflow loads. Figures 19 to 22 show the comparison of load among soil horizons for the major cations, calcium, magnesium, potassium and sodium. The total average load of calcium produced by the A horizon was the largest compared to all other horizons (Figure 19). Also, the total calcium load released in the A horizon flow was higher than magnesium or any other base cation load from the A. This was probably due to biological activity that decomposes calcium-rich organic matter.

The total average load of calcium and magnesium produced by the B horizon was about the same. The magnesium was most likely supplied by biogeochemical weathering, which may have resulted in additional ionic exchange with the increase of water volume in contact with the clay in this horizon. The source of B horizon calcium was likely A horizon percolation. This can be contrasted with the A horizon, which contained organic matter, hence a higher calcium load.

The total average load from the C horizon showed that the magnesium load increased compared to the B horizon while calcium load decreased. This indicates that the C-horizon may have a geological source of magnesium. The load of potassium remained unchanged within the different soil horizons due to the reserve or exchange with sodium, which increased with depth. Geochemical weathering was a possible source of sodium leading to increased concentration and load with depth from the A through C horizons.

The C-horizon produced a larger load of magnesium than any other horizon most likely due to geochemical weathering of the parent material. This suggests that magnesium-rich sources in the C-horizon contributed to the total average load of magnesium in streamflow, with geochemical weathering being the predominant mechanism for introduction of magnesium into the stream. The conclusion that the streamwater chemistry was influenced strongly by the C horizon flow based on concentrations of magnesium, is further confirmed by the results of the load of magnesium from the C horizon to the streamflow. These results support the assumption that the total average load calculations could be used to identify the sources of flow that combined to generate streamwater.

Figures 23 to 26 show the total average loads of hydrogen and the major anions. The total average load of hydrogen introduced by precipitation relative to the export by streamflow indicates an accumulation of hydrogen within the watershed. Hydrogen retention was probably caused by ion exchange in the canopy and litter layer (Kress, 1990). The total average load of major anions (sulfate, chloride and nitrate) indicates that the anions were accumulated in the watershed. The accumulation of nitrate-N was most likely caused by direct plant and microorganisms uptake in the canopy and the litter layer. The total average load of sulfate indicated that the accumulation of sulfate occurred in the watershed. This was probably due to biological uptake in the litter layer and adsorption by the clay in the B horizon. Foster (1985) reported that sulfate ions are retained in acid soils due to adsorption on soil exchange sites. Chloride was accumulated as flow passed through the soil horizons. Although geochemical weathering contributed to the loads of sulfate and chloride, as reflected in C horizon loads of these constituents, the streamwater exported smaller quantities of anion loads than were imported through precipitation.

Seasonal Storm Load Variation

Hydrological and chemical processes are greatly influenced by distinct seasonal patterns in the study area. Biological activity is at a maximum, with high soil moisture content and high temperature in the summer. The canopy undergoes a seasonal transformation, with the largest leaf surface at maturity during the summer. Fully developed canopies intercept dry deposition and the leaf surfaces are washed by incoming precipitation.

Precipitation was the major source of nutrient input and the driving force for nutrient movement within the ecosystem. Clearly, amount of precipitation was seasonal with maximum input during spring and minimum input during the late summer. The highly variable storms influenced the seasonal loads through precipitation volume and the varying levels of biogeochemical weathering. Geochemical weathering is strongly influenced by the amount of water moving through the ecosystem and in contact with the parent materials.

Figures 27 to 31 show the seasonal loads of selected ions in precipitation, throughfall and by source of flow. The calcium load exported in winter streamflow was greater than for other seasonal storms. This was probably due to reduced biological activity in the organic layers and minimal plant uptake. In addition, geochemical weathering of parent materials in the C-horizon released greater amounts of calcium during the winter due to the higher water volume moving through the soil horizons. In summer and spring, the load of calcium increased with soil depth but not in the winter, presumably due to the retention of exchangeable calcium by adsorption onto the clay soil sites in the B horizon. In summer, the output load of calcium was equal to the input load by precipitation due to the maximum microorganism and plant uptake and less flow of water through the soil horizon.

The magnesium load exported by winter streamflow was greater than spring and summer, also due to the greater volume of water in contact with and passing through the C horizon and less biological activity at low temperature. The magnesium load in throughfall was highest in the summer due to the wash out of dry deposition and exchange of base cations by hydrogen ions in the dense canopy. The load of magnesium in subsurface flow increased with soil depth for all three seasons. This increase may be explained by the exchange of calcium by magnesium, in addition to the biogeochemical factor. Calcium is required by plants, especially during the growing season. The output load in the streamflow was higher than the input load by precipitation due to the geochemical weathering contribution. Likens et al., (1977), and Wooldridge and Larson (1980) reported that geochemical weathering is the major source for cations.

Potassium loads in throughfall, subsurface flow and streamflow varied seasonally. Spring storm resulted in the greatest potassium load in throughfall, probably because of the high mobility of potassium which resulted in high leaching rates from the fresh leaves and the effect of precipitation acidity (Lowrance, 1981). The load of potassium exported by streamflow during the growing season, summer and spring, was less than in the winter, most likely because of increased plant and microorganisms uptake of potassium and higher evapotranspiration rates which reduced flow volumes.

The accumulation of sulfate during the three seasonal storms resulted in smaller loads exported in the streamflow than were introduced by precipitation. This may indicate that the input of sulfate by atmospheric pollution was higher than the geochemical weathering source of the lower soil horizons in this watershed, or the adsorption of sulfate ion by the clay in the B horizon was very high. Apfelbeck (1987) reported that sulfate adsorption correlated with clay content and the B soil horizon of Ouachita Mountain soil adsorbed 0.3 meq sulfate/g of soil. On similar Oklahoma watersheds, Kress et al., (1990) found that the soil accumulated sulfate ions. He reported that the input of sulfate ions by bulk precipitation was 50 meq/m^2 while the output by streamflow was 46 meq/m^2, and stated that this accumulation was due to the adsorption to the clay in the lower horizons.

NO3-N was exported in minute quantities in streamflow, but was introduced in relatively large quantities in precipitation. The accumulation of nitrate-N within the watershed was probably because it was either consumed by the plants and microorganisms or stored within the canopy and in the litter layer. The load of nitrate-N in throughfall during the winter storm was greater than in summer and spring storms. The increase of about 200 g/ha was likely due to the absence of leaves in the canopy during the winter which reduced the uptake of NO3-N. The appearance of nitrate-N in the C-horizon flow in the winter, was probably due to one of the following:

1) Less biological activity occurred in winter and spring seasons with a resultant reduction in the consumption of nitrate by microorganisms and plants.

2) Macropores may have channeled nitrate-N from the organic layers directly to the C-horizon under the wet soil conditions.

Overall, biological activity, plant uptake, organic matter storage and low flow volumes contributed to the small litter flow loads of nitrate-N. Kress et al., (1990) reported that biological uptake contributed to the accumulation of nitrate and ammonia ions at the Oklahoma watershed.

Cation - Anion Balance

Theoretically, an equivalent difference of 5 percent or less should exist between the cations (meq/l) and the anions (meq/l) in the samples collected from the sources of water examined in this study. The imbalance of measured cations and anions in throughfall, litter, A, B, C, and stream samples (Table XVI through XVIII) were the result of higher concentrations of cations. The greater cation concentrations measured in throughfall and soil horizon flows were probably due to the leaching from the canopy, the additional cations provided by geochemical weathering and due to unmeasured dissolved organic carbon (DOC) which was present in significant amounts in the upper soil horizons. Apfelbeck (1987) found that cations in flow through soil horizons were greater than anions due to unmeasured bicarbonate and organic acids in solution.

A cation - anion balance was obtained for precipitation samples for all three seasonal storms. As in most natural water, small amounts of organic material (DOC and TOC) is present compared to dissolved inorganic solute concentrations, but even the small amounts of organic material can influence the chemical properties of water (Hem, 1985). The only significant imbalance caused by anions concentration being greater than cations was in throughfall samples collected during the winter storm (Table XVII). This cation - anion imbalance was probably associated with sulfate, nitrate or organic anions that are leached and not retained by the least active canopy which associated with the absence of leaves during the winter season.

A greater percent difference occurred between cations and anions in the litter and A horizon flow (upper soil horizons), than the B and C horizon flow (lower horizons) (Figure 31 and 32). This difference is likely due to the presence of more dissolved organic carbon in the upper horizons than the lower horizons. Further support for this explanation is that the color of the samples from the upper horizons were darker and had higher DOC values.

CHAPTER VII

CONCLUSION

Water is the driving force for the movement of chemical constituents in the watershed. Enough water must be introduced into the system through precipitation to satisfy soil storage, evapotranspiration, and any other factors which consume water before any excess can move through the system and leave via streamflow. Flow from all four soil horizons contributed to streamflow. The amount of contribution however varied from horizon to horizon. By studying hydrological processes and the chemistry of the water sources, the percent contribution of different sources to streamflow can be quantified. The following conclusions can be made based on the observations made in this study:

- Subsurface flow was the major source contributing to streamflow.
- The subsurface flow contribution to streamflow is greater in winter than in spring and summer.
- The contribution of flow and chemical constituents of soil horizons to streamflow is greater than the upper horizons.
- Precipitation was found to be slightly acidic with a pH less than 5 for all storms.

- pH in subsurface flow increases with soil depth.
- The pH of flow from the C-horizon is similar to the streamwater pH.
- Hydrogen and sulfate were the dominant ions in the precipitation.
- Precipitation input of calcium, magnesium and sodium concentrations were higher during the summer storm than the winter and spring storms.
- In summer and spring storms an enrichment of all ions except hydrogen and nitrate-N occurred as precipitation passed through the canopy.
- The litter layer flow was dominated by calcium and sulfate.
- The A-horizon flow was also dominated by calcium and sulfate.
- The B-horizon and C-horizon flow was dominated by magnesium and sulfate.
- Concentration of magnesium and sulfate were greater in C horizon flow than in B horizon flow .
- Nitrate-N concentration decreased with depth and was below the detection limit in the subsurface flow and streamflow, except from the C-horizon during the winter storm.
- Streamflow was dominated by magnesium and sulfate.
- Chemical weathering and biological activity were the sources for calcium, magnesium and potassium in the upper soil horizons, while geochemical

weathering was the major source in the lower soil horizons.

- Two overall patterns of input and output chemical loading were evident in the watershed. The base cation output loads of calcium, magnesium, potassium and sodium in streamflow exceeded precipitation loads. Secondly hydrogen and all anions were accumulated within the watershed.
- Nitrate-N accumulated within the forest canopy during the growing season.
- The litter layer of the forest floor acted as the accumulator for all the ions.
- The greatest percentage of the streamflow chemical load was contributed by the B and C horizons.
- Organic acid and dissolved organic carbon, which is produced in the upper soil horizon, influenced the cation - anion balance.
- Streamwater chemistry reflected the chemistry of the lower soil horizons (B and C horizons).

Since the streamwater quality is strikingly similar to the chemistry of water from the B and C horizons, subsurface flow must be the major contributor to streamflow. As reported by Williams (1990), subsurface stormflow, or saturated interflow, may release large quantities of water to streamflow through either macropore flow or piston displacement of old water with new. Since the chemistry of direct precipitation and throughfall differ from the streamflow chemistry, significant amounts of water must be received from saturated interflow, especially from the B and C horizons. Additional studies will be required to completely characterize the nature of the geochemical processes in soil horizons to understand and quantify the chemical uptake and release.

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APPENDIX A

SUBSURFACE FLOW CONTRIBUTION SUMMARY TABLES

TABLE XIX

THE SUBSURFACE FLOW CONTRIBUTION PER LAYER TO THE TOTAL FLOW FOR THE THREE SEASONAL STORMS

Summer Storm

Layers	L-Site cm	U-Site cm	MAWF* cm
L	0.02	0.00	0.01
A	0.25	0.02	0.07
B	0.24	0.20	0.21
C	0.25	0.59	0.52
Total	0.8	0.8	0.8

Winter Storm

Layers	L-Site cm	U-Site cm	MAWF* cm
L	0.04	0.68	0.53
A	0.25	3.27	2.64
B	3.54	3.11	3.20
C	0.54	3.17	2.62
Total	4.4	10.2	9.0

Spring Storm

Layers	L-Site cm	U-Site cm	MAWF* cm
L	0.00	0.16	0.13
A	0.03	0.82	0.65
B	2.19	2.30	2.27
C	0.89	3.75	3.16
Total	3.1	7.0	6.2

* MAWF = Mean Area Weighted Flow

TABLE XX

SUBSURFACE FLOW BY HORIZON AS PERCENTAGE OF TOTAL SITE FLOW FOR SUMMER STORM (7/17/89)

	ThF	L-Site		U-Site	
		% of Total Flow			
Layers	cm	cm	%	cm	%
L	4.1	0.02	3	0.00	0
A		0.25	33	0.02	3
B		0.24	31	0.20	25
C		0.25	33	0.59	72
Total		0.76	100	0.81	100

TABLE XXI

SUBSURFACE FLOW BY HORIZON AS PERCENTAGE OF TOTAL SITE FLOW FOR WINTER STORM (3/06/90)

	ThF	L-Site		U-Site	
			% of Total Flow		
Layers	cm	cm	%	cm	%
L	10.0	0.04	1	0.68	7
A		0.25	6	3.27	32
B		3.54	81	3.11	30
C		0.54	12	3.17	31
Total		4.38	100	10.22	100

TABLE XXII

SUBSURFACE FLOW BY HORIZON AS PERCENTAGE OF TOTAL SITE FLOW FOR SPRING STORM (5/01/90)

	ThF	L–Site			U–Site
			% of Total Flow		
Layers	cm	cm	%	cm	%
L	15.2	0.00	0	0.16	2
A		0.03	1	0.82	12
B		2.19	70	2.30	33
C		0.89	29	3.75	53
Total		3.11	100	7.03	100

APPENDIX B

SUBSURFACE CHEMISTRY SUMMARY TABLES

TABLE XXIII

VOLUME-WEIGHTED MEAN CONCENTRATION OF MAJOR CATIONS AND ANIONS IN SOIL HORIZONS

Seasonal Storm	Source of Water	Ca	K	Mg	Na	H	Cl	NO3-N	SO4
					meq/l				
Summer 7-17-89									
	Litter	0.137	0.017	0.055	0.033	0.0053	0.0121	0.0004	0.0418
	A-HORIZON	0.131	0.019	0.045	0.037	0.0098	0.0335	0.0029	0.0445
	B-HORIZON	0.051	0.011	0.064	0.068	0.0116	0.0345	0.0002	0.0599
	C-HORIZON	0.057	0.012	0.067	0.055	0.0067	0.0524	0.0005	0.0740
Winter 3-06-90									
	Litter	0.125	0.018	0.033	0.015	0.0113	0.0124	0.0007	0.0434
	A-HORIZON	0.101	0.016	0.037	0.036	0.0124	0.0274	0.0001	0.0541
	B-HORIZON	0.048	0.017	0.038	0.027	0.0144	0.0201	0.0001	0.0515
	C-HORIZON	0.028	0.013	0.052	0.039	0.0071	0.0197	0.0006	0.0515
Spring 5-01-90									
	Litter	0.053	0.013	0.042	0.032	0.0171	0.0128	0.0001	0.0520
	A-HORIZON	0.101	0.015	0.041	0.031	0.0169	0.0309	0.0002	0.0659
	B-HORIZON	0.044	0.012	0.048	0.032	0.0134	0.0249	0.0000	0.0672
	C-HORIZON	0.045	0.010	0.060	0.043	0.0048	0.0342	0.0005	0.0729

TABLE XXIV

THE AVERAGE CHEMICAL LOADS BY SOURCE FOR THE THREE SEASONAL STORMS BASED ON VOLUME-WEIGHTED MEAN CONCENTATIONS

Source of Water	Ca	Mg	K	Na	H	SO4	NO3-N	Cl	Total
		(values in equivalents per hectare)							
Prcp.	11.4	6.6	3.7	13.9	25.2	38.4	6.0	17.8	123.0
ThF	16.3	16.7	17.4	17.3	16.6	38.1	2.2	18.4	143.0
L	2.5	0.8	0.4	0.4	0.3	1.0	0.0	0.3	5.7
A	11.4	4.3	1.8	3.9	1.5	6.3	0.0	3.2	32.3
B	8.8	8.1	2.8	5.7	2.6	11.0	0.0	4.3	43.4
C	8.2	12.0	2.4	8.9	1.2	13.4	0.1	6.2	52.5
Strm.	27.4	32.4	6.4	16.1	1.9	19.7	0.0	10.3	114.2

TABLE XXV

THE AVERAGE CHEMICAL LOADS BY SOURCE FOR THE THREE SEASONAL STORMS BASED ON VOLUME-WEIGHTED MEAN CONCENTATIONS

Source of Water	Ca	Mg	K	Na	H	SO4	NO3-N	Cl	Total
			(values in grams per hectare)						
Prcp.	229.3	79.9	143.8	320.2	25.4	1843.1	368.9	631.5	3642.1
ThF	327.0	202.4	679.5	397.0	16.7	1830.8	137.2	652.5	4243.1
L	50.7	9.6	15.1	9.6	0.3	49.1	0.8	10.0	145.4
A	228.2	51.7	69.5	90.3	1.5	302.4	1.5	112.1	857.2
B	176.5	98.9	109.4	131.2	2.7	528.4	0.9	151.5	1199.3
C	163.5	145.9	93.6	204.0	1.3	645.5	7.1	220.6	1481.5
Strm.	549.4	394.1	248.6	369.5	1.9	946.9	1.1	365.0	2876.6

VITA

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