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Chemical Quality Variation in a Small Mountain Watershed

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CHEMICAL QUALITY VARIATION IN A
SMALL MOUNTAIN WATERSHED

by

David C. White

A thesis submitted in partial fulfillment
of the requirements for the degree

of

MASTER OF SCIENCE

in

Watershed Science

Approved:

[redacted]

UTAH STATE UNIVERSITY
Logan, Utah

1977

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David C. White

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ABSTRACT

Chemical Quality Variation in a Small Mountain Watershed

by

David C. White, Master of Science

Utah State University, 1977

Major Professor: Dr. Richard H. Hawkins
Department: Forestry and Outdoor Recreation

The purpose of this study was to quantify the chemical nature of the Chicken Creek waters, and to investigate the variability and causes of that observed chemistry. The three objectives of the study were: 1) inventory the chemistry of the water produced by the subject watersheds, 2) determine chemical budgets for the watersheds, and 3) identify the sources of the primary chemical components.

Chemical surveys were made: 1) on the stream exiting from each gaged watershed, 2) at various points within the West Branch drainage network, 3) of the atmospheric inputs (rain, snow, and dust), 4) of the soil solution, and 5) of the soil itself. Data were also collected on the volume and distribution of rain and snow entering the watersheds, and the volume and timing of the streamflow leaving.

Streams were found to be dilute solutions with nearly neutral pH, containing Ca, Mg, Na, K, HCO_3, SO_4, and Cl; with NO_3 and PO_4 present in lesser quantities. The observed chemistry was quite dynamic with the

$CO_2/CO_3/HCO_3$ equilibrium system having a significant influence. In a more general sense, the water chemistry appeared to be a mixture of surface runoff, with chemistry approaching that of precipitation; and subsurface flow, with chemistry near that of soil solution.

The watersheds themselves are the source of most of the chemical constituents, with only NO_3 and PO_4 appearing to be consumed within the watersheds. On a per unit area basis, the West Branch watershed was shown to produce significantly more water, of higher chemical concentration than the East Branch. Possible explanations for such variability are discussed, e.g., non-uniform distribution of the snow pack and varying chemical activity of soils.

(105 pages)

INTRODUCTION

Nature of the Problem

The intermountain area is one in which water plays a critical, if not limiting, role in human activity. The amount of effort expended in the management and utilization of the water resource is tremendous. Historically, the greater portion of the concern has been with water quantity. Water quality has been of concern only when it became so extreme that the use of the water was limited.

As the population expands, the pressure on the water resource must necessarily increase, requiring that the quality, as well as the quantity, of a given water supply be considered for its full utilization. The quality considerations will include both biological and chemical components, either of which may be limiting for a particular use (McKee and Wolf, 1963). The biological component has long been of concern in natural waters because of its potential for causing disease. Little attention has been given to the chemical component of water quality, particularly of natural water from wildland source areas.

As Snyder (1974) pointed out, some of the difficulties in meeting new state and federal water quality standards, when applied to land management, arise not from the guidelines suggested by the laws, but from inadequate baseline water quality information (i.e., insufficient knowledge about natural chemical water quality).

Most of the studies that have been done are far removed from the intermountain area, and natural variability is so great that applying those findings to the intermountain conditions is inappropriate. There seems to be a real need for the collection and analysis of baseline water quality data from the intermountain area. In the past, such information has not been extensively obtained and quantified. Corresponding to this lack of basic data is a similar lack of investigation into the sources and processes active in producing the natural water chemistry.

Purpose

The purpose of this study was to survey some of the important chemical water quality parameters of the water produced by a pair of small mountain watersheds located in the intermountain area. The survey also attempted to identify and describe some of the agents and processes bringing about the observed chemical quality.

The specific objectives of this study were:

1. To inventory the chemical quality of the water produced by the subject watersheds.
2. To determine chemical budgets for the watersheds.
3. To identify the sources of the primary chemical components.

The Site

Selection criteria

In an article, "Nutrient Cycling," published in the January, 1967, issue of Science, Drs. Bormann and Likens discuss the use of small watersheds in the study of the biogeochemistry active in ecosystems (Bormann and Likens, 1967). The authors presented requisite qualities of a watershed that would make it an appropriate study subject in such research. Included in those qualities were: obvious surface boundaries, being underlain by a water-tight stratum, and draining so that water produced can be conveniently monitored. These qualities enable the researcher to confidently define his "subject" which can then be dealt with as a system, and can be examined, monitored, and manipulated much like any other system that might be studied. Bormann and Likens suggest that because of practical considerations, research watersheds already established for hydrologic studies are logical candidates for biogeochemical studies. The East and West branches of Chicken Creek, on the Davis County Experimental Watershed in Northern Utah, are examples of just such recommended candidates.

Since the branches of Chicken Creek seem to meet the requirements of the research procedures and are located in an area of the country needing study, the use of these watershed in this study is quite appropriate.

The Chicken Creek study area

The specific area of this study is a paired set of research watersheds located on the Davis County Experimental Watershed (U. S. Forest Service) in Northern Utah. The immediate area of interest is the East and West branches of Chicken Creek. The location of the area is shown in Figure 1, and a more local description is shown in Figure 2.

The Davis County Experimental Watershed has been intensively studied since its establishment in 1930. The research on the watershed has been almost entirely of a physical hydrology nature: flood control, water budgets, descriptive climatology, sedimentation, vegetation/hydrologic cycle interactions, and management techniques research. An inclusive bibliography of this research has been compiled by DeByle and Hookano (1973). These publications were invaluable sources of background information on the area.

The Chicken Creek watersheds are the subject areas for a presently ongoing watershed management experiment. In conjunction with this research Johnston and Doty (1972) published a thorough description of the watersheds. In their publication Johnston and Doty included a summary of the chemical water quality. This discussion of water quality was rather brief, but the interest shown initiated the study described in this thesis. Because the interest in the chemistry of the waters of the Chicken Creek watershed was very general at the time of this study; broadly focused survey techniques were adopted to examine the nature of this chemistry.

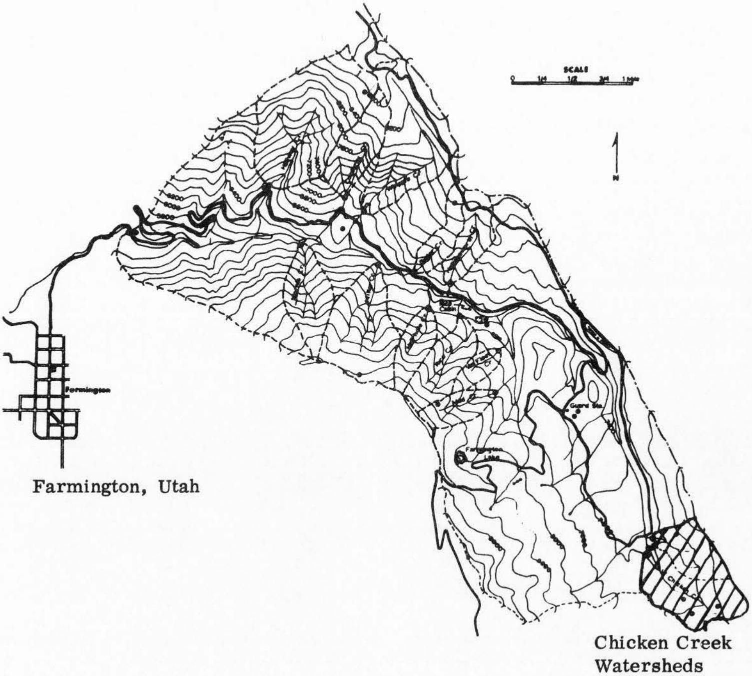

Figure 1. Location of study area.

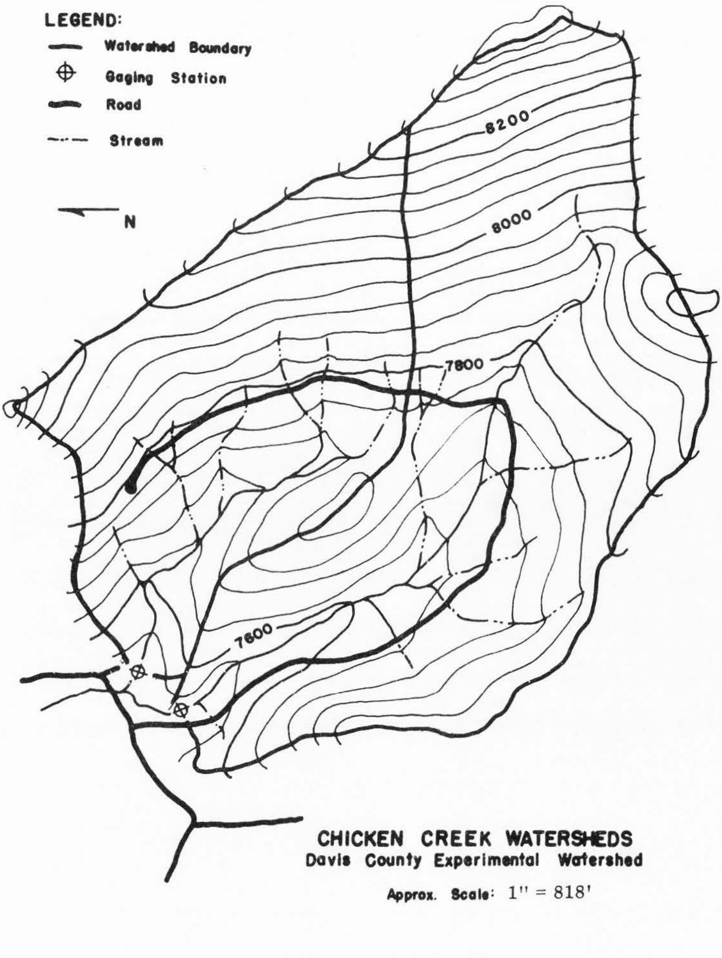

Figure 2. Topographic map of study site.

REVIEW OF LITERATURE

General Description of Surface Water Chemistry

Before undertaking a study of a particular water, it is necessary to understand the chemistry of natural water in general.

Factors controlling chemical composition

The environmental factors influencing the chemistry of observed natural waters have been variously categorized by researchers. Hem (1970) grouped the influences into three main areas: climate, biota, and geology. Gorham (1961) also recognized climate and biota, but saw a usefulness for a further breakdown of geology into (mineral) geology and topography. Gorham also added time to his list. However, the authors chose to group the factors, the message always emphasized the need to appreciate the complexity of natural processes.

Such attempts at categorizing environmental influences are concepts used by researchers to help visualize complex and invisible processes. If such concepts are to have any validity, the mechanisms must be shown, through which the environmental factors can have a causal relationship to the character of the water being studied. These mechanisms, then, are the actual chemical reactions resulting from water being exposed to the natural environment.

Chemical processes involved

Hem (1970) classified the reactions active in controlling the composition of natural water. That classification is briefly summarized in the following outline.

I. Reactions having energy relationships and rates of reaction such that in the environment of the earth's surface they form dynamic equilibria--constantly adjusting to the changing environment.

  A. Reactions that water itself does not enter into.

    1. Reversible solution of solid crystalline material.

      e.g., $NaCl \leftrightarrow Na^{+} + Cl^{-}$

    2. Molecular dispersion of solids or gases.

      e.g., $N_{2\ (gas)} \leftrightarrow N_{2\ (aqueous)}$

    3. Reactions among aqueous species or complexes.

      e.g., $Ca^{+2} + SO_4^{-2} \leftrightarrow CaSO_{4\ (aqueous)}$

    4. Sorption-desorption and ion-exchange reactions.

      e.g., $Na_2X + Ca^{+2} \leftrightarrow CaX + 2Na^{+}$

  B. Reversible solution and desorption reactions in which water molecules are broken down into H^{+} and OH^{-}.

    1. Simple hydrolysis

      e.g., $CaCO_3 + H_2O \leftrightarrow Ca^{+2} + HCO_3^{-} + OH^{-}$

    2. Dissociation of acid-forming solutes.

      e.g., $CO_{2\ (aq)} + H_2O \leftrightarrow HCO_3^{-} + H^{+}$

3. Hydrolysis of weakly basic ions.

   e.g., $Al(H_2O)_6^{+3} \leftrightarrow AlOH(H_2O)_5^{+2} + H^+$

C. Reversible solution and deposition reactions or ion reactions involving changes in oxidation state.

1. No hydrolysis involved.

   e.g., $Fe^{+3} + e^- \leftrightarrow Fe^{+2}$

2. Hydrolysis involved.

   e.g., $Fe(OH)_3 + e^- + 3H^+ \leftrightarrow Fe^{+2} + 3H_2O$

II. Reactions that are not readily reversible under the natural environment of the earth's surface. The reactions do not appear reversible because of either slow reaction rates or the need for energy input.

A. Complicated processes.

   e.g., weathering of sodium feldspar

   $2NaAlSi_3O_8 + 2H^+ + 9H_2O = 2Na^+ + H_4Al_2Si_2O_9 + 4Si(OH)_{4\,(aq)}$

B. Life processes.

   e.g., $C_6H_{10}O_5 + 6O_{2\,(aq)} = 6CO_2 + 5H_2O$

The first of the two major categories, those reactions that are readily reversible, yield to investigations that assume chemical equilibria. The less readily reversible reactions are likely to be so far from equilibrium that that very concept is inappropriate. These reactions then must be studied in terms of their rates of reaction and the mechanism involved (Hem, 1970).

Major constituents

In order to study the composition of a natural water, a researcher must be able to inventory his subject with a reasonable degree of completeness. Researchers disagree somewhat on the exact numbers, or percentages, involved but they agree that the vast bulk of the inorganic chemical load of natural fresh water is made up of seven ions. The cations are calcium (Ca^{+2}), magnesium (Mg^{+2}), potassium (K^{+1}), and sodium (Na^{+1}). The anions are bicarbonate (HCO_3^-), sulfate (SO_4^{-2}), and chloride (Cl^-). Other ions, such as iron (Fe^{+x}) can have local significance and must be considered (Conway, 1943). However, in the case of the water that is the subject of this study, the seven ions mentioned above account for most of the measured chemical load.

Discussion of Major Constituents

Calcium

In most natural fresh water, calcium is the principal cation. It is a common constituent of rock and soil minerals found worldwide.

Sources. Calcium is an essential constituent of many igneous-rock minerals, especially chain silicates, pyroxene and amphibole; and the feldspars. It also occurs in silicate minerals formed by netamorphism. Therefore, water in contact with igneous or metamorphic rock would be expected to contain some calcium, but because the rate of reaction of these minerals is slow, the concentration of calcium in the water is usually low. Naturally occurring feldspars are mixtures of the calcium and sodium types, and yield both calcium and sodium to the reacting water (Hem, 1970).

In sedimentary rocks, the common forms of calcium are carbonates, either calcite (or aragonite) $CaCO_3$, or dolomite $CaMg(CO_3)_2$. Other calcium minerals are sulfates (gypsum or anhydrite) and fluorides (fluorite). Calcium is also found in some clay mineral structures. Due to their relatively rapid reaction rates, these sedimentary and clay minerals are primary mineral sources of the calcium ion in natural water (Hem, 1970).

Chemical controls. Carbonate equilibria are the primary controlling factors in calcium solubility. The controls on the equilibria, and therefore the calcium concentration in water, are the carbon dioxide content of the earth's atmosphere and the rate at which it dissolves in water (Ruttner, 1963). Examination of these carbonate equilibria involves measurement of pH and CO_2 partial pressure. These measurements are difficult and the parameters themselves are very changeable. The pH can be controlled by the atmosphere (a compounding influence of CO_2), or by processes such as the oxidation of sulfur or sulfides. The partial pressure of CO_2, important in itself and in its control over pH, varies considerably from approximately 0.0003 atmosphere in normal air to commonly 10-100 times that concentration in soil air (Hem, 1970).

Cation-exchange reactions generally exert a great deal of control over the calcium concentrations found in natural fresh water. In small, source-area watersheds, these reactions are most active in the soil profile. In the more complex solutions of larger rivers, a continued influence has been noted involving cation-exchange on suspended sediment (Hem, 1970).

Dissolved species. Calcium does not readily from a hydrated species. It generally occurs as the ion Ca^{+2} (Gorham, 1961). Except in waters having ionic concentrations exceeding 1000 mg/l, the presence of calcium in ion pairs with CO_3/HCO_3 or SO_4 is insignificant (Hem, 1970).

Magnesium

While magnesium is usually thought of as very similar to calcium, its geochemical behavior is quite different.

Sources. Igneous rocks contain magnesium in such minerals as olivine, pyroxenes, amphiboles, and some micas. In metamorphic minerals, species containing magnesium include chlorite, montmorillonite, and serpentine. Sedimentary magnesium minerals are such as magnesite, hydromagnesite, and dolomite; which are all carbonate compounds. Magnesium is much less abundant in all rock types than calcium and is, therefore, less available for solution. Ruttner (1963) states that except in areas of dolomitic minerals, magnesium forms rarely exceed 20 percent of the total carbonate.

Controls. Since the dissolved species of magnesium are comparable to those of calcium, it can be expected that the environmental influences would be the same. This is generally the case, but the controls, such as pH and CO_2 partial pressure, do not exert as straightforward control over magnesium reactions as they do over calcium equilibria. Reactions involving magnesium are often non-reversible under normal conditions, making them more difficult to model (Hem, 1970).

Ion-exchanging minerals may adsorb magnesium even more readily than calcium, but their control over magnesium concentrations does not appear to be too important in observed natural waters (Hem, 1970).

Dissolved species. Magnesium generally occurs, as a solute in natural water, in the form of the hydrated ion $Mg(H_2O)_6^{+2}$ (generally written as Mg^{+2}). It will form ion pairs, similar to calcium, with both SO_4 and CO_3/HCO_3, but in dilute solutions these are not significant (Hem, 1970).

Sodium

The amounts of sodium found in both igneous and sedimentary rocks can not account for the relative abundance of sodium in the waters in contact with those minerals. The explanation for this situation is in sodium's unique chemistry. Sodium is very susceptible to attack by water and, once in solution is not readily either reincorporated or precipitated (Hem, 1970).

The result of this chemistry is the transport of sodium to salt, or alkali, flats or to the ocean. This process has developed the observed worldwide situation where much of the sodium present near the earth's surface is contained in these sodium sinks. It also argues for sodium often being a recirculated constituent, introduced into a given watershed by precipitation (Gorham, 1961).

Sources. An important igneous rock source of sodium is plagioclase, a sodium feldspar. Sodium feldspars are quite susceptible to solution. Sodium sources in most sedimentary rocks are either incorporated sea salts or precipitates that act as cementing materials. Either type source yields readily available sodium (Hem, 1970).

Controls. Sodium reacts so readily with water that the only really controlling influence is the availability of the sodium.

Species. $NaHCO_3$, Na_2CO_3 and NaCl are the most common sodium containing species found in natural waters. These can be found both dissociated and as ion pairs (Hem, 1970).

Potassium

While potassium is only slightly less common than sodium in igneous rocks and much more common in sedimentary rocks, its concentration in water is far less than sodium. This indicates that the chemical behavior of potassium must differ considerably from sodium. In general, potassium is less readily brought into solution than sodium and is much more likely to be reincorporated into minerals produced by weathering (Hem, 1970).

Sources. Feldspars (orthoclase and microcline), micas, and feldspathoid leucite are the major source minerals for potassium among igneous rocks. Among sediments, potassium is found in unaltered igneous particles and in some clay minerals. Evaporite rocks can include potassium salts.

Potassium is also an essential plant nutrient and can be found in plant material in fairly high concentrations (Hem, 1970).

Controls. In dilute waters with sodium present in concentrations less than 10 mg/1, potassium has been commonly found to one-half to one-tenth that of sodium. Such concentrations are peculiar to these dilute waters, with potassium concentration falling to the level of tenths of mg/1, as total salt concentration increases. Potassium concentration remains at essentially the same low level until total salt concentration becomes exceedingly high. The mechanism by which such consistently low concentrations are maintained is not clear. General tendencies already mentioned are probably controlling factors--resistance to solution and preferential incorporation of potassium into clay or mica mineral structures (Hem, 1970).

Species. The subject of the chemical nature of potassium in water presents more questions than answers. Little is really known about the behavior of the potassium ion in the water environment.

Carbonate/bicarbonate

The carbonate/bicarbonate equilibrium reactions are, some of the most important factors active in controlling water chemistry. Under most environmental conditions, these equilibria are frequently dynamic enough and sensitive enough to bring about measureable changes.

Sources. Although CO_3^{-2} is found in some rock minerals, the primary source of CO_3/HCO_3 is generally thought of as the CO_2 in the atmosphere. The concentration of CO_2 in the aquatic environment is dependent on the partial pressure of CO_2 in contact with the water. This partial pressure can vary considerably between atmospheric conditions and soil, or subsurface, conditions (Hynes, 1970).

Controls. As the aqueous CO_2 is constantly equilibrating with gaseous CO_2, the interrelated HCO_3^{-1} and CO_3^{-2} concentrations must also adjust (Hem, 1970).

$$CO_2 \rightleftharpoons CO_{2(aq)} \rightleftharpoons HCO_3^{-} + H^{+} \rightleftharpoons CO_3^{-2} + 2H^{+}$$

Species. The importance of the equilibria illustrated above is the control these related concentrations have over the solubility of all of the cations common in natural water. The CO_3^{-2} and HCO_3^{-} ions can be found associated with Ca^{+2}, Mg^{+2}, Na^{+}, and K^{+} (Hynes, 1970).

Chloride

Of the halogen group of elements, including fluorine, bromine, and iodine; chlorine is the only one with any importance in natural water. Its importance is in spite of the fact that chlorides are present in all rock types in lower concentrations than any other major component of natural water.

Sources. Igneous rocks, at least those at all near the earth's surface, have chloride concentrations too low to be significant sources of the anion in surface waters. Sedimentary rocks are much more important as sources of chloride. Of particular significance are evaporites and deposited formations with trapped sea water or included salts (Hem, 1970).

An important source of chloride is precipitation. Reports vary on how important this source is--from being the only significant source, to accounting for only a fraction of observed stream water concentrations. It has been demonstrated that, on occasion, man (through such uses as road salts) supplies a considerable portion of the chloride found in some waters (Hem, 1970).

Controls. Chloride behavior in natural waters is deceptively simple. It does not significantly enter into most of the kinds of reactions that complicate the modeling of other water constituents--chloride is not an important reactant in redox reactions, it does not normally form precipitates, and it does not play any significant role in biochemical processes (Hem, 1970).

Concentrations of chloride in the rocks at the earth's surface is a basic control. A discrepancy between high concentrations of chloride in minerals from deep within the earth and the much lower chloride concentration in minerals nearer the surface, suggests that the volatility of the element plays an important role in its behavior. The large size of the chloride ion influences the transport of the element. For example, the ion can be physically trapped within clay structures, while the water filters through. Because chloride is so chemically inactive, and largely controlled by physical processes, it has been suggested that the element is cyclic, i.e., that its presence in fresh waters is the result of its integration into the hydrologic cycle. There is considerable disagreement over how completely this theory explains the observed chloride concentrations in fresh water (Hem, 1970).

Species. The most common species of chloride found is sodium chloride.

Sulfate

Because the element sulfur plays a major role in life processes, its biogeochemistry is extremely complex.

Sources. Sulfur is not a major constituent of the minerals found at the earth's surface, but it is widely distributed and occurs occasionally in very high concentration. These occurrences are in the form of metallic sulfides. Since sulfur is readily oxidized, these are sources of the oxidized sulfate ion (SO_4^{-2}). Fossilized materials, such as coal, are also geologic sources of sulfides and, therefore, eventually sulfates.

Sulfate itself is present in rock minerals. Igneous rocks such as the feldspathoids contain sulfate ions. More important are evaporite sediments. Calcium sulfate; hydrated, as gypsum, or without structural water, as anhydrite; compose a considerable part of such sediments (Hem, 1970).

The atmosphere introduces significant quantities of sulfate into any watershed system (Hynes, 1970). The ultimate source of this atmospheric sulfate (oceanic emissions, terrestrial dusts, or biologic processes) is uncertain. Another uncertainty is the significance of this atmospheric sulfate, relative to other sources of sulfate within the watershed system. This also appears quite variable from one case to another (Hem, 1970).

Man's activities supply considerable quantities of sulfur to the atmosphere (Hynes, 1970). These can be oxidized to sulfate, therefore, their impact must be reckoned with in any attempt to study sulfate occurrence.

Controls. Changes in the oxidation state of sulfur seem to occur slowly--often only with energy supplied by some biologic activity. This tendency makes the relationship between a potential sulfate supply, and its actual availability difficult to predict. Generally, however, sulfides found in rock minerals are oxidized as the minerals become aerated. The sulfates thusly formed are then available for leaching and solution in natural water. The equilibrium between the rate of sulfate formation and its subsequent leaching is, to a large extent, dependent on the aridity of the area studied (Hem, 1970), with the upper limit of SO_4^{-2} concentration in waters being determined by gypsum solubility (Turrner, 1963).

Once sulfate (SO_4^{-2}) is dissolved in water it is relatively stable. However, existing complications are its tendencies to form ion pairs (with metal ions), and to enter into aquatic life processes (Hem, 1970).

Species. Although sulfate (SO_4^{-2}) forms an equilibrium with bisulfate (HSO_4^{-1}), in the pH range of most natural waters only the SO_4^{-2} form is of concern (Hem, 1960).

SO_4^{-2} tends to form complex ions and ion pairs, for example: $NaSO_4^-$, $CaSO_4^0$, and $MgSO_4^0$. The fact that some of these species (e.g., $CaSO_4^0$) are lacking electrical charge complicates the electrical conductivity/ total dissolved solids relationship of the water (Hem, 1970).

Nitrate

While nitrate is not one of the commonly recognized major constituents of natural water, it is of importance. Nitrate is very closely related to biological activity. Its behavior within the subject watershed is of concern because of interest in the role played by vegetation in controlling water chemistry.

Nitrogen occurs in natural water in several forms, both organic and inorganic. Nitrate is the most fully oxidized form commonly found in natural water. Dissolved nitrate (NO_3^-) is a major nutrient for vegetation, and the element is essential to all life (Hem, 1970).

Sources. Some plants convert atmospheric nitrogen into reduced compounds which are subsequently oxidized to nitrate. The atmosphere is also a source of nitrate itself. Once nitrate from these sources enters into a biological cycle, it is effectively retained within that cycle of growth, decay, and uptake (Hem, 1970).

Controls. The overriding controls of nitrate concentration in natural water are biological interactions. These interactions comprise the sources of most of the nitrate, control the rate of availability of the ion, and determine the fate of that available nitrate.

Phosphate

Phosphate is not a major constituent in the chemical make-up of unpolluted streams. Like nitrate, it is a biologically critical chemical.

Sources. The most common rock mineral source of phosphate is apatite (calcium orthophosphate). This mineral is widespread in both igneous and sedimentary rocks (Hem, 1970). Phosphate presence in natural water is normally determined by biological processes. Life cycles are both local sources and local sinks for the dissolved phosphorus species (Hynes, 1970).

Species. The chemistry of phosphate in water is basically that of a dissociation equilibrium for phosphoric acid (Hem, 1970).

Controls. Though phosphate does form complexes with inorganic compounds, which then are often precipitated; the primary control over dissolved phosphate concentrations is biological.

pH

The hydrogen ion activity, expressed as pH, is one of the most important summarizing parameters commonly used to characterize water. It expresses the acid or alkaline condition of a solution.

Sources. The pH of a water represents the result of the interrelation of several chemical equilibria. As examples of such equilibria found in stream water, Hem (1970) mentions: the dissociation of dissolved species of carbon dioxide, reactions involving oxidation of sulfur, hydrolysis reactions involving silicates, and oxidation of ferrous iron. At times oxides of nitrogen and sulfur can significantly, even drastically, lower the pH of precipitation (Likens, Bormann, and Johnson, 1972). The relative dominance of these equilibria varies considerably, but carbon dioxide influence can be expected universally in surface water.

Range. Most natural surface water has a pH between 6.5 and 8.5. In waters whose pH is less than 4.5, equilibria involving species other than carbon dioxide become dominant, e.g., equilibria of sulfur oxides are commonly present in such acid waters. During periods of the day when photosynthesis lowers the concentration of carbon dioxide, pH may rise to 9.0. Surface waters with pH much over 9.0 or below 4.5 are unusual, and are products of some unique local chemistry (Hem, 1970).

Similar Studies

Many researchers have been involved in the investigation of chemical quality of wildland streams. They have been primarily interested in measuring the impacts of man's activities (logging, road building, etc.) on the streams. The East has been the most active area of the United States for these investigations. Research of this nature has been carried out at Hubbard Brook Experimental Forest in New Hampshire (Bormann, Likens, and Eaton, 1969; Fisher, Gambell, Likens, and Bormann, 1968; Likens, Bormann, Johnson, and Pierce, 1967; Likens, Bormann, Johnson, Fisher, and Pierce, 1970;

Likens, Bormann, and Johnson, 1972), at Fernow Experimental Forest in West Virginia (Aubertin and Patric, 1974), at Coweeta Hydrologic Laboratory in North Carolina (Johnson and Swank, 1971), and at Pennsylvania State University (Lynch, Sopper, Corbett, and Aurand, 1975).

The Western United States has not been as intensively studied. The bulk of the activity that has occurred, has taken place in Oregon and Washington. This research has occurred at the H. J. Andrews Experimental Forest in Western Oregon (Fredriksen, 1970), at the Alsea River Watersheds also in Oregon (Marston, 1967), and at the Cedar River Watershed in Washington (Cole and Gessell, 1963; Cole, Gessel, and Dice, 1967). There have also been projects in Nevada (Skau, Meeuwig, and Humphrey, 1971) and Montana (Weisel and Newell, 1970).

The real significance of this previous research, to this thesis, is not in the data obtained. The numerical results previously published vary considerably from one region of the country to another and, therefore, are of little use in evaluating data obtained in an area remote from any of them. However, the research methods used and the models suggested do have more universal application, and establish the state-of-the-art in which this thesis was developed.

An exception to the above generalizations is a study that was done on another area in Northern Utah (Hart, Southard, and Williams, 1973). This study was near enough to the Davis County Experimental Watershed to allow more direct comparison of results. Numerous references to this study are made in the Results section of this thesis.

METHODS AND PROCEDURES

Field Procedures

Use of paired watersheds

The Chicken Creek watersheds had been established, studied, and calibrated for an ongoing streamflow enhancement experiment. This water chemistry investigation was undertaken to add a water quality dimension to that experiment. While the objectives of this study of water chemistry do not indicate any need for paired watersheds, using the data from both of them allowed considerable additional analysis through comparison.

To collect the paired watershed data, samples were taken at both stream gages. The samples were collected periodically from November 9, 1972, to April 10, 1973, and then weekly through the summer of 1973.

In addition to the sampling at the gage, the chemistry of the West Branch was variously surveyed on a weekly basis throughout the summer of 1973.

Survey of tributaries of West Branch

In an attempt to identify and characterize any local variation in water chemistry within the watershed, intermittent tributaries were sampled. These tributaries and their respective sampling points are shown in Figure 3. Samples were obtained from these tributaries as long as they flowed.

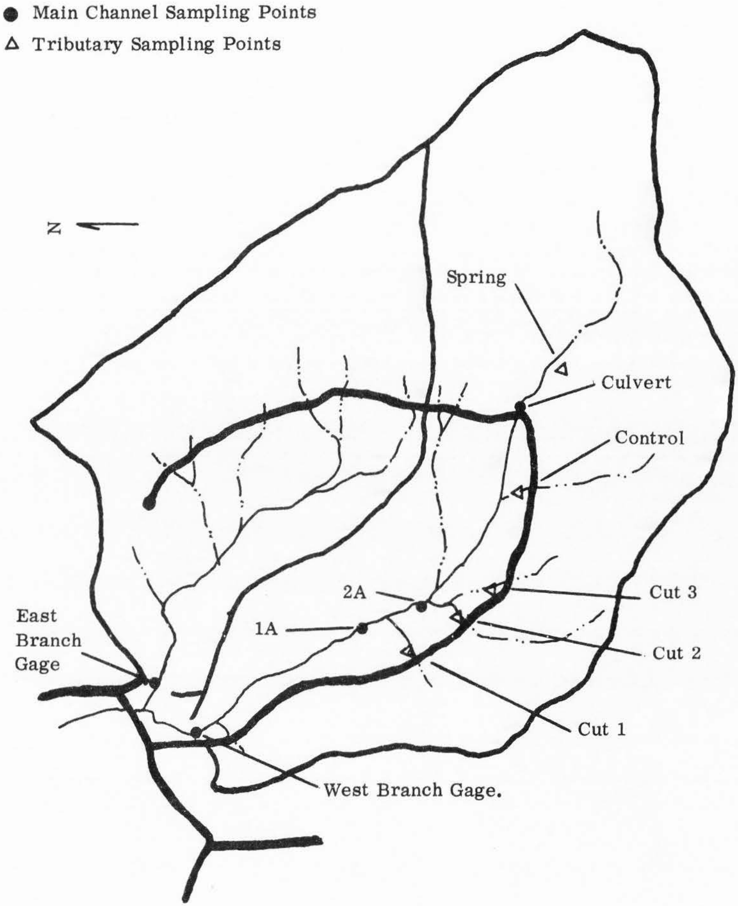

Figure 3. Stream and tributary sampling points.

Survey over the length of West Branch

As the summer progressed and one after another of the tributaries dried up, additional sampling points were established in the main channel. A station was located immediately below where each of the tributaries had been entering. The five stations eventually located over the length of the main channel of the West Branch were maintained so that linear variability within the channel could be observed. The locations of these stations are shown in Figure 3.

Sampling schedules

Samples were collected only periodically during the winter (November through April) because of limited accessibility. From early May through October, the sampling was performed weekly. Superimposed on this weekly summer schedule were four diurnal cycles.

On July 16 and 17, July 23 and 24, August 27 and 28, and September 3 and 4; four complete sets of samples were taken on the West Branch Watershed. These samples were collected at 6 hour intervals to complete the 24 hour cycles.

Precipitation samples

Precipitation, both rain and snow, was collected and analyzed. Snow was collected periodically during the winter. These collections were made from the snow already on the ground, rather than by intercepting falling snow.

Rainfall was collected in three collectors, at two sites on the watersheds (Figure 4). At the northern site, an open collector was used. This collector consisted of a plastic funnel, plastic tubing, and a plastic jug. The funnel was mounted on a steel fence post so that its mouth was approximately 4 feet above the ground. The mouth of the funnel was covered with an inert screening material to exclude any large particles or insects.

The second site consisted of a collector identical to the one described above, and a Wong Gage Precipitation Sampler. The Wong Gage is a commercial instrument, constructed with a precipitation sensitive circuit that operates a valve covering the collection apparatus. This enables the instrument to open only during precipitation and thereby exclude any material, such as dust, that might settle from the atmosphere between periods of rainfall.

Soil solution sampling

Samples of soil solution were obtained from six sites located on the West Branch watershed. The location of these sites will be shown in the discussion in the Results section. Each location consisted of four tubes. The tubes were a length of PVC pipe with a porous ceramic cup attached to the lower end.

The sampling procedure amounted to applying a vacuum to each tube, leaving the vacuum on overnight, then extracting the soil solution that had been drawn into the tube. This procedure was repeated four times through the summer of 1973.

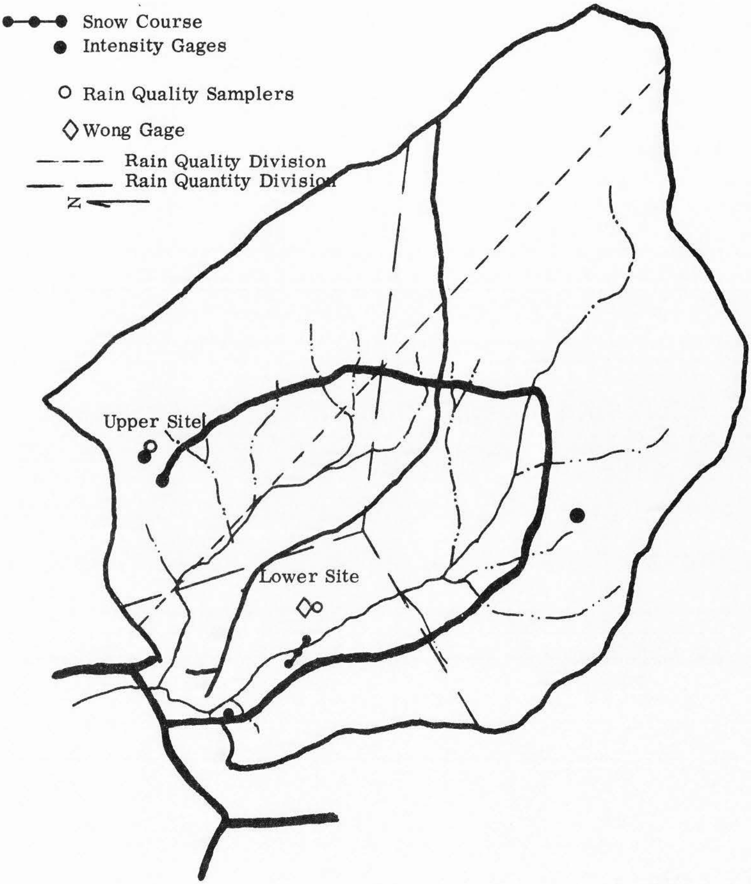

Figure 4. Precipitation gaging and sampling sites.

Sample transport and storage

As the samples were collected, in inert polyethylene bottles, they were immediately placed on ice and transported to the laboratory in that condition. As the samples were brought to the laboratory, they were stored at 4 C until analyzed.

Precipitation quantities

Rainfall amounts were recorded on recording rain gages located as shown in Figure 4. Two of these were 7-day gages. The third recorder was located near the stream gage and was a 30-day recording gage.

Snow quantities were estimated from data collected at a snow course maintained at 7,600 feet elevation on the West Branch. In addition, snow distribution was measured with the use of a network of thirty-five snow depth stakes scattered over both watersheds.

Streamflow data

The streamflows were measured through the use of an "H" type flume. The data was "recorded continuously on Fisher-Porter analog-to-digital punch tape recorders at 15-minute intervals from April through October, and 30-minute intervals during the remainder of the year." (Johnston and Doty, 1972, p. 20) For the purpose of this study, the streamflow measurement coinciding at the time that the water sample was taken has been used.

Laboratory Procedures

The chemical analyses were performed in the laboratory of the U.S. Forest Service Forest and Range Experiment Station in Logan, Utah. The methods used are shown in the following table.

Table 1. Chemical analysis methodology

Analysis	Method*
pH	Glass Electrode
Specific Conductance	Wheatstone Bridge
Calcium	Atomic Absorption
Magnesium	Atomic Absorption
Sodium	Atomic Absorption
Potassium	Atomic Absorption
Total Alkalinity	pH Meter
Sulfate	Turbidmetric Method
Nitrate	Brucine Method
Orthophosphate	Ascorbic Acid Method
Chloride	Mercuric Nitrate Method
Sediment	Gravimetric

*Source: Standard Methods for the Examination of Water and Wastewater, 1971.

RESULTS

Inventory of Chemical Constituents

The only real test of a chemical inventory is whether or not it is complete. Two different general relationships were examined to test the completeness of the inventories presented in Table 2.

Anion-cation balance

In theory, the cation equivalents should balance the anion equivalents. In practice, for waters with total concentrations in excess of 250 mg/l this balance should be within a couple of percent of the total ionic concentration. However, with waters having total ionic concentrations less than 5 meq/l, larger discrepancies can be expected (Hem, 1970).

The summary in Table 3, indicates that the Chicken Creek waters each contain far less than 250 mg/l total dissolved load and far less than 5 meq/l total ionic concentration. In light of the discussion concerning what could be expected, the cation-anion imbalances seem acceptable.

Another relationship discussed by Hem (1970), is that 100 times the total of either the cations, or the anions in equivalents, is equal to the electrical conductivity (micromhos/cm). This is quite close, in both branches, for anions. In both cases the cations are somewhat higher.

Table 2. Average ion composition of Chicken Creek branches (November 192-November 1973

	East Branch		West Branch	
Ion	mg/l	meq/l	mg/l	meq/l
Ca^{+2}	13.60 ± 1.21	0.68	21.81 ± 1.97	1.09
Mg^{+2}	3.74 ± 0.46	0.31	4.71 ± 0.58	0.39
Na^{+}	7.29 ± 0.68	0.32	5.95 ± 0.63	0.25
K^{+}	1.22 ± 0.31	0.03	1.13 ± 0.27	0.03
Total Cations	25.85	1.34	33.70	1.76
HCO_3^-	55.33 ± 7.10	0.91	79.00 ± 6.25	1.29
SO_4^{-2}	6.84 ± 0.60	0.14	5.69 ± 0.69	0.12
Cl^-	5.58 ± 0.69	0.16	5.10 ± 0.69	0.14
NO_3^-	0.44 ± 0.12	0.01	0.22 ± 0.08	0.00
PO_4^-	0.05 ± 0.01	0.00	0.39 ± 0.01	0.00
Total Anions	66.24	1.21	90.40	1.55
Total Ions	92.09	2.55	124.10	3.31

Note 1: HCO_3^- concentrations were calculated from measured alkalinity using the method described on page 336 of Chemistry for Sanitary Engineers (Sawyer and McCarty, 1967).

Note 2: Mg/l concentrations are presented with 95 percent confidence intervals, n = 20.

Table 3. Summary of ion compositions

Location	Total Ion Conc. (meq/l)	Ion* Inbalance %	TDS** (mg/l)	Cond. (μmhos)	TDS Cond.
East Branch	2.55	5	63.87	116	.55
West Branch	3.31	6	83.81	154	.54

*Ion Imbalance $= \frac{\text{Cations - Anions}}{\text{Cations + Anions}} \text{ X } 100\%$

**TDS is computed by summing the individual ion concentrations (mg/l), with the HCO_3 concentration multiplied by .49 to approximate HCO_3 being volatilized to CO_3 during a standard evaporative analysis for TDS (Hem, 1970)

It occurs to me that a possible reason for this exists in the analysis procedures. All of the anions were measured by chemical procedures. All of the cations were measured using atomic absorption. Perhaps the atomic absorption method fails to differentiate between ionic and complexed or molecular species of the cations.

TDS/conductivity

A "normal" range of values for the ratio of total dissolved solids (mg/l) to electrical conductivity (micromhos/cm) is from .55 to .75. If the anions are composed mostly of HCO_3^- and Cl^-, the ratio will tend to be nearer the .55 value (Hem, 1970). This appears to be the case with the Chicken Creed waters (Table 3) (TDS/Cond. of 0.55 and 0.54).

If the ratios had fallen far outside the normal range, it would indicate that one, or more, important constituent had not been measured.

Chemical Budgets of Watersheds

Assumptions and calculations

The chemical budgeting process is based on a very simple model. The following diagram illustrates the concept. The differences between the chemistry of the incoming water and the water flowing out is attributable to processes internal to the watershed. The budgeting process achieves an overall quantification of the effects of these processes but not necessarily insight into the processes themselves.

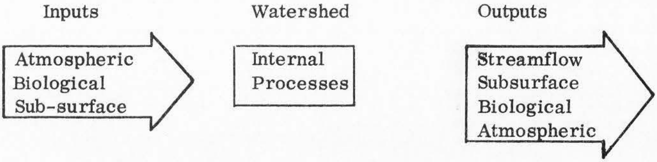

Figure 5. Conceptual model of the functioning of a watershed.

Certain inputs and outputs are extremely difficult to monitor, e.g., biological vectors and subsurface leaks into, or out of, the basin. In order to handle these uncertainties, some assumptions must be made.

Considerable care must be taken in the selection of watersheds for such budget studies. The bedrock underlying the watershed should be tight and the watershed should be of such a shape that the outlet, both surface and sub-surface, can be controlled and the flow monitored. Once this care has been taken and gross water budgets (as opposed to chemical budgets) do not indicate large discrepancies, the assumption is made that subsurface flow is inconsequential (Likens and Bormann, 1972).

Biological vectors (wildlife, insects, etc.) are simply assumed to be balanced. Some natural transport of chemicals, by plant and wildlife activities, will undoubtedly be occurring across watershed boundaries, but there is no reason to think that there would be any net transport in either direction.

Inputs. In the conceptual model, the categories of possible inputs are sub-surface, biological, and atmospheric. Of these input possibilities, sub-surface and biological are assumed to have no net influence. This leaves only the atmospheric category to be investigated and quantified. This category is further broken down into rain, snow, and dust. The procedures actually used to collect data on each of these input sources were explained in the Methods and Procedures section of this thesis. Now the calculations used to expand that data to cover the two watersheds will be explained.

In the case of snow, the quality samples that were taken were used to obtain an average chemical composition that was assumed to represent all of the water contained in the snowpack. The volume of the water in the snowpack was calculated by first developing a map (Figure 6) showing snow depth contours (in inches of water). The total volume of water in the snowpack was then calculated by summing the products, of the areas between adjacent contours multiplied by the average depth of snow between those contours.

This method was made possible by the relatively large number and the distribution of the depth samples taken. The process also illustrated the

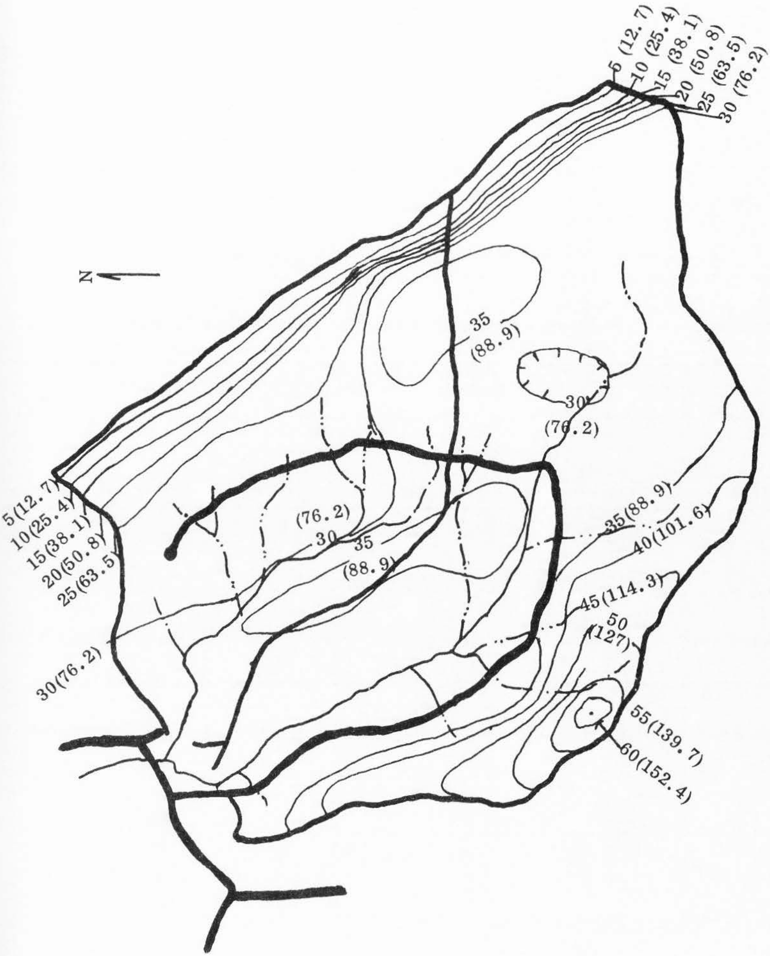

Figure 6. Total snow depth contours in inches (centimeters), Winter of 1972/1973.

distribution of the snowpack. This, in itself, is significant and will be discussed later.

No attempt was made to measure the distribution of the snowfall over time, or to determine variations in the quality of the snow from one storm to the next. While this information might be of interest, the study area is too remote to make an investigation of this sort practical.

The make-up of the snow chemistry is further discussed in the next section. The total chemical inputs of the snow are shown in Tables 4 and 5.

The data analyses and calculations were considerably more complex in dealing with the inputs made by rain. Rain volume information was not collected at enough points to allow the use of contours to expand the data. The Theisson polygon method was used to expand the information collected at the three gages. Rain quality data was expanded similarly from only two collection sites. These superimposed polygons are illustrated in Figure 4. Because of the artificiality of the polygon method of data expansion, the calculations were made only to determine average rainfall and average quality on each watershed. These averages were then used to calculate the input into the chemical budget made by rain.

The investigation of the chemical input occurring in the form of dust raised more questions than it answered. The intent was to distinguish between dry fallout and rain solution. So much of the meaning of this investigation is pure speculation that no attempt was made to conclude any quantities of dust

Table 4. 1973 chemical budget of West Branch of Chicken Creek

				(Kg/Hect.)							
	Ca	Mg	Na	K	NO_3	SO_4	Cl	HCO_3	PO_4	TDS	Water (cm)
Inputs											
Snow	14.2	1.5	3.3	4.5	4.4	8.7	4.5	23.4	.24	49.3	79.5
Rain	5.4	1.1	3.8	0.7	3.5	6.1	6.8	5.5	.11	26.7	24.5
Total	19.6	2.6	7.1	5.2	7.9	14.8	11.3	28.9	.35	76.0	104.0
Outputs											
Stream	107.6	20.7	24.3	9.2	1.8	43.5	24.8	350.0	.02	402.0	68.4
Net Change	-88.0	-18.1	-17.2	-4.0	+6.1	-28.7	-13.5	-321.1	+.33	-326	+35.6

Table 5. 1973 chemical budget of East Branch of Chicken Creek

				(Kg/Hect.)							
	Ca	Mg	Na	K	NO_3	SO_4	Cl	HCO_3	PO_4	TDS	Water (cm)
Inputs											
Snow	10.0	1.1	2.3	3.1	3.5	6.2	3.1	16.9	0.17	34.8	56.1
Rain	5.0	1.2	3.7	0.6	3.5	6.7	6.2	1.2	0.23	26.1	21.8
Total	15.0	2.3	6.0	3.7	7.0	12.9	9.3	18.1	0.40	60.9	77.9
Outputs											
Stream	34.3	9.4	18.6	5.6	0.9	27.4	14.4	114.2	0.02	165.9	36.6
Net Change	-19.3	-7.1	-12.6	-1.9	+6.1	-14.5	-5.1	-96.1	+0.38	-105	+0.38

for the purpose of the chemical budget. Precipitation inputs in the budget include both material dissolved in the rain and between-storm dry fallout.

Outputs. According to the model (Figure 5), the visualized routes by which a watershed produces chemical outputs are: streamflow, subsurface, biological, and atmospheric. As previously described, for the purpose of chemical budgeting, the sub-surface and biological transport of chemicals are ignored. The loss of chemicals from the watershed into the atmosphere is assumed to be minimal, when compared to loss through streamflow.

Certainly the primary mode of transport of chemicals out of the watershed is through streamflow. Quantifying this output was accomplished by measuring the outflow of water and analyzing its chemical makeup. The methods used to accomplish this were previously described.

The calculation of the total annual chemical output was accomplished with the following formula:

$$\text{Chemical Output} = \sum_{i=1}^{n} (Q_i \times C_t)$$

Q = stream discharge

C = chemical concentration

i = interval number

n = number of intervals = $\frac{\text{year}}{t}$

t = length of interval

The available stream hydrograph supplied a nearly continuous (down to approximately a 15-minute interval) record of discharge. On the other hand, chemical concentration information was available only on an irregular basis. The problem consisted of expanding the available concentration information so that each discharge (Q_i) would have its own associated concentration (C_1).

Attempts were made to correlate concentration to streamflow, so that the concentration data could be mathematically expanded to represent all flow conditions. The correlation coefficients that were obtained (Tables 6 and 7) were not high enough to justify the use of this method.

The precision and insight represented by the stream quality (concentration) data seemed to justify only a rather rough breakdown of the year's information into monthly averages. Using monthly totals of stream discharge and a monthly average concentration, chemical discharges were calculated.

Budgets

The chemical budgets developed for the East and West Branches of Chicken Creek are presented in Tables 4 and 5. The quantities are expressed on a per unit area basis so that the two watersheds can be compared.

Investigation of Sources

Data produced by each of the sampling schemes described earlier were examined for any evidence that they might yield concerning sources of chemicals.

Table 6. Correlations of water quality parameters, West Branch gage (November 1972-November 1973)

	Flow	pH	Cond.	Sediment	Alkalinity	Calcium	Magnesium	Sodium	Potassium	Phosphorus	Nitrate	Sulfate
pH	-.50											
Cond.	-.63	.82										
Sediment	.87	-.50	-.60									
Alkalinity	-.46	.78	.80	-.47								
Calcium	-.30	.50	.61	-.35	.60							
Magnesium	-.38	.45	.67	-.31	.45	.56						
Sodium	-.67	.55	.52	-.61	.37	-.02	.26					
Potassium	.13	-.31	-.36	.06	-.25	-.36	-.24	-.02				
Phosphorus	-.07	-.22	-.20	-.03	-.17	-.22	-.12	.11	-.06			
Nitrate	.00	.15	.01	-.13	.09	.16	-.09	.08	-.06	.26		
Sulfate	.52	-.52	-.57	.44	-.37	-.38	-.41	-.49	.19	.08	-.15	
Chloride	-.46	-.06	-.07	-.49	-.09	-.26	.02	.50	.10	.44	.11	-.18

Note: At n = 27, correlation coefficients having an absolute value ≥.39 are significant at 95 percent confidence level.

Table 7. Correlations of water quality parameters, East Branch gage (November 1972-November 1973)

	Flow	pH	Cond.	Sediment	Alkalinity	Calcium	Magnesium	Sodium	Potassium	Phosphorus	Nitrate	Sulfate
pH	-.66											
Cond.	-.81	.68										
Sediment	-.04	.06	.05									
Alkalinity	-.78	.73	.99	.06								
Calcium	-.74	.67	.86	.06	.87							
Magnesium	-.62	.46	.70	.16	.71	.61						
Sodium	-.81	.65	.97	.09	.95	.84	.64					
Potassium	.08	-.18	-.04	.07	-.03	-.01	-.04	-.04				
Phosphorus	-.04	-.42	.14	-.06	.08	.03	.15	.16	-.13			
Nitrate	-.25	.52	.25	-.26	.29	.27	.13	.30	-.32	-.20		
Sulfate	.36	-.43	-.60	-.40	-.63	-.58	-.55	-.57	-.29	-.03	.06	
Chloride	-.54	.56	.85	.40	.83	.72	.51	.86	-.00	.14	.09	-.68

Note: At n = 27, correlation coefficients having an absolute value $\geq .39$ are significant at 95 percent confidence level.

Atmospheric sources

The chemical budget just developed determined a comparative quantity of the chemical "inputs" to the watershed, relative to the quantity of chemicals picked up by the water in transit through the watershed.

To further break the "input" sources into dust and precipitation, the chemical data generated by three collectors at two different sites were examined.

Open collector versus Wong gage. As previously described in the Methods and Procedures section, the Wong gage is instrumented to collect precipitation samples only during storm events. This capability should allow the gage to obtain samples free of between-storm fallout.

The open collectors could be expected to pick up both the between-storm fallout and the input by storms. Ideally, then, the between-storm fallout (dust) could be quantified by subtracting the Wong gage results from the open gage results.

Table 8 shows the results of this comparison. "t" tests were run on each parameter. The significant difference appears to be only in the quantity of Ca present (the pH difference probably just reflects the Ca difference). This single difference, though significant, did not seem to justify difference, though significant, did not seem to justify any attempt to quantify the chemical input of the dust during the budget calculations.

Upper versus lower precipitation collector. A second open precipitation collector was maintained to obtain information concerning areal

Table 8. Analysis of dust (Summer 1973)

Parameter	Average Open	Average Wong gage	Open-Wong*	Level of Sig.
Cond. (μmhos)	24.42	27.50	-3.09	N.S.
pH	5.71	4.86	+0.85	@.995
HCO_3^- (mg/1)	2.20	0.61	+1.55	N.S.
Ca^{++} (mg/1)	1.41	0.83	+0.58	@.975
Mg^{++} (mg/1)	0.39	0.42	-0.03	N.S.
Na^{++} (mg/1)	1.59	1.73	-0.14	N.S.
K^+ (mg/1)	1.01	1.57	-0.56	N.S.
$NO_3^=$ (mg/1)	1.46	1.51	-0.05	N.S.
$SO_4^=$ (mg/1)	2.82	2.51	+0.31	N.S.
Cl^- (mg/1)	3.72	3.05	+0.67	N.S.
PO_4^{-x} (mg/1)	0.03	0.03	0.00	N.S.

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*The difference between the open collector and the Wong gage collector should be the particulate material collected between precipitation events. Only positive differences would be expected, the negative values indicate imprecision in sampling and/or analysis techniques.

variability of atmospheric input. The two collectors were located approximately 1/2 kilometer apart. The results (Table 9) of comparing the samples obtained at the two sites add further confusion to trying to explain the atmospheric processes.

Since only one of the sites was equipped with a Wong gage (to quantify the dust), there is no way to assess its areal variability. The significant differences seen between the two sites could, therefore, be caused by local variations in dust, local variations in precipitation chemistry, or some combination of the two.

Precipitation chemistry versus time. The comparison between rain and snow is relatively straight forward. The results (Table 10) show that chemical input from the atmosphere is significantly greater during the summer months. Some questions that were not answered include: Is the seasonal difference the result of a difference in the source areas of the storms? (Summer precipitation is typically from thunderstorms that originate along the Wasatch Range. Winter weather is associated with more general frontal patterns) (Eaton, 1974). Or, is the seasonal difference the result of more local phenomena such as exposure of dust sources as the snows melt, or increased biological activity occurring during the summer months?

Further investigations into atmospheric inputs were suggested by an analysis done by Hart, Southard, and Williams (1973). These authors proposed three methods of atmospheric transport of chemicals: "bonding with water vapor and delivery of incorporated elements with rainfall; dry fallout

Table 9. Analysis of areal variability of precipitation chemistry (Summer 1973)

Parameter	Average Upper (n = 5)	Average Lower (n = 5)	Upper-Lower	Significance
Cond. (μmhos)	67.9	24.4	43.5	@.975
pH (units)	4.12	5.74	-1.62	@.995
HCO_3^- (mg/1)	0.00	2.20	-2.20	@.995
Ca^{+2} (mg/1)	2.13	1.41	0.72	@.900
Mg^{+2} (mg/1)	.57	.39	0.18	N.S.
Na^+ (mg/1)	1.94	1.59	0.35	N.S.
K^+ (mg/1)	.37	1.01	-0.64	N.S.
NO_3^- (mg/1)	1.86	1.46	-0.40	@.975
SO_4^{-2} (mg/1)	3.56	2.82	0.74	@.900
Cl^- (mg/1)	3.01	3.72	-0.71	N.S.
PO_4^{-x} (mg/1)	0.09	3.09	-3.00	@.900
TDS (mg/1)	10.53	16.57	-6.04	N.S.

Table 10. Differences between rain and snow chemistry (1973 data)

Parameter	Average Rain (n = 5)	Average Snow (n = 4)	Rain-Snow	Significance
Cond. (μmhos)	46.7	9.7	37.0	@.995
pH (units)	4.93	5.27	-0.34	N. S.
HCO_3^- (mg/1)	2.20	3.79	-1.59	N.S.
Ca^{+2} (mg/1)	1.79	3.68	-1.89	@.950
Mg^{+2} (mg/1)	.49	0.28	0.21	@.900
Na^+ (mg/1)	1.78	0.49	1.29	@.990
K^+ (mg/1)	0.34	0.60	-0.26	N. S.
NO_3^- (mg/1)	1.68	0.58	1.10	@.995
SO_4^{-2} (mg/1)	3.21	Snow was not analyzed for $SO_4^=$		
Cl^- (mg/1)	2.81	1.26	1.55	@.900
PO_4^{-x} (mg/1)	0.06	0.03	0.03	N.S.
TDS[*] (mg/1)	11.88	8.29		

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[*] Calculated TDS is shown but not analyzed because of the missing SO_4^{-2} values.

of particulate matter between storms; or as particulate matter washed out (scavenging) by rainfall." Their research suggested that the major contributing process, at least in their area of study, was dry fallout between storms. Since attempts at actually measuring dust on the Chicken Creek Watershed failed, the correlation analyses (storm size and between-storm period versus conductivity) used by the above-mentioned authors were tried.

The number of storms having data available for this investigation varied from seven at the upper collector, to five at the lower collector, to four at the Wong gage. With such small samples, correlation coefficients would have had to have been extremely large to prove significant. The results of the analyses are shown in Table 11.

Table 11. Correlation of conductivity with storm size and inter-storm period (Summer 1973)

	P vs Cond.	ΔT vs Cond.	ΔT/P vs Cond.
Upper (n = 7) Collector	R = -.75 (-.95 = R = -.24)	R = +.39 (+.46 = R = +.84)	R = +.88 (+.40 = R = +.97)
Lower (n = 5) Collector	R = -.50 (-.93 = R = +.57)	R = +.53 (-.57 = R = +.92)	R = +.86 (+.15 = R = +.97)
Wong (n = 4) Gage	R = -.86 (-.98 = R = +.35)	R = +.20 (-.84 = R = +.93)	R = +.45 (-.77 = R = +.94)

P = Storm size in inches of precipitation.
ΔT = Days since last storm.
Cond. = Electrical conductivity
R = Correlation coefficient (95% confidence belt).

Recognizing that the correlation statistics are far from irrefutable, the trends hinted at make for some interesting speculation. The data seem to indicate super-imposed processes. The precipitation versus conductivity correlations suggest the airborne incorporation of materials. Whether the source of these materials is local scavenging during rainfall, or uptake and incorporation during cloud formation; the sources appear to be limited and their impact diluted in the larger storms. The Wong gage, that was closed between storms, does not show as great a correlation between inter-storm period/precipitation ($\Delta T/P$) and conductivity as the two open collectors. This suggests that between-storm dry fallout also can account for a portion of the observed chemistry.

Storm-to-storm variability was quite evident. Conductivity ranged from 3.9 to 144 micromhos. pH ranged from 6.40 to one storm that was so strongly acidic that it corroded and destroyed the moisture sensing grid on the Wong gage (pH was less than 3.0).

Measurements of pH less than 4.5 indicate hydrogen ion sources other than the equilibria expected in unpolluted natural precipitation (Hem, 1970). The extremely low pH readings suggest the incorporation of "unnatural" materials of some type. The normal summer storm patterns in the area (from southwest to northeast) could transport such materials, picked up over the industrialized Salt Lake Valley, and deposit them on the study area.

Yet, as great as the storm-to-storm variability was, it did not mask the local differences. The data collected at the two sites are not well explained by any single one of the proposed mechanisms. The consistent differences between the two sites (Table 9) indicate the presence of some quite local phenomenon. The chemical parameters that exhibit the significant differences do not clearly point toward any particular source. The highly significant difference in conductivity suggests that the upper collector receives more ionic inputs. The pH difference suggests that this ionic input is acidic. The NO_3^-, $SO_4^=$, and orthophosphate differences suggest that these inputs were perhaps HNO_3, H_2SO_4, and H_xPO_x. If this line of reasoning is valid, what is a reasonable source of such chemicals? What kind of particulates would be of such composition? If these chemicals are transported into the area by the general storm pattern, why is there such a significant local variation in the quantities deposited?

In searching for possible explanations for the observed local trends, the following differences were noted: 1) The northern site is 200 feet higher than the southern site. 2) The vegetation immediately surrounding the northern site is sagebrush, while that of the southern site is grasses and forbs. 3) The higher, northern site is more exposed to prevailing winds, to normal weather patterns, and to local turbulence that can be expected in mountainous terrain. 4) The soils immediately surrounding the northern site (perhaps very local sources of dust) are gneissic loams, while the southern site is located on deep alluvium. How these observed site differences might act to influence the nature and quantity of atmospheric inputs is open to speculation.

Terrestrial sources

East Branch versus West Branch. A comparison of the hydrologic and chemical budgets of the two watersheds (Tables 4 and 5) indicates that the West Branch is producing not only more streamflow per unit area, but also that water is of higher chemical concentration.

An inspection of the quantities of precipitation shows that most of the difference in the total water quantity is accounted for in the unbalanced precipitation distribution. The greater portion of this precipitation imbalance is in the distribution of snow. The West Branch received approximately 80 cm of snow, while the East Branch received only 56 cm.

The snow depth contour map (Figure 6) illustrates the snow distribution pattern. This pattern suggests an explanation for the second part of the disimilarity between the watersheds--the higher concentrations found in the West Branch stream. The contours show that the snow that fell on the West Branch watershed tended to accumulate in the upper reaches of the watershed away from the outlet. Just the opposite is true in the East Branch basin. This would mean that the average travel distance and probability of contamination, would be greater for the melting West Branch snowpack. In fact, a rough comparison of the distances of the snowpacks from their respective main channels indicates that the snow in the West Branch basin averaged approximately 1.5 times as far from its main channel as did the East Branch snow.

Another effect of the distribution is that a much greater quantity of snow in the West Branch watershed was accumulated on a protected northern aspect. This means that the rate of melt, in the spring, would be slower. This condition would, once again, assure maximum opportunity for the precipitation input in the form of snow to become exposed to the soil profile--rather than rapidly run off as surface flow.

The greater travel distance and slower melting rate, together could explain much of the observed differences in chemistry.

Correlation of parameters. Simple linear correlation analysis was run on the data collected at each of the stream sampling sites.

Temperature data were not included in the correlation analyses. It was felt that within the range of temperatures measured (1-19 C), any direct effect of temperature change on chemical concentrations would be beyond the sensitivity of the laboratory analyses. Hem (1970, p. 22) states:

> The effects of moderate departures from standard conditions (a few atmosphere pressure and ± 10-15 C) are not large enough to preclude the direct application of standard conditions to most natural water environments. Unavoidable errors of sampling and analysis generally can be expected to affect equilibrium calculations at least as much as these small departures from standard temperature and pressure.

Tables 6, 7, 12, and 13 reflect data collected throughout the entire year. The data, therefore, shows the impact of flow fluctuations inherent in the annual hydrograph. A model incorporating water chemistry into a flow hydrograph, might be described by the following argument: Assume that there are essentially two chemically distinct waters present on the watershed. One

Table 12. Correlation of water quality parameters sampled at the West Branch "Spring" (November 1972-November 1973)

Note: At n = 31, correlation coefficients having an absolute value ≥ .38 are significant at 95 percent confidence level.

	Flow	pH	Cond.	Sediment	Alkalinity	Calcium	Magnesium	Sodium	Potassium	Phosphorus	Nitrate	Sulfate
pH	-.07											
Cond.	-.63	.29										
Sediment	.32	.06	-.07									
Alkalinity	-.45	.58	.69	-.06								
Calcium	-.39	.06	.63	-.13	.50							
Magnesium	-.40	.41	.66	.13	.53	.45						
Sodium	-.55	.00	.42	-.53	.38	.40	.10					
Potassium	-.05	-.29	-.10	.26	-.31	-.12	.07	-.41				
Phosphorus	.31	.10	-.03	.49	-.08	-.02	-.02	-.37	-.20			
Nitrate	-.45	.12	.70	-.41	.41	.54	.46	.32	-.14	-.14		
Sulfate	.59	-.20	-.67	.28	-.54	-.32	-.42	-.44	.27	.27	-.45	
Chloride	-.21	.04	.53	.25	.14	.43	.53	.10	.02	.20	.24	-.28

Table 13. Correlations of the water quality parameters sampled at the West Branch "Culvert" (November 1972-November 1973)

pH	-.17											
Cond.	-.79	.02										
Sediment	-.41	.23	.46									
Alkalinity	-.73	.29	.63	.37								
Calcium	-.53	-.06	.55	.24	.49							
Magnesium	-.47	.22	.53	.07	.55	.62						
Sodium	-.71	.12	.60	.22	.64	.65	.38					
Potassium	-.20	-.16	.56	-.03	.33	.30	.48	.20				
Phosphorus	-.09	-.16	.14	.12	-.04	-.30	-.14	-.20	.21			
Nitrate	.33	.10	.34	-.10	-.29	-.21	-.19	-.25	-.18	.03		
Sulfate	.32	-.21	-.11	-.28	-.08	-.04	.12	-.03	.54	-.04	.28	
Chloride	-.56	-.01	.63	.05	.56	.52	.62	.66	.36	-.10	-.18	.09
	Flow	pH	Cond.	Sediment	Alkalinity	Calcium	Magnesium	Sodium	Potassium	Phosphorus	Nitrate	Sulfate

Note: At n = 28, correlation coefficients having an absolute value $\geq .39$ are significant at 95 percent confidence level.

might be described as precipitation--relatively uncontaminated, unexposed to the soil. The second would be groundwater--this water has had some exposure to the biogeophysical processes that occur in a soil profile. The streamwater chemistry measured at various flow stages is a mixture of these two types of water. Measurements taken during baseflow are dominated by "groundwater." Measurements taken during floodflow reflect "groundwater" that is being diluted by waters (overland flow, snowmelt, etc.) that are nearer the "precipitation" type.

An examination of how the various chemical parameters are correlated to flow tends to support this general concept. The concentrations of the bulk of the ions are negatively correlated with flow. pH also displays a negative correlation, illustrating how the acid, poorly buffered precipitation is neutralized by exposure to the soil.

The nitrate ion appears to be an exception. The behavior of the nitrate ion does not, however, disagree with the model. Since precipitation actually contains higher concentrations of nitrate (.38 mg/l) than groundwater (.17 mg/l), it is reasonable to expect the nitrate concentration in streamwater to increase as the proportion of overland flow increases.

The sulfate ion, even more dramatically than the nitrate ion, refuses to react to flow change as the dilution model would predict. This illustrates the inadequacy of so simple a model. There are other processes occurring simultaneously with the seasonal flow fluctuations. One of the most obvious of these processes is biological activity. Sulfate is a constituent whose availability could be greatly affected by seasonal changes in vegetation. This could conceivably account for the exhibited behavior of sulfate.

The overall chemical nature (indicated by conductivity and pH) of the stream water seems to be most directly correlated to the concentrations of metallic cations (calcium, magnesium, and sodium), rather than being dominated by anions such as sulfate. This suggests that the water chemistry is primarily a CO_3/HCO_3 equilibrium system.

Tables 14, 15, 16, 17, and 18 all present correlation coefficients calculated from spring runoff data. Because of the extreme changes in flow during this period and the fact that the data were entirely from the short runoff period (reducing confusion from seasonal biological influences), these correlations reflect better the simplistic dilution model than did the annual cycle.

Tables 19 and 20 present correlations observed during the summer low flow period. As can be seen, these correlation coefficients do not reflect as clear a picture as the spring runoff data presented. Flow is not as dominating. Summer precipitation has higher ion concentrations and, therefore, is a less effective dilutant. And, there are undoubtedly many more biological or meteorological processes adding to the confusion.

Chemical changes over stream length. Samples were taken at five sites along the length of the main channel of the West Branch. The locations of the sample sites are shown in Figure 7. The stiff diagrams (Hem, 1970) associated with each site graphically present the relative concentrations of

Table 14. Correlation of water quality parameters sampled at East Branch gage (Spring melt period, 1973)

	Flow	pH	Cond.	Sediment	Alkalinity	Calcium	Magnesium	Sodium	Potassium	Phosphorus	Nitrate	Sulfate
pH	-.75											
Cond.	-.90	.81										
Sediment	.82	-.84	-.76									
Alkalinity	-.88	.75	.99	-.76								
Calcium	-.69	.69	.74	-.80	.77							
Magnesium	-.65	.62	.87	-.52	.89	.67						
Sodium	-.95	.85	.97	-.85	.95	.70	.79					
Potassium	.14	-.29	-.22	-.11	.14	.13	-.14	-.17				
Phosphorus	.52	-.32	-.56	.50	-.60	-.72	-.31	-.47	-.09			
Nitrate	-.33	.71	.34	-.55	.26	.08	.10	.48	-.22	.14		
Sulfate	-.12	.14	-.16	-.07	-.27	-.37	-.51	.00	-.14	.25	.55	
Chloride	-.10	.39	.40	-.01	.38	.09	.61	.31	-.69	.19	.21	-.41

Note: At n = 5, correlation coefficients having an absolute value ≥.87 are significant at 95 percent confidence level

Table 15. Correlation of water quality parameters sampled at West Branch gage (Spring melt period, 1973)

	Flow	pH	Cond.	Sediment	Alkalinity	Calcium	Magnesium	Sodium	Potassium	Phosphorus	Nitrate	Sulfate
pH	-.73											
Cond.	-.81	.72										
Sediment	.88	-.65	-.74									
Alkalinity	-.82	.76	.98	-.71								
Calcium	-.79	.60	.79	-.78	.81							
Magnesium	-.74	.54	.91	-.61	.94	.77						
Sodium	-.91	.68	.72	-.92	.71	.62	.65					
Potassium	.08	-.43	-.46	-.02	-.47	-.37	-.42	.06				
Phosphorus	-.20	-.37	.08	-.14	.02	-.17	.17	.28	.56			
Nitrate	.47	-.28	-.44	.42	-.56	-.55	-.68	-.45	-.10	-.09		
Sulfate	.22	-.09	.24	.01	.25	.29	.34	-.21	-.41	-.30	-.38	
Chloride	-.31	-.10	-.23	-.41	-.26	-.02	-.25	.45	.76	.43	.00	-.61

Note: At n = 5, correlation coefficients having an absolute value ≥ .87 are significant at 95 percent confidence level.

Table 16. Correlation of water quality parameters sampled at tributary "Cut 1" of West Branch (Spring melt period, 1973)

	Flow	pH	Cond.	Sediment	Alkalinity	Calcium	Magnesium	Sodium	Potassium	Phosphorus	Nitrate	Sulfate
pH	-.30											
Cond.	-.91	.56										
Sediment	.62	-.67	-.63									
Alkalinity	-.91	.44	.98	-.59								
Calcium	-.33	-.28	.01	-.40	.05							
Magnesium	-.87	.60	.95	-.63	.91	.05						
Sodium	-.46	.37	.66	-.61	.69	-.13	.42					
Potassium	-.07	.07	.14	.37	.10	.17	.34	-.15				
Phosphorus	.83	-.54	-.85	.60	-.81	-.21	-.93	-.35	-.46			
Nitrate	.89	-.21	-.73	.57	-.72	-.34	-.65	-.48	.24	.76		
Sulfate	.53	-.64	-.68	.83	-.73	.07	-.59	-.73	.48	.45	.40	
Chloride	-.62	-.06	.41	-.38	.41	.51	.27	.41	-.24	-.48	-.88	-.16

Note: At n = 8, correlation coefficients having an absolute value $\geq .70$ are significant at 95 percent confidence level.

Table 17. Correlation of water quality parameters sampled at tributary "Cut 2" of West Branch (Spring melt period, 1973)

	Flow	pH	Cond.	Sediment	Alkalinity	Calcium	Magnesium	Sodium	Potassium	Phosphorus	Nitrate	Sulfate
pH	-.92											
Cond.	-.96	.93										
Sediment	.95	-.96	-.93									
Alkalinity	-.92	.89	.94	-.87								
Calcium	-.90	.82	.89	-.81	.94							
Magnesium	-.87	.85	.93	-.81	.96	.94						
Sodium	-.73	.76	.81	-.77	.88	.83	.88					
Potassium	-.44	.44	.47	-.33	.69	.70	.70	.58				
Phosphorus	.30	-.44	-.40	.32	-.43	-.44	-.54	-.38	-.63			
Nitrate	.97	-.81	-.90	.86	-.83	-.84	-.77	-.60	-.33	.12		
Sulfate	.32	-.08	-.21	.06	-.20	-.36	-.23	.17	-.39	.30	.41	
Chloride	.32	-.35	-.35	.29	-.28	-.35	-.40	-.12	-.41	.87	.20	.57

Note: At n = 9, correlation coefficients having an absolute value $\geq .67$ are significant at 95 percent confidence level.

Table 18. Correlation of water quality parameters sampled at tributary "Cut 3" of West Branch (Spring melt period, 1973)

	Flow	pH	Cond.	Sediment	Alkalinity	Calcium	Magnesium	Sodium	Potassium	Phosphorus	Nitrate	Sulfate
pH	-.74											
Cond.	-.77	.99										
Sediment	.40	-.65	-.61									
Alkalinity	-.36	.89	.85	-.70								
Calcium	-.69	.87	.89	-.74	.77							
Magnesium	-.66	.96	.95	-.57	.89	.93						
Sodium	-.70	.93	.95	-.41	.80	.93	.97					
Potassium	-.66	.69	.64	-.57	.55	.70	.73	.62				
Phosphorus	.28	-.50	-.42	.92	-.59	-.47	-.45	-.28	-.72			
Nitrate	.56	-.56	-.49	.31	-.40	-.42	-.56	-.43	-.85	.47		
Sulfate	.63	-.55	-.51	.84	-.37	-.23	-.35	-.25	-.55	.62	.56	
Chloride	-.48	.82	.77	-.69	.82	.67	.81	.73	.76	-.67	-.53	-.55

Note: At n = 7, correlation coefficients having an absolute value $\geq .75$ are significant at 95 percent confidence level.

Table 19. Correlation of water quality parameters sampled at Each Branch gage (Summer low flow, 1973)

	Flow	pH	Cond.	Sediment	Alkalinity	Calcium	Magnesium	Sodium	Potassium	Phosphorus	Nitrate	Sulfate
pH	.18											
Cond.	-.72	.12										
Sediment	.01	.03	-.08									
Alkalinity	-.61	.43	.85	-.03								
Calcium	-.29	.18	.23	.00	.34							
Magnesium	-.02	-.11	.01	.17	.11	-.10						
Sodium	-.61	-.05	.71	.05	.55	.15	-.21					
Potassium	-.06	-.16	.10	.11	.00	-.14	.00	.03				
Phosphorus	-.30	-.77	.08	-.08	-.13	-.12	.11	.14	-.17			
Nitrate	.24	.45	-.11	-.30	.03	.08	-.11	.03	-.43	-.28		
Sulfate	.48	.06	-.03	-.50	-.10	.09	-.17	-.06	-.50	-.33	-.33	
Chloride	-.46	.05	.60	.55	.41	.18	-.11	.66	.14	.05	-.37	-.39

Note: At n = 17, correlation coefficients having an absolute value $\geq .48$ are significant at 95 percent confidence level.

Table 20. Correlation of water quality parameters sampled at West Branch gage (Summer low flow, 1973)

Note: At n = 17, correlation coefficients having an absolute value $\geq .48$ are significant at 95 percent confidence level.

	Flow	pH	Cond.	Sediment	Alkalinity	Calcium	Magnesium	Sodium	Potassium	Phosphorus	Nitrate	Sulfate
pH	-.52											
Cond.	-.48	.82										
Sediment	.16	-.20	-.18									
Alkalinity	-.49	.76	.73	-.25								
Calcium	.01	.50	.61	-.23	.55							
Magnesium	-.13	.35	.58	.04	.30	.53						
Sodium	-.75	.40	.24	.01	.19	-.22	.01					
Potassium	.10	-.23	-.26	-.07	-.12	-.38	-.16	.19				
Phosphorus	-.02	-.28	-.34	.10	-.22	-.24	-.17	.07	-.16			
Nitrate	-.02	.17	.02	-.31	.13	.23	-.08	.02	-.04	.26		
Sulfate	.20	-.40	-.64	-.07	-.36	-.60	-.45	.09	.51	.19	-.06	
Chloride	.07	-.55	-.67	-.12	-.43	-.47	-.21	.01	.17	.53	.05	.47

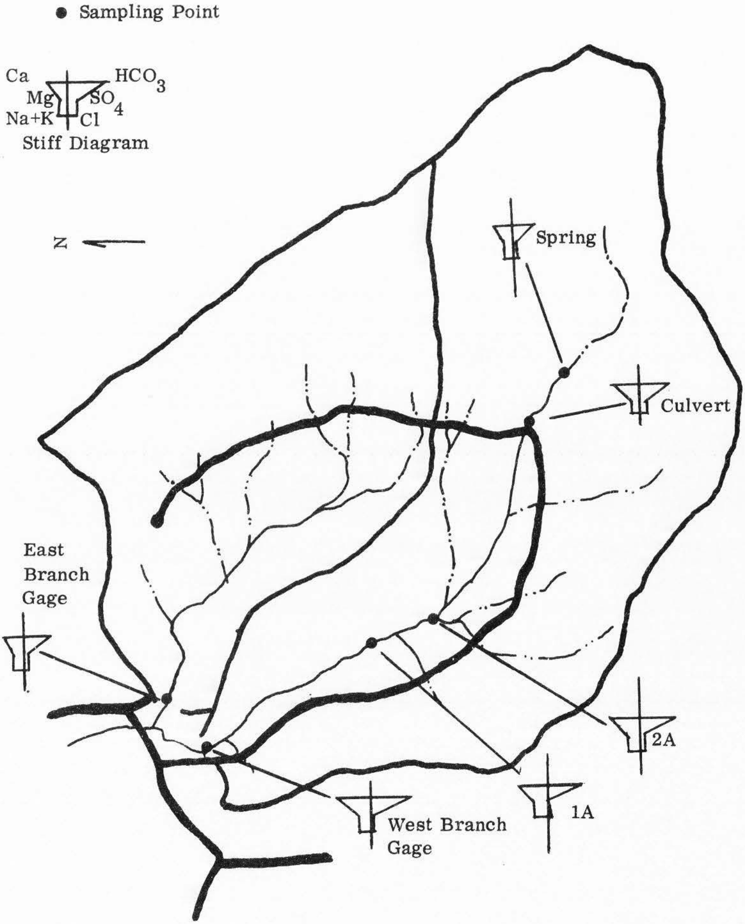


Figure 7. Relative ion concentrations within West Branch and at both gages (Summer 1973).

the major constituents. More detailed information concerning the chemistry is presented in Table 21.

As can be seen by the map, there was no attempt to evenly space the sampling sites. An examination of the average concentrations obtained at each site indicates that the changes that occur are not a function of length of channel. The changes seem more like a mapping of inflows. Throughout the length of the stream the flow is being augmented by groundwater--groundwater that is of varying chemical make-up.

Comparisons of tributaries. If the chemical changes that occurred over the length of the main channel were caused by inflow, of groundwater or tributaries, of varying quality; an investigation of the tributaries ought to reflect such variability. Table 22 resulted from such an investigation of West Branch tributaries. The concentrations displayed are averages of several samples taken from each of the tributaries over a period of weeks. The locations sampled are identified in Figure 8. Flow measurements were not taken at the tributary sampling point.

Comparing the tributaries, parameter by parameter, with the value obtained at the gage, the effluent concentration lies within the range of values measured at the tributaries. The concentration seen at the gage can, therefore, be explained as a mixture of the tributary inputs.

An incidental observation that can be made from this data is the close association of Na^+ and Cl^-. Their concentrations vary similarly from

Table 21. Comparisons of water chemistry over the length of West Branch (low flow averages, 1973)

	Spring	Culvert	2A	1A	Gage
pH	6.98	7.50	7.68	7.76	7.86
Cond. (μmhos)	108	141	153	155	167
HCO_3^- (mg/1)	50	63	74	77	85
Ca^{+2} (mg/1)	10.43	14.79	17.32	18.14	22.05
Mg^{+2} (mg/1)	3.10	3.97	5.21	4.84	4.89
Na^+ (mg/1)	6.24	7.14	7.73	7.24	7.03
K^+ (mg/1)	.64	1.04	1.04	.93	.93
Cl^- (mg/1)	4.72	5.55	5.97	5.88	5.21
SO_4^{-2} (mg/1)	5.72	5.81	5.29	5.56	4.70
NO_3^- (mg/1)	1.24	.40	.22	.27	.27
PO_4^{-x} (mg/1)	0.02	.03	.01	.01	.03

Note: Single line means significantly different at .95.
Double line means significantly different at .99.

Table 22. Comparisons of water chemistry between tributaries of West Branch (Spring 1973)

	Spring	Control	Cut 3	Cut 2	Cut 1	Gage
pH	$\underline{\underline{6.78}}$*	6.95	$\underline{7.03}$	7.50	$\underline{\underline{7.74}}$**	7.43
Cond. (μmhos)	$\underline{\underline{73.3}}$	$\underline{\underline{52.8}}$*	$\underline{\underline{86.3}}$	$\underline{\underline{168.0}}$	$\underline{\underline{363.0}}$**	148.0
HCO_3^-	$\underline{\underline{26.0}}$	$\underline{\underline{16.5}}$*	$\underline{\underline{38.7}}$	$\underline{\underline{96.5}}$	$\underline{\underline{213.5}}$**	76.9
Ca^{+2}	$\underline{\underline{7.58}}$	$\underline{\underline{6.00}}$*	$\underline{\underline{12.70}}$	$\underline{\underline{30.06}}$	$\underline{\underline{59.00}}$**	23.00
Mg^{+2}	$\underline{\underline{2.41}}$	$\underline{\underline{1.70}}$*	$\underline{\underline{2.82}}$	5.34	$\underline{\underline{9.27}}$**	4.90
Na^+	$\underline{\underline{4.87}}$**	$\underline{\underline{3.61}}$	4.39	$\underline{\underline{2.56}}$*	$\underline{\underline{2.65}}$	4.09
K^+	0.78	0.84	$\underline{1.06}$**	$\underline{.63}$	$\underline{\underline{.58}}$*	0.80
NO_3	$\underline{0.53}$**	$\underline{0.30}$	0.19	$\underline{0.06}$*	0.17	0.18
SO_4^{-2}	7.59	7.36	7.72**	$\underline{4.17}$	$\underline{\underline{4.09}}$*	6.73
Cl^-	$\underline{4.44}$**	$\underline{2.70}$	$\underline{\underline{2.89}}$	$\underline{\underline{1.71}}$*	$\underline{\underline{1.86}}$	3.39

*Minimum values.

**Maximum values.

Note: Tributaries were compared, parameter by parameter, with the water at the gage. If the tributary parameter is significantly different from the gage, it is underlined. One line = 95 percent significance. Two lines = 99 percent significance.

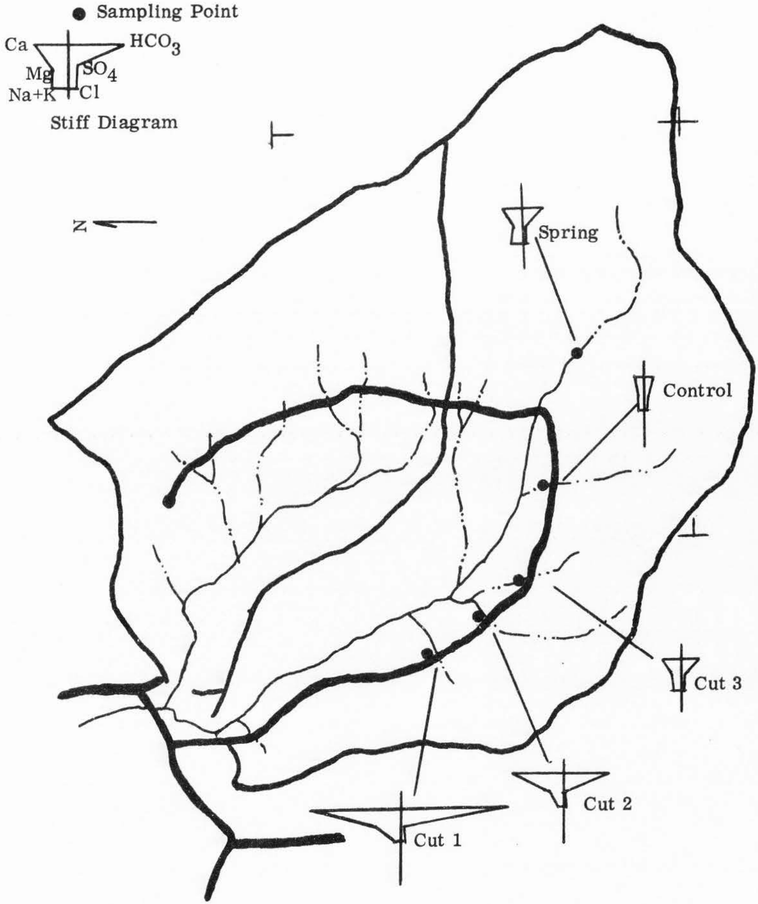


Figure 8. Variation of major ion concentrations between tributaries (Spring 1973).

tributary to tributary, indicating the probability that they are present in the form of NaCl.

The difference between the water flowing from Cut 1 and the other tributaries is worth noting. The essential difference appears to be in the Ca^{++} and Mg^{++} content (pH, conductivity, and alkalinity values simply reflect the Ca^{++} and Mg^{++}). Cut 2 shows the same tendency but to a lesser degree. An examination of the soil map for the watershed (Figure 9) shows a soil type change adjacent to the Cut 2 tributary. This means that the drainage area of Cut 2 is composed of both soil types, while Cut 1 is entirely within shale and siltstone soil type.

The sharp discontinuity in stream chemistry coinciding with just as sharp a discontinuity in soil type seems strong evidence of the basic control that the nature of the soil has over water quality. This is further investigated in the following sections.

Soil solution samples. Soil solution samples were obtained on four occasions during the summer, at six separate plots. Each plot consisted of four access tubes. The locations of the plots are indicated in Figure 10. The average values for each of the parameters analyzed are shown in Table 23.

The discontinuity of soil types mentioned in the analysis of tributaries is again evident in these soil solution results. Plot 1 displays the same markedly greater content of Ca^{++} and Mg^{++} (and their associated values for pH, conductivity, and alkalinity).

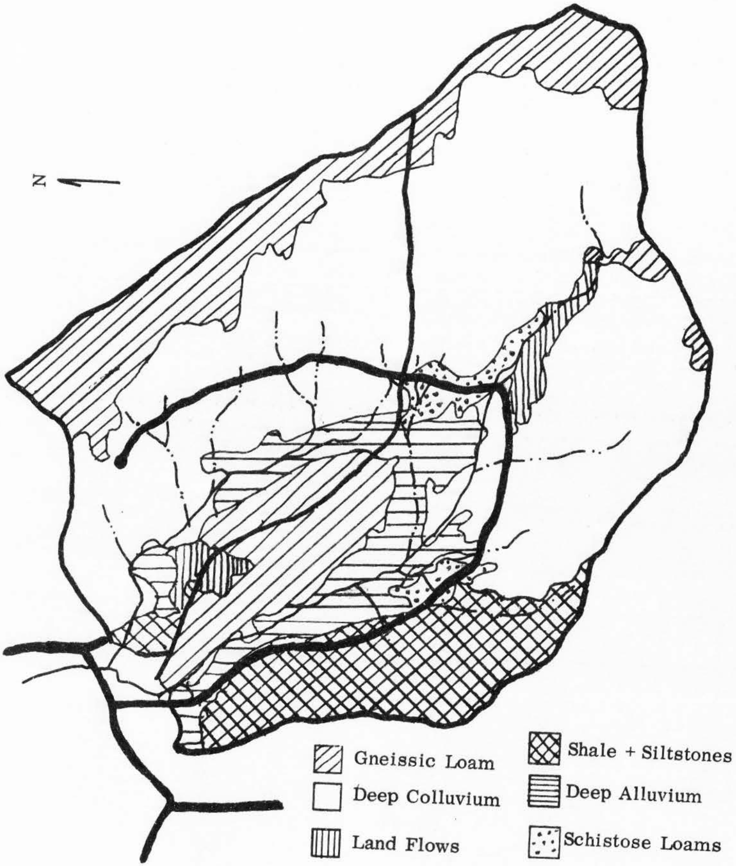


Figure 9. General soils map.

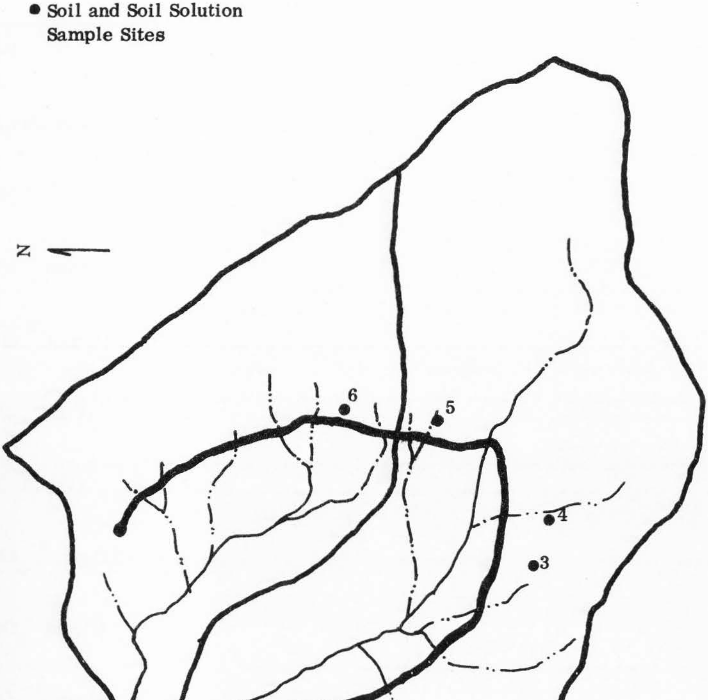


Figure 10. Soil chemistry sampling sites.

Table 23. Soil solution analyses (1973)

	Plot 1	Plot 2	Plot 3	Plot 4	Plot 5	Plot 6
pH	7.25**	6.70	5.47*	6.04	5.89	5.55
Cond. (μmhos)	285.7**	122.09	119.91	70.44*	86.70	144.25
HCO_3^- (mg/1)	147.32**	32.12	7.01*	11.93	9.76	10.44
Ca^{+2} (mg/1)	52.28**	18.69	8.81	7.48	7.04*	14.53
Mg^{+2} (mg/1)	7.09**	3.28	2.17	1.82*	1.94	2.27
Na^+ (mg/1)	2.91	2.73*	6.08	3.48	6.17**	4.98
K^+ (mg/1)	0.57*	0.78	0.83	3.32	0.65	3.65**
PO_4^{-x} (mg/1)	0.03	0.03	0.06	0.18**	0.00*	0.03
NO_3^- (mg/1)	0.35	0.13	0.09*	0.40	1.06	2.39**
SO_4^{-2} (mg/1)	4.80	5.20	8.40**	4.72	4.65	3.97*

Note: Not all samples were fully analyzed. This resulted in some missing data and, therefore, these averages are of 10-16 pieces of data. Too few samples of Cl^- were obtained to calculate meaningful averages.

*Minimum.

**Maximum.

Soil analyses. Chemical analyses were run on soil profiles obtained near each of the soil solution plots (Figure 10). Each profile was analyzed for the extractable fraction and the water soluble fraction of Ca^{++}, Mg^{++}, Na^{+}, and K^{+}. Two different summaries of the data obtained yield some insight into the chemical processes occurring.

The first summary (Table 24) simply displays the average concentrations measured at each site. A comparison of the water soluble averages, from one site to another, reveals the same trend observed earlier--soil profile 1, soil solution plot 1, and tributary "Cut 1" all contain markedly higher concentrations of Ca^{++}, than do the other sites or tributaries. The similar trend of Mg^{++} concentrations is not as clear-cut, but may be just as real.

As was pointed out earlier, the mapped change in water chemistry coincides with a mapped change in soil type. Is the water chemistry difference the result of a difference in the total amounts of Ca^{++} and Mg^{++} present, or is it that the one soil somehow makes the cations more readily available?

The soil profiles were also analyzed for total extractable fractions of each of the cations. This analysis more closely indicates the total quantities of the elements present, not just the water soluble fraction. Since the average concentrations obtained via this analysis fail to again indicate the marked uniqueness of profile 1, it seems likely that the basic mineral make-up of the soils is not that different. Therefore, the difference must be in the relative rates at which these soils make the cations available.

Table 24. Soil chemistry analyses

Plot	Ca^{++}	Mg^{++}	Na^{+}	K^{+}
		Water Soluble (meq/100 gr)		
1	0.21	0.05	0.025	0.030
2	0.08	0.03	0.024	0.029
3	0.14	0.03	0.024	0.028
4	0.10	0.03	0.020	0.029
5	0.13	0.05	0.023	0.041
6	0.10	0.03	0.027	0.029
		Extractable (meq/100 gr)		
1	17.67	1.90	0.53	0.22
2	15.16	1.99	0.64	0.23
3	16.06	2.87	0.71	0.24
4	14.62	2.58	0.89	0.25
5	15.43	3.05	0.78	0.24
6	13.97	2.11	0.99	0.26

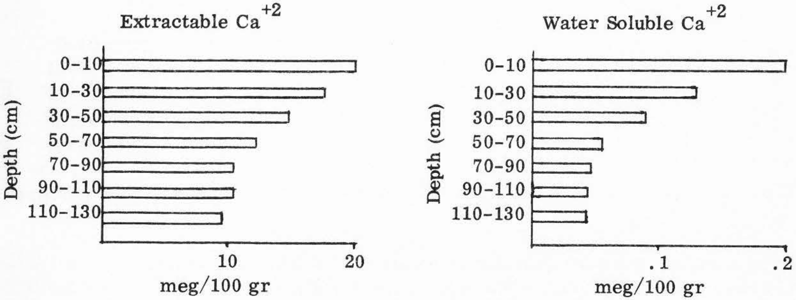
A difference in biological activity, or soil drainage characteristics might explain such a difference in cation availability. However, the vegetative cover found on all the soils is quite similar (aspen, grasses, and forbs), and all of the soils are described as "well drained" (Johnston and Doty, 1972).

There is a definite difference in texture between the two mapped soil types. The soil, typical of profiles 2 through 6, is described as Pachic Cryoboroll (coarse loamy mixed) with various horizons described as sandy loam, gravelly heavy sandy loam, cobbly sandy loam, and cobbly loamy sand (Johnston and Doty, 1972). The soil in which profile 1 is located, is described as Argic Cryoboroll (fine loamy mixed) with various horizons described as loam, clay loam, and sandy clay loam (Johnston and Doty, 1972).

The cation exchange capacity of a soil rests primarily in clay sized particles. Therefore, the measured textural differences between the soils seems a reasonable explanation for the observed differences in water chemistry.

The second type of summary of the soil chemistry data (Figures 11, 12, 13, and 14) illustrates the average vertical distribution of the cations within the soil profile. The vertical distribution of the cations might be the result of greater microbial activity or higher oxidation rates near the surface. Or, it may be the result of a nutrient pump action carried on by deep rooted higher forms of vegetation. The data did not allow testing of these theories.

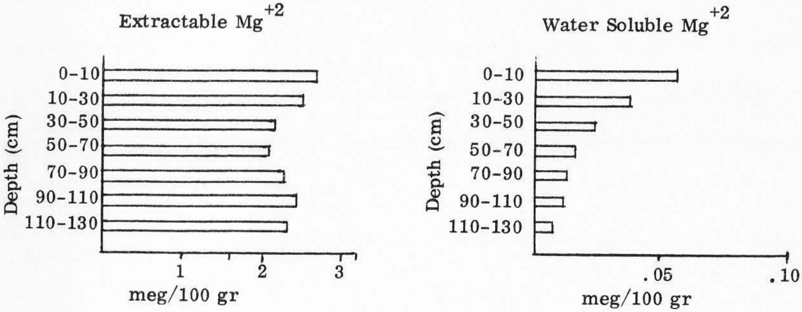
Regardless of how the distributions came about, the relative importance of the horizons near the surface, as cation sources is evident.



Extractable Ca^{+2}

Water Soluble Ca^{+2}

Figure 11. Calcium distribution in soil profile.



Extractable Mg^{+2}

Water Soluble Mg^{+2}

Figure 12. Magnesium distribution in soils profile

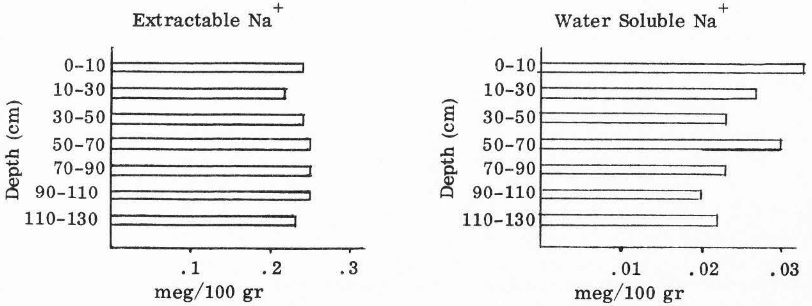


Figure 13. Sodium distribution in soil profile.

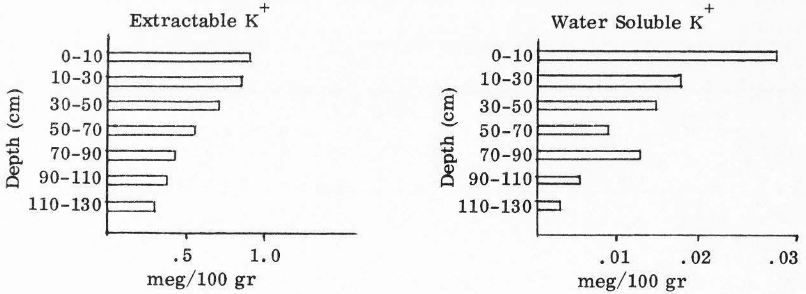


Figure 14. Potassium distribution in soil profile.

Changes of chemistry with time. One of the intentions of the scheme used in collecting the water quality samples was to be able to chart the fluctuations in quality through an entire annual cycle. The graphs that resulted from this effort are displayed in Figures 15 through 24. Many of the data analyses that have been previously described were first suggested by the observed seasonal fluctuations in one, or more, of the measured parameters.

Several approaches were also suggested for attempting to model these fluctuations, but for one reason or another they proved inadequate. The factors that might conceivably affect the quality of the water emanating from a watershed are numerous, variable, complex, and interactive. With the amount of water quality data available, and the even fewer measurements of the corresponding watershed dynamics, modeling efforts were frustrated.

The stream hydrograph (Figure 15) is an example of both a valuable observation and a picture that is too simple to serve many needs. It displays quite well the timing of streamflow fluctuations, how extreme the change in flow is during spring runoff, and allows a graphic comparison between the two drainages. However, because the hydrographs were developed from weekly data (corresponding to the weekly water quality data), the smaller fluctuations associated with summer thunderstorms were lost. These relatively minor flow fluctuations are suspected to account for many of the sharp changes in stream chemistry observed during the summer. However, the sampling routine did not allow the modelling or testing of the suspected process.

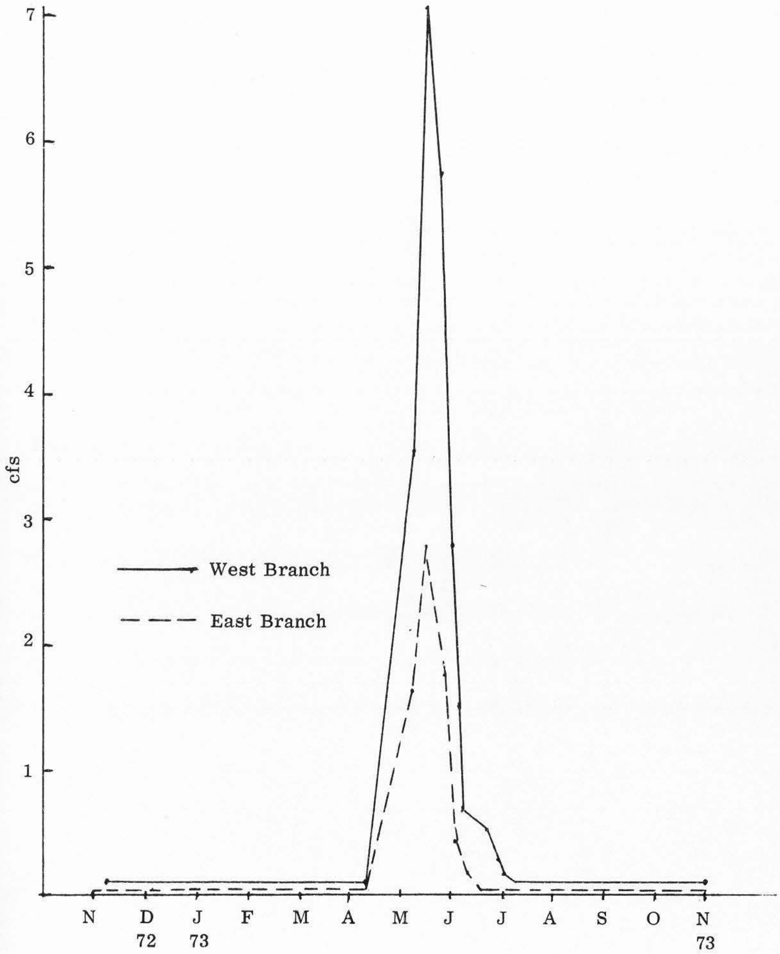


Figure 15. Annual hydrographs for branches of Chicken Creek (November 1972-November 1973).

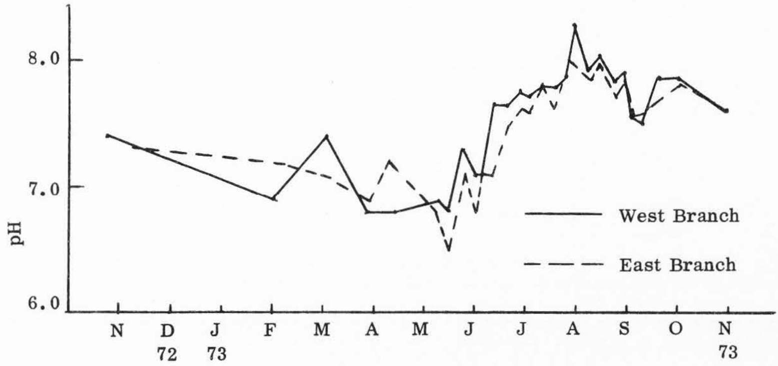


Figure 16. Annual pH cycles (November 1972-November 1973).

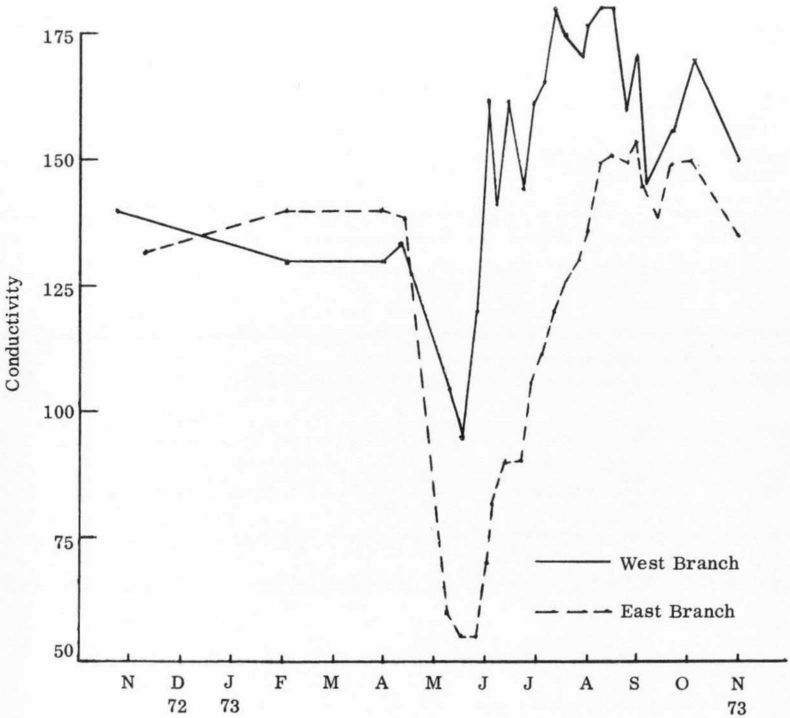


Figure 17. Annual cycle of conductivity (November 1972-November 1973).

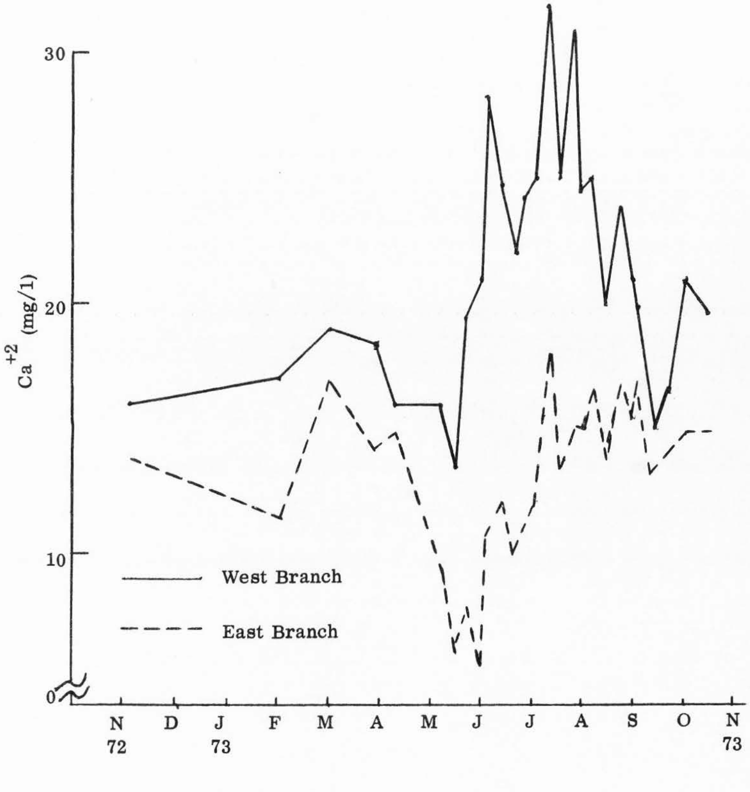


Figure 18. Annual cycle of calcium concentrations (November 1972-November 1973).

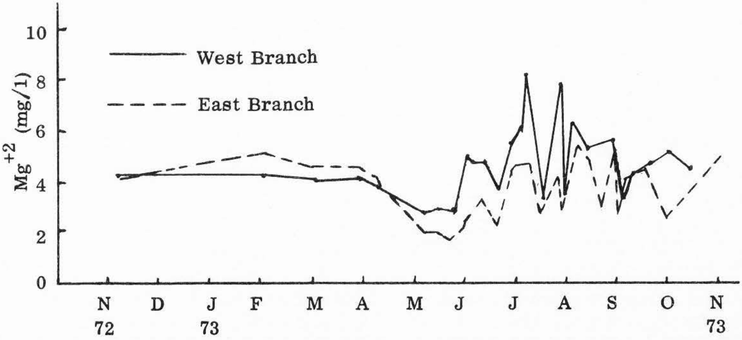


Figure 19. Annual cycle of magnesium concentration (November 1972-November 1973).

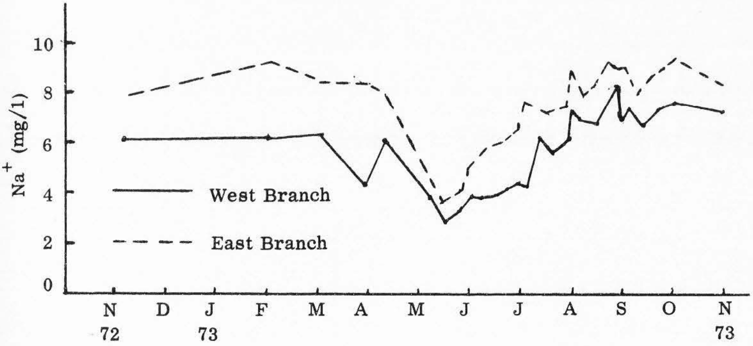


Figure 20. Annual cycle of sodium concentrations (November 1972-November 1973).

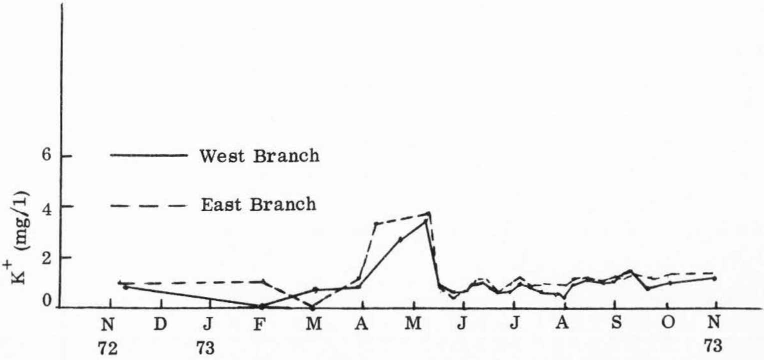


Figure 21. Annual cycle of potassium concentration (November 1972-(November 1973).

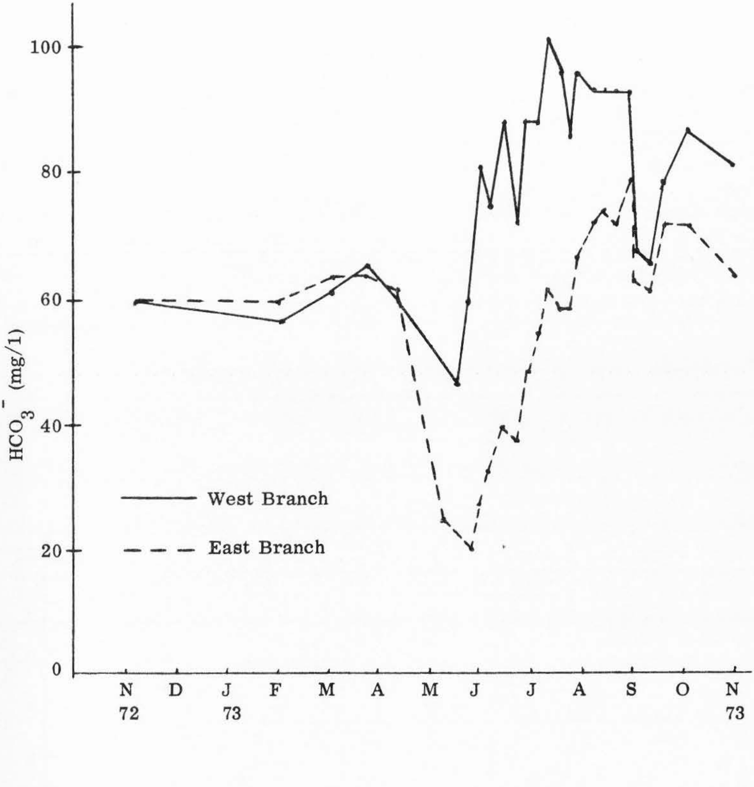


Figure 22. Annual cycle of bicarbonate concentration (November 1972-November 1973).

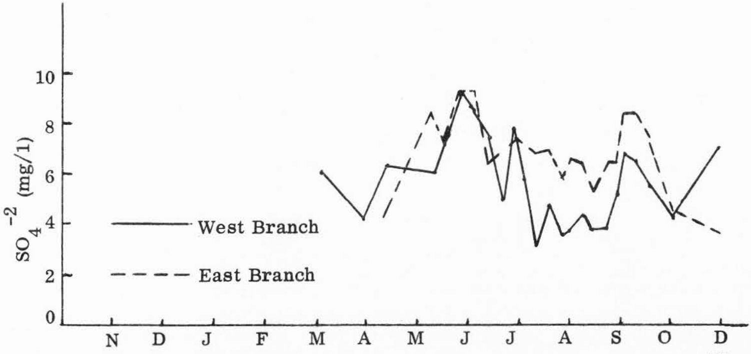


Figure 23. Annual cycle of sulfate concentration (November 1972-November 1973).

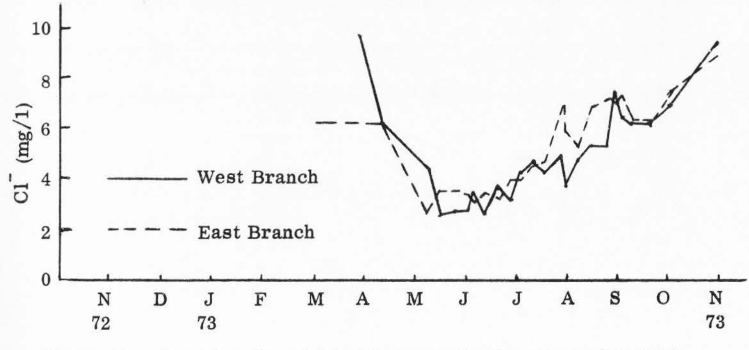


Figure 24. Annual cycle of chloride concentration (November 1972-November 1973).

A discussion similar to the above could be made of each of the annual charts, but it is sufficient to say that their value is the picture that they present of a naturally dynamic system.

Diurnal samples. The four dirunal cycles of sampling that were superimposed on the weekly sequence produced one insight into the chemical processes. The data were obtained as four separate 24 hour cycles, within which samples were taken 6 hours apart. There were differences among the data, but the only fluctuation that occurred consistently was stream temperature.

During the four diurnal cycles monitored, the temperature ranged an average of 7 C. The maximum fluctuation measured was 11.5 C. Comparing the daily fluctuations to the annual range of 18 C Figure 25 gives some perspective to the dynamics of stream temperature. Stream temperature varied, on a daily basis, 64 percent of the observed annual variation, and yet failed to produce any significant fluctuation in water chemistry. This observation seems to support the proposition made earlier that water temperature could safely be ignored in the search for explanations for variations in water chemistry.

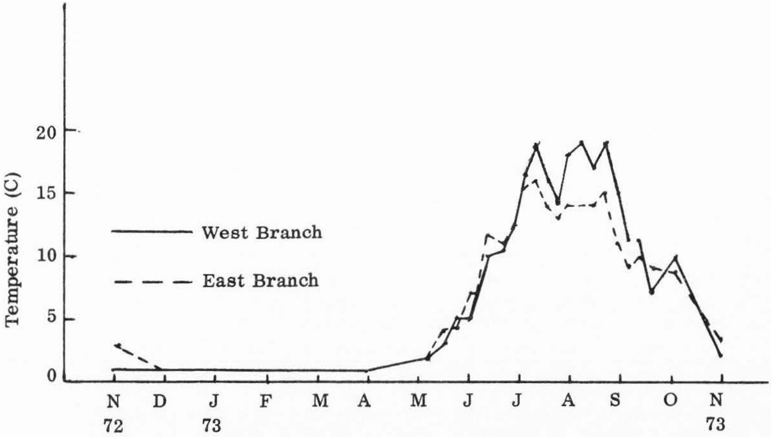


Figure 25. Annual cycle of instantaneous stream temperatures, measured at the time of chemical sampling (November 1972-November 1963).

SUMMARY, CONCLUSION, AND RECOMMENDATIONS

Summary

The purpose of this study was to quantify the chemical nature of the waters from the Chicken Creek watersheds, and to investigate the variability and causes of that observed chemistry. Three objectives were set:

1. To inventory the chemical quality of the water produced by the subject watersheds.
2. To determine chemical budgets for the watersheds.
3. To identify the sources of the primary chemical components.

To gather the necessary data, procedures were established for a series of surveys. The series included chemical surveys of: the stream exiting from each gaged watershed, various points within the West Branch drainage network, the atmospheric inputs to the watersheds (rain, snow, and dust), the soil solution, and the soil itself. The procedures also included measuring the volume and distribution of rain and snow entering the watersheds, and the volume and timing of the streamflow leaving.

The chemical surveys were accomplished by collecting grab samples, on schedules that varied with the subject of each individual survey. These samples were collected, transported, stored, and analyzed using accepted techniques. The snowfall was measured using a snow course (for water content) and a network of depth stakes (for total volume and distribution).

Rainfall was measured by three recording rain gages. Streamflow was measured by H-type flumes and automatic stage recorders.

The Chicken Creek waters are quite dilute, neutral to slightly alkaline solutions containing primarily calcium, magnesium, sodium, potassium, bicarbonate, sulfate, and chloride (nitrate and phosphate are also present at much lower concentrations). The dynamics of the solutions are controlled by the $CO_2/CO_3/HCO_3$ equilibrium system. Within the limits of these stated characteristics, the waters are extremely variable. The variability can be seen over time, and from location to location.

The annual chemical budgets indicate that the watersheds are suffering a net loss of all the chemical constituents, except nitrate and phosphate. Nitrate and phosphate are either accumulating on the watersheds, or are leaving the watersheds in some way other than streamflow. The West Branch watershed not only produces almost twice as much water per unit area, but the water is more chemically concentrated.

Snow versus rain, and storm-to-storm variations in precipitation chemistry were significant. Variation in rain chemistry from area to area also appeared significant, and nonrandom.

The soil appears to be the primary source of the observed water chemistry. Even though the basic mineral composition of the soils were similar throughout the watershed, the chemical productivity varied. The productivity seemed closely and positively related to the clay content of the soil.

Conclusion

The water flowing from the study watersheds are the result of the integration of many variable, complex, and superimposed processes. Limitations of the number of sampling points, of the frequency of sampling, of the length of the study period; and the insensitivity of the sampling to flow change make the findings of this study a first approximation. More thorough investigations may bring the functioning of the watershed into much sharper focus.

Recommendations

The observed variation in precipitation chemistry, both with season and with location, do not appear to be random. This variability is intriguing and seems worthy of further investigation.

Any future study of stream water quality should be designed to be flow sensitive. The variation of water chemistry with a storm hydrograph is a phenomenon that this study failed to document. Had the effects of summer storm flow been known, they might have changed the results of this study considerably.

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