KARST SOLUTION IN THE SOUTHERN CANADIAN ROCKIES

HYDROLOGY AND KARST SOLUTION
IN THE
SOUTHERN CANADIAN ROCKIES

By

JULIAN JOHN DRAKE, B.A., M.Sc.

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AUTHOR: Julian John Drake, B.A. (Oxford University)
M.Sc. (McMaster University)

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This study seeks to achieve an understanding of the factors which control the rate and nature of karst solution in the Alpine setting of the southern Canadian Rockies. Theoretical controls of the process are reviewed quantitatively in order to ascertain the effects which they can be expected to exert. The value of techniques of hydrochemical analysis which have been developed for use in other environments are examined from the point of view of karst hydrochemistry.

The process of karst solution in two large river basins (the Athabasca and the North Saskatchewan) is described with particular reference to the effects of the hydrological regime of the area and to the theoretical controls of the process. The findings are shown to be similar in kind to those which are presented for a number of small holokarstic basins within the same area. The hydrochemical behaviour

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of karst basins at both scales can be described in terms of the interaction of a small number of distinct hydrochemical environments in which the hydrodynamics of solution plays a determining role.

The implications of this conclusion with reference to the extent and distribution (both spatial and temporal) of karst solution within the southern Canadian Rockies are described. Karst solution is shown to be the most important single geomorphic process presently operating in the area. Improved estimates of the rate of this process are presented.

ACKNOWLEDGEMENTS

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DEDICATION

This dissertation is dedicated to the memory of Cameron D. Allen, a good friend and colleague who was tragically killed in the course of the research for his doctorate.

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CHAPTER I

INTRODUCTION

The study of small, local karst terrains in which the dominant geomorphic process is solution has been intensive. Especially in Europe numerous workers, exemplified by Corbel (1956, 1959), have concerned themselves with the detailed description of various karst morphologies and have provided semi-quantitative explanations of their genesis. The basics of the karst solution process, and in particular that of limestone, have been known for a considerable time. Tillmans (1932) and Frear and Johnston (1929) provided detailed measurements of the solubility of calcite in water containing carbon dioxide. Since that time the solution of calcite has become a well-documented process, and recently the more difficult problem of the solubility of magnesium-calcium carbonates has been substantially resolved. The relevant theoretical solubility products of most of the common karst minerals are now specified to an accuracy of 1%.

Unlike many other agents of geomorphic change, therefore, the main agent of karst landform development is known and is quantified. The thrust of karst research is now turning from the investigation of the manner in which the process acts upon the natural environment. Because the solution of a karst terrain is essentially a mass-transfer problem, much of the preliminary work along these lines has been contributed by a growing group of workers who are not karst geomorphologists. A petroleum geologist, Weyl (1958), introduced the basic concepts of the mass-transfer approach to the problem of sub-surface karst development and since that time two engineers, Curl (1968) and Wigley (1971b, c) have extended it. As is the case for the problem of the solubility of karst minerals the theoretical mass-transfer aspects of the interaction between water and the karst terrain are now known.

The facts that one known process is dominant in the evolution of a karst terrain and that the manner in which this process acts upon the terrain is known in a number of simplified situations (such as sheet-flow over and pipe-full flow through the rock) make the study of karst landforms one of the least imprecise in geomorphology. The processes acting to produce, for example, a specific hill-slope morphology are many, their interactions are complex and for the most part they are undefined and therefore cannot be quantified. In a similar manner the measurement of the rate of removal of the products of the solution process from a karst terrain is often easier and more accurate than corresponding measures of the erosion due to other processes. Also in contrast to other agents of geomorphic change there is very limited re-deposition or re-working of the eroded material produced by the solution process. Although in certain circumstances significant amounts of eroded material may be deposited in the form of travertine or tufa, in climates other than tropical and/or with non-hydrothermal waters, the re-deposition of karst materials is only a minor part of the overall process. Because the products of other agents of erosion are likely to be re-deposited within the terrain, floods or other catastrophic events often give rise to a sudden and large increase in the amount of material being moved within or removed from an area. In contrast the amount of solution attributable to rare events is limited, as evidenced by the relative conservatism of the amount of dissolved material carried from a basin by streamflows of various magnitudes. Douglas (1964) well illustrates the contrast.

The aim of most of the present hydrologic and geomorphic work in karst terrains is to integrate a known body of theoretical knowledge with hypothesized morphogenetic processes to determine the nature of the development of the present landscape, and to understand the observed relationships and patterns in the hydrologic and hydrochemical regimes of the terrain. The practical problems of applying theoretical considerations to the development of a karst terrain are several, but in broad terms they may be grouped into two sets: 1) the determination of the environmental controls of the process, and 2) the determination of the location of the major part of the solution within the terrain. The two sets are not, of course, independent. The environmental controls change as the water passes into and through a karst aquifer. In many areas the controls may also change seasonally. In Alpine or Arctic areas in particular the extreme seasonality of hydrologic events can be expected to be mirrored in a marked difference in the rate or nature of karst development.

Since the development of the theoretical analysis of the karst solution process, one of the tools of the karst geomorphologist has been the analysis of the hydrochemistry of water flowing from a karst basin or aquifer. Hydrochemical analysis in other contexts is in a relatively advanced state. Back (1960, 1961, 1966) has demonstrated that lithologic facies can give rise to hydrochemical facies in groundwater bodies, and several workers such as Hall (1970, 1971) have shown that the hydrochemistry of many streams may be viewed as the result of the mixing of a number of components. This approach has also been used to separate basin outflow hydrographs into their component parts such as groundwater discharge and surface runoff. There has long been an implied assumption in karst geomorphology that waters flowing in a number of situations within a karst terrain should exhibit different chemical characteristics. This is the basis for much of the work by Ashton (1966) who has attempted to define the nature of a karst aquifer by the analysis of the hydrochemical behaviour of its discharge during floods, and for various mechanisms proposed to explain the apparent reactivation of the solution process deep within the aquifer. The most discussed of these has been Bogli's (1964) concept of 'mischungskorrosion'. The assumption referred to above has recently received much support from Drake and Harmon (1973) and Harmon et al. (1972b) who have demonstrated that the hydrologic zonation of a karst aquifer system is paralleled by a hydrochemical zonation.

The essential elements for the hydrochemical analysis of the discharge from a karst aquifer or basin are therefore present in the form of characteristic zones. The southern Canadian Rockies are largely composed of carbonate materials and they form a large karst area. Small elements of this area have been studied by Ford and co-workers at McMaster University (Ford, 1971a, b; Ford et al., 1972; Brown, 1972a), and it has been suggested that the altitudinal zonation of vegetation gives rise to a number of characteristic karst hydrochemical environments. It is the purpose of this thesis to investigate the nature of the overall karst development of the southern Canadian Rockies utilising the methods and techniques developed for the hydrochemical analysis of streams fed by a number of chemically different components. The area also demonstrates a marked seasonality in its hydrologic regime and the relationships between this and the seasonal variation in the effects and controls of the karst solution process are also analysed. The observed characteristics of the runoff from the southern Canadian Rocky Mountains are related to the theoretical controls of the karst solution process and to the behaviour exhibited by the small, holokarstic areas previously studied by others.

This thesis is arranged into six main chapters. Chapters II and III review the major elements of the karst solution process and its environmental controls and of the techniques of hydrochemical analysis in both karst and non-karst areas. Chapter IV describes the pertinent features of the study area and of the study basins. Because one of the most important features in the determination of the nature of karst landform development is the hydrologic regime of the area, Chapter V provides an analysis of the hydrologic regime of basins in the southern Canadian Rockies. Chapter VI describes the use of the techniques reviewed in Chapter III in the analysis of the seasonal behaviour of the hydrochemistry of the Athabasca and North Saskatchewan River basins which together drain 8000 sq mi of the area. Chapter VII combines the results of the analyses in the two previous chapters and relates the karst solution process exhibited in the area at the small scale to characteristics shown by the small basins that have been described by previous workers. Chapter VII also draws the conclusions resulting from the preceding chapters.

CHAPTER II

KARST SOLUTION

2.1 Introduction

The most commonly occurring minerals which are susceptible to solution, and in which solution is likely to be the dominant geomorphic process, are limestone, dolomite, gypsum and anhydrite and halite. The carbonate minerals are by far the most widespread but the sulphate minerals are important in some areas of North America such as west Texas and east Nova Scotia. Examples of the extensive development of karst features in chloride rocks are uncommon because of the limited surficial distribution of these rocks. The general process of solution of all of the karst minerals is, however, the same. In the following sections the nature of this process and of the controls upon it are described. The general principles of the solution process in naturally occurring rocks are dealt with by many texts such as Garrels and Christ (1965) and Krauskopf (1967). Because karst landforms develop most frequently in carbonate rocks the carbonate solution process has received the most attention, and most of the specific examples of the manner in which environmental controls may affect the karst solution process are drawn from studies of carbonate karst areas.

The solution of gypsum or anhydrite and of halite (in water) is a two-phase ionic dissociation:

$$CaSO_4 \rightleftharpoons Ca^{2+} + SO_4^{2-} \qquad (2.1.1a)$$

$$NaCl \rightleftharpoons Na^+ + Cl^- \qquad (2.1.1b)$$

Although the solution of limestone (and dolomite) may be represented in the same way, as

$$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-} \qquad (2.1.2)$$

the process is complicated by the instability of the CO_3^{2-} ion in the range of pH encountered in most natural waters in karst areas. Because the Cl^- and SO_4^{2-} ions are stable in the natural situation the solution of gypsum or anhydrite and of halite is completely described by equations 2.1.1. The stable form of the carbonate species in water with a pH of between 7 and 9 is the bicarbonate ion, HCO_3^-, which then accounts for over 80% of the total dissolved carbonate species (see, e.g., Krauskopf 1967, Figure 2-2). The solution of these carbonate minerals in water can be represented by two reactions:

$$H_2O \rightleftharpoons H^+ + OH^- \qquad (2.1.3a)$$

and $$CaCO_3 + H^+ \rightleftharpoons Ca^{2+} + HCO_3^- \qquad (2.1.3b)$$

Any acid present in water in the natural environment will dissociate to produce H^+ ions. Because these ions associate with the CO_3^{2-} ions produced by the dissociation of the carbonate mineral, the carbonate solution process is pH dependent. The most commonly occurring acid present in the natural environment where no substances are introduced by pollution or other extraneous factors is carbonic acid. All water in contact with the atmosphere reacts with carbon dioxide:

$$H_2O + CO_2 \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \qquad (2.1.4)$$

The carbonate solution process may be represented as the sum of two subsystems - the production of carbonic acid and its reaction with the mineral:

$$H_2O + CO_2 \rightleftharpoons H^+ + HCO_3^- \qquad (2.1.5a)$$

$$CaCO_3 + H^+ \rightleftharpoons Ca^{2+} + HCO_3^- \qquad (2.1.5b)$$

or, summing,

$$CaCO_3 + H_2O + CO_2 \rightleftharpoons Ca^{2+} + 2HCO_3^- \qquad (2.1.6)$$

The basic solution reactions of the most common karst minerals are thus represented by equations 2.1.1 and 2.1.5.

2.2 Geochemical Measures of Mineral Saturation

The chemical characteristics of water in a karst setting may be expressed in terms of the concentrations of the various ions in solution. A more useful measure in many cases is, however, the extent to which the water is saturated with respect to the minerals in the terrain. This approach can indicate the conditions under which the water entered and reacted with the terrain or aquifer, and whether any further solution can take place.

Chemical reactions may be described by the Law of Mass Action. Thus, if

$$aA + bB \rightleftharpoons cC + dD \qquad (2.2.1)$$

where lower case letters indicate the combining numbers of the substances represented by capitals, then at equilibrium

$$\frac{[C]^c\ [D]^d}{[A]^a\ [B]^b} = K \qquad (2.2.2)$$

where [ ] represents the activity of the enclosed species. K is known as the equilibrium constant of the reaction given in equation 2.2.1, or in the case of the simple ionic dissociations represented by equations 2.1.1 and 2.1.5 it is termed the solubility product. The equilibrium expressed by equation 2.2.2 is the thermodynamic equilibrium and arises when the two reactions of equation 2.2.1 (that is, one reaction from left to right and another from right to left) are occurring at the same rate. In this situation there is evidently no further net production of either the substances A and B or of the substances C and D. Although both reactions are continuing, and individual molecules of any of the substances may be recombined, the reaction as a whole is in a state of dynamic equilibrium and the equilibrium concentrations of each of the substances is constant. It is this constancy of the concentrations of the component substances of the solution reactions of karst minerals that makes the consideration of the thermodynamic equilibrium state important and useful.

If the activities of the substances involved in a particular reaction are known, an ion-activity product (K_{iap}) can be calculated from equation 2.2.2. In general this value will not be the same as the equilibrium constant. Only if the reaction is in the thermodynamic equilibrium state will the two values be equal. If $K_{iap} < K$ the reactions of equation 2.2.1 will proceed in sum to the right; if

$K_{iap} > K$, to the left. The solution of gypsum, described by equation 2.1.1a provides an example of the use of this principle in the study of karst waters. The ion-activity product may be calculated from measured values of $[Ca^{2+}]$ and $[SO_4^{2-}]$ by

$$K_{iap} = \frac{[Ca^{2+}][SO_4^{2-}]}{[CaSO_4} \qquad (2.2.3)$$

or, because the activity of a solid or of an undissociated substance is by definition unity,

$$K_{iap} = [Ca^{2+}][SO_4^{2-}] \qquad (2.2.4)$$

If this value for K_{iap} is less than the known value of K for the reaction (the solubility product of gypsum) the reactions of equations 2.1.1a will in sum proceed to the right and more gypsum will be dissolved in the system until thermodynamic equilibrium is established. Conversely, if the calculated value of K_{iap} is greater than K, then the reactions will proceed in sum to the left and gypsum will be formed. A comparison between K_{iap} and K in the case of the mineral solution in a karst terrain can thus give an indication of whether further solution, precipitation or neither is likely to occur.

The accuracy of any such measure of the equilibrium state of the solution reaction of a karst mineral depends ultimately on the accuracy with which K can be determined, but there are also several complicating factors in the determination of K_{iap}. The most significant of these are, firstly, the necessity to consider the relationship between the activities of the relevant species and their (measured) concentrations and, secondly, to account for all significant ion-pairing in the system. Recently, many workers have detailed the essential steps in deriving an estimate of the saturation state of karst solutions (e.g. Garrels and Christ, 1964; Picknett, 1964; Drake, 1970; Langmuir, 1971; Wigley, 1971a). Details of the computational scheme used in this study are shown in Appendix 1. Since the solution of carbonates is greatly enhanced by the presence of carbon dioxide in the solution, the procedure to derive an estimate of the saturation state is not a single step. For karst areas where the only readily soluble minerals occurring in significant amounts are calcite, dolomite and gypsum (or anhydrite), the advent of the computer has enabled the calculation of 'saturation indices' from field measurements of pH, Ca^{2+}, Mg^{2+}, HCO_3^- (or alkalinity), SO_4^{2-} and temperature:

for gypsum $SI_g = \log \{([Ca^{2+}][SO_4^{2-}])/Kg\}$ (2.2.5)

for calcite $SI_c = \log \{([Ca^{2+}][HCO_3^-]K_2/[H^+])/K_s\}$ (2.2.6)

and for dolomite $SI_d = \log \{([Ca^{2+}][Mg^{2+}][HCO_3^-]^2K_2^2/[H^+]^2)/K_d\}$ (2.2.7)

where K_g, K_2, K_s, K_d are the theoretical dissociation constants for gypsum, H_2CO_3, calcite and dolomite respectively. Similar measures may be defined for any other mineral.

There has been doubt as to the true meaning of a saturation index with respect to a given, pure mineral. Some workers, notably Stenner (1969, 1971), have advocated a different technique in which a fine powder of the host rock is added to a water sample and changes in a parameter (such as the concentration of Ca^{2+}) noted. Whilst this procedure can produce a numerical value for the additional amount of mineral dissolved in or precipitated from the solution it seems to be less desirable than the thermodynamic saturation index approach for four main reasons:

1) the reaction can take an extended period of time to reach a new equilibrium, during which time characteristics of the water sample (e.g. temperature) may change,

2) the particular sample of host rock used may be no more representative of the whole than is a pure mineral,

3) the determination cannot be repeated, whereas saturation indices may be recomputed from field measurements,

and

4) the resulting measure is not universal, whereas a thermodynamic measure may be reproduced from field data by any other worker.

Although the thermodynamic saturation indices are preferable, there remains some problem in assessing the value of an index with respect to, for example, calcite, when most natural environments do not exhibit a single, pure mineral phase. There is evidence (e.g. Terjesen et al., 1961) that heavy metals such as copper present in the system in trace amounts can significantly reduce the solubility of calcite. Plummer (1972) reports that calcite containing some magnesium is more soluble than pure calcite or dolomite, a conclusion also demonstrated qualitatively by Picknett (1972).

Notwithstanding these observations, evidence that the theoretical solubilities do in fact constitute real limits to the solution of limestones, dolomites and gypsum in the natural environment is accumulating. Langmuir (1971), Drake and Harmon (1973) and Wigley et al. (1973) have used the technique with considerable success, and it is also commonly used in the high ionic strength environment of ocean waters (e.g. Li et al., 1969). One of the criteria for a satisfactory saturation index is that it should not show oversaturation in a stable environment. Although waters saturated with respect to calcite in a high P_{CO2} environment may become oversaturated when removed to a lower P_{CO2} environment, water in equilibrium with its surroundings cannot be. Plummer (1972) considers that an oversaturation of 2^x is necessary in the case of calcite to overcome the energy barrier to precipitation presented by the nucleation potential. In this case, then, equilibriated waters should never exhibit $SI_c > 0.30$. In stable environments it seems that this is in fact a reasonable upper limit to the observed values (see, e.g., data presented in Langmuir, 1971; Back et al., 1964).

The accuracy and precision of the derived saturation indices are dependent upon the accuracy and precision of the contributing measurements. As shown in Appendix 2, a conservative estimate of the accuracy of SI_c is ± 0.10. A similar accuracy is reasonable for SI_d. A precision of 0.02 is again a conservative estimate based upon the claimed precision of many field pH meters. SI_g is potentially more accurate since the error-prone pH measurement does not enter into the calculation.

2.3 Environmental Controls of Solution

The solution system for limestones and dolomites is different from that for gypsum in that it is three- rather than two-phase. The addition of the extra (gaseous) phase adds further controls to the system, and complicates the basic mechanisms. The potential controls may be divided into two groups:

1) those which influence the chemical reaction itself, such as temperature and, for the carbonate system, the availability of CO_2,

and 2) those which influence the intermixing of the solute and solvent, such as the type of fluid flow, the geometry of the interface and, for the carbonate system, whether the system is open or closed.

The various controls are not independent. For example, the ambient temperature influences the availability of CO to the system, as well as itself being a controlling factor. Moreover, no control has a unique influence - any change in the equilibrium state of the solution system can be produced by changes in any or all of the various determining factors. It is important to separate intra- and inter-environment variations in solution. For two separate environments the most significant differentiating factors may well not be those which influence seasonal or other temporal variation within each environment. Whereas the controls are common to both situations, their relative importance is not necessarily the same.

2.3.1 Temperature

The temperature of any dissolution influences not only the rate of the reaction, but also the final equilibrium state. In general, the solubility constant, K, is temperature dependent. For a solid - liquid system the dependence is positive such that more of the solute may be dissolved with an increase in temperature, while for a gas - liquid system the reverse is true. Langmuir (1971) and Wigley (1972) quote temperature-dependent forms for K_c, K_d, K_2, and K_g from which the variation in solubility of these minerals with temperature may be computed. Figure 2.1 illustrates the theoretical temperature dependence of the equilibrium Ca^{2+} concentrations of the gypsum - water and calcite - water systems, using the values for the dissociation constants given by Wigley (1972). It is apparent that the solubility of gypsum increases with temperature (within the range considered) whilst that of calcite decreases. For the case of calcite (or dolomite) solution the magnitude of the temperature dependence of the carbon dioxide - water subsystem represented by equation 2.1.5a is greater than that of the H_2CO_3 - calcite subsystem represented by equation 2.1.5b, resulting in an overall negative Ca^{2+} - temperature relationship. This fact has been noted by many workers including Tillmans (1932), whose calculations of carbonate equilibria presaged much of the early European karst research, including that of Trombe (1952). Corbel (1959) considered that this temperature dependence was the single most important control on the rate of limestone solution in different environments:

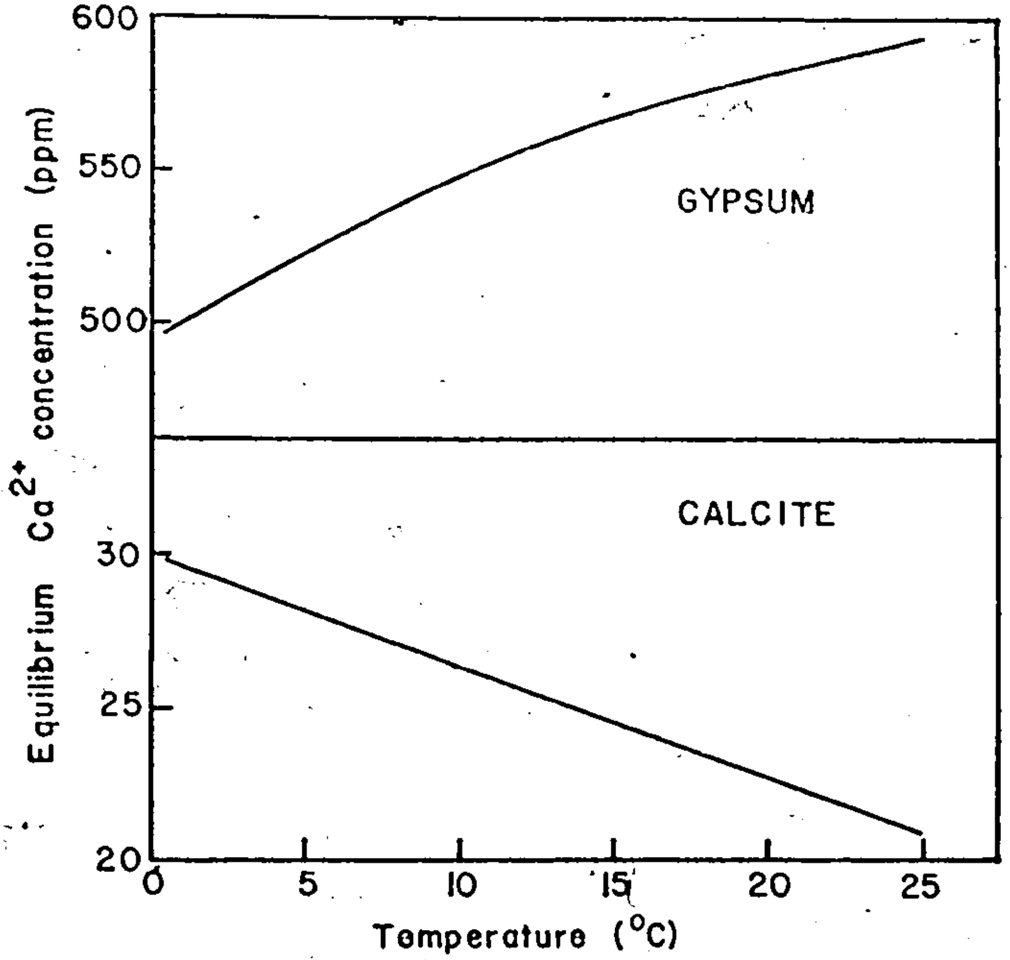


Figure 2.1

Temperature dependence of the solubility of calcite and gypsum

> "On peut donc conclure que, dans son ensemble, la karstification en région froide est plus rapide que la karstification en région chaude." (p. 118)

In a given environment, however, the range of temperatures encountered during the year is often much less than would be required to explain the variation observed in the solute concentrations, a fact apparent in the data presented by Paterson (1972). In a number of studies it has been observed that the solubility of carbonates in different environments is apparently a positive, rather than a negative, function of temperature (Pitty, 1966; Kotarba, 1972; Pulina, 1972; Harmon et al., 1972a). It is evident that temperature is not the overriding factor that Corbel considered it to be.

2.3.2 Carbon Dioxide Partial Pressure

Figure 2.2 shows the average Ca^{2+} concentrations of spring waters in several different environments, together with the temperature dependent equilibrium values for different partial pressures of CO_2. As the ambient temperature of the various environments increases, so does the partial pressure of CO_2 with which the water is in equilibrium. This trend is most evident in comparisons between environments in different climatic regions, but it is also apparent within a given environment as the annual march of temperature progresses. Ford (1971a) illustrates the seasonal change in the equilibrium P_{CO_2} of waters in the vicinity of Crowsnest Lake, Alberta. He suggests that the controlling factor in the availability of CO_2 is not temperature per se, but rather the vegetal cover associated with a particular temperature regime. A control by

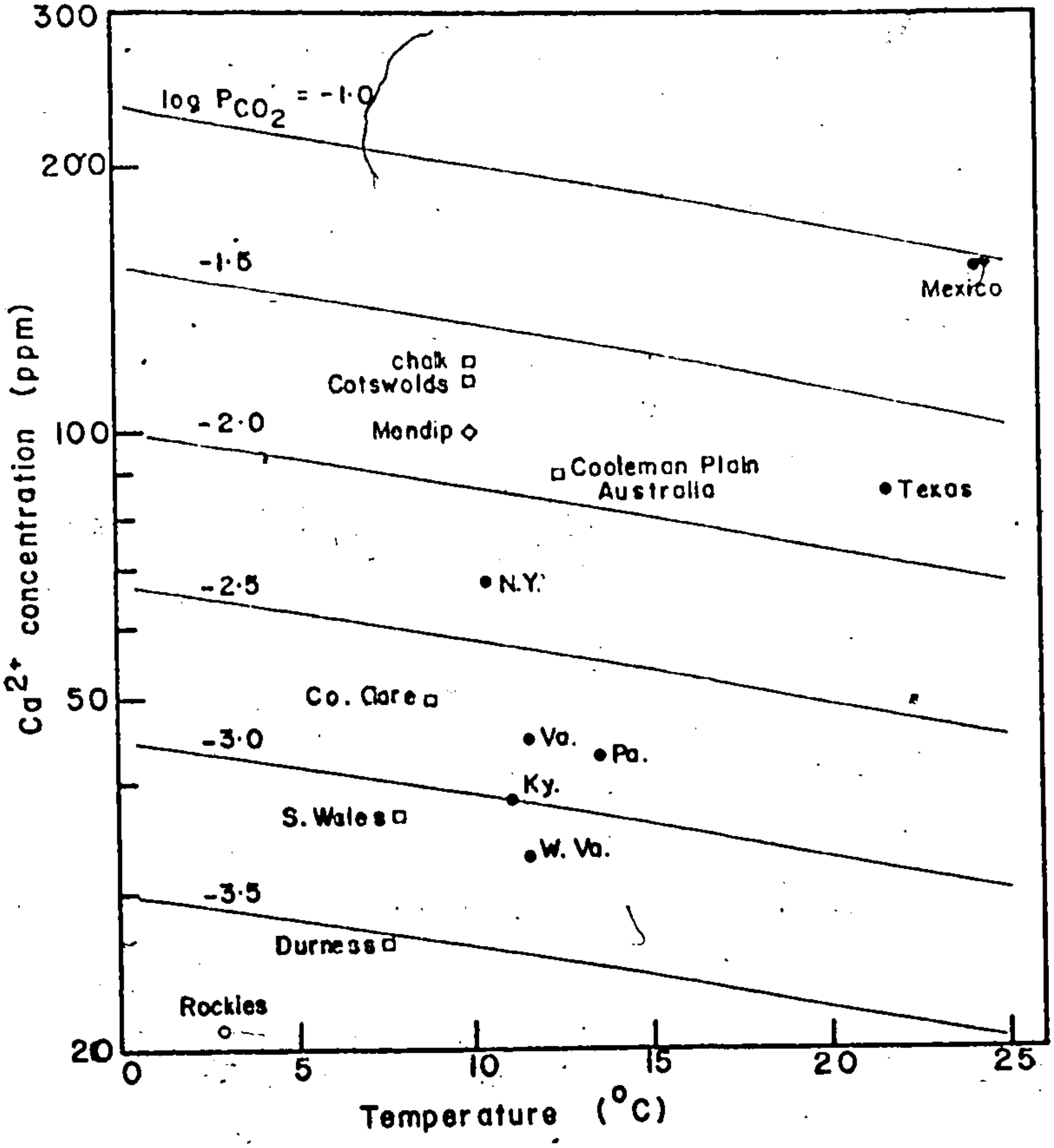


Figure 2.2

Theoretical and observed temperature dependence of calcite solution in different environments. Data sources Ford, 1966 (◇); Ford, 1972 (○); Harmon et al., 1972 (●); Sweeting, 1964 (□).

vegetally produced CO_2 is similarly suggested by several other authors such as Ek (1964) and Sweeting (1966). Measured values of the CO_2 concentrations of soil air in various environments support this view (Smith and Mead, 1962; Pitty, 1966). Data from the Canadian Rockies (D.C. Ford, McMaster University and F.D. Miotke, Technical University of Hannover, pers. comm.) are shown in Figure 2.3, together with water sample data from Ford (1971a,b). Improved estimates of the equilibrium P_{CO_2}, recomputed using Wigley's (1972) program, are used here. The figure demonstrates that in general the concentration of CO_2 in the soil air decreases with altitude and strongly suggests that the causative factor is the altitudinal change in vegetation from forest to tundra. Also, the CO_2 concentration of the atmosphere measured at various altitudes is very close to the figure of 0.03% atm. (or $10^{-3.52}$ atm.) usually given as the global mean atmospheric value. Allowance for the decrease of atmospheric pressure with altitude is according to tables given by List (1968). The values shown for the CO_2 concentration of the atmosphere within the snowpack are considerably less than those for samples of the open air at the same sites. The water samples from the same altitude show that the range of P_{CO_2} with which water can be in equilibrium in the area spans the range found in snow and open air. Cogley (1972) suggests that, in the Arctic snowpack, CO_2 concentrations decrease with time. Ford et al. (1970) note that delicate calcite precipitates formed beneath the margins of glaciers in the Mt. Castleguard, Alberta, area show little sign of resolution by meltwater from snow accumulation during

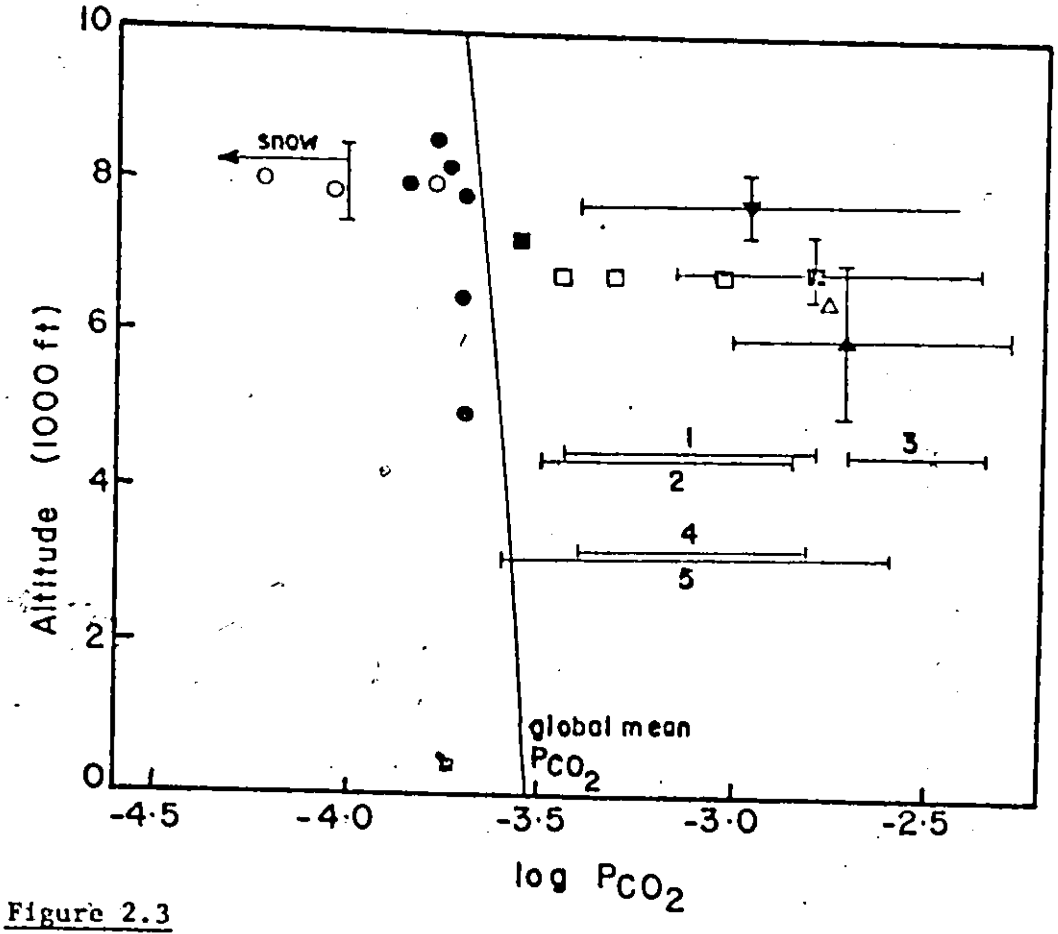


Figure 2.3

Altitudinal dependence of P_{CO_2} in air and water samples. Symbols indicate mean and bars indicate range.

- ● open air
- ▼ soil air in tundra
- ■ soil air in alpine meadows
- ▲ soil air in forest

- ○ water above treeline
- □ water in alpine meadows
- △ water in forest

1. Crowsnest Creek
2. Crowsnest River
3. Old Man River Rising
4. Athabasca River
5. North Saskatchewan River

the winter. The very low P_{CO_2} values shown in Figure 2.3 for air in snow suggest that in a snowmelt environment, solution is likely to be extremely limited. The survival of the precipitates is thus not unexpected.

The equilibrium CO_2 partial pressures calculated from data given by Ford (1971a) for the waters of Crowsnest Creek and Crowsnest River show that the range is from the value found in forest soils to one slightly above the atmospheric mean. This suggests that at various times during July, 1969, these streams were fed by different amounts of soil- and runoff-water. This corresponds to the hydrologic conditions at the time - in the early part of the month, much water was contributed to the streams by runoff from heavy rains which fell during the previous week, whilst at the end of July the streamflow was almost entirely derived from ground- and soil-water storage. Old Man River Rising (O.M.R.R.) is a large karst spring which exhibits an almost constant temperature of 42°F, and has a much more constant discharge than either of the surface streams. Figure 2.3 shows that during the period of observation the CO_2 partial pressure remained within the range given for forest soils. Surface waters might also be expected to show a lower P_{CO_2} value than springs in most instances since water in contact with the atmosphere will tend to de-gas CO_2 until equilibrium with the atmosphere is attained. This point is also clearly demonstrated by Drake and Harmon (1973).

The peculiarities of the carbonate solution process are such that the type of conditions under which the reaction takes place are pertinent. Garrels and Christ (1965) define five cases of carbonate equilibria, two of which are applicable to a natural environment in which the only geochemical controls are those of the process itself. These are cases 2 and 5 - "calcium carbonate - water, with externally fixed pressure of CO_2" and "equilibrium in a system of water originally open to atmospheric CO_2, then closed before the addition of $CaCO_3$" respectively. Smith and Mead (1962) considered the same point using the terms 'equilibrium' and 'anaerobic' solution. The process of carbonate solution in contact with a (theoretically) infinite reservoir of air with a fixed P_{CO_2} dissolves further CO_2 as that in the water is combined into HCO_3^- ions. This absorption of CO_2 continues until equilibrium is reached. If, however, there is no (or only a very limited) atmospheric reservoir, then the P_{CO_2} of the water will decrease as solution progresses, resulting in less solution than in the former case. Langmuir (1971) shows the two paths to equilibrium taken by the two cases for various initial P_{CO_2} values. His Figure 4 is reproduced as Figure 2.4. It can be seen that for $P_{CO_2} = 10^{-2}$ atm the difference in equilibrium HCO_3^- concentrations is approximately 150 ppm. There is, however, evidence which suggests that the equilibrium system in most environments is open. In order to achieve final equilibrium concentrations of $Ca^{2+} > 60$ ppm, P_{CO_2} values of more than 0.24% ($10^{-2.6}$) atm are required in the open system case, whilst the closed system equilibrium requires the P_{CO_2} to be more than 3.0% ($10^{-1.5}$) atm. Figure 2.3 shows that $10^{-2.6}$ atm (ten times that of the global mean atmosphere) is a reasonable approximation to the mean values measured in forest and alpine meadow soils, whilst $10^{-1.5}$ atm was not reached by any soil air sample.

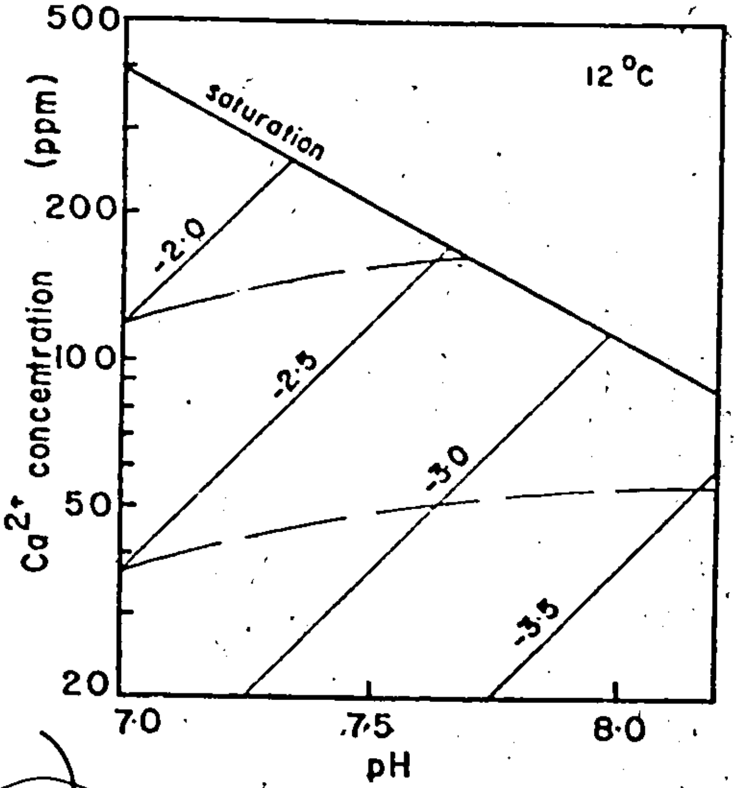


Figure 2.4

Approaches to calcite saturation in open (——) and closed (- -) systems.

Ford (1971a) quotes the Ca^{2+} concentrations of groundwaters in the Crowsnest Pass area as being of the order of 60 ppm. Langmuir (1971) similarly concludes that the groundwaters in central Pennsylvania originate under open system conditions, and Harmon (1973) makes the same claim on the basis of a study of stable carbon isotopes. That the source of the CO_2 in karst waters in excess of that in the atmosphere is indeed of vegetal origin is strongly supported by Harmon et al. (1973), who demonstrate that aquatic plants consume biogenic CO_2 during the daylight (photosynthetic) period. Holland et al. (1964) reached the same conclusion.

2.3.3 Geologic Controls

Many aspects of the geology of karst rocks are liable to influence the rate or extent of the solution process. Structure is one of the main determining factors in the secondary permeability of a karst aquifer, and thus exerts considerable control via the hydrologic nature of groundwater flow. This action is considered in a later section. The physical and chemical properties of the rock itself are also potentially important controls. Sweeting (1966), considering the morphology of limestone pavements in N.W. England, writes:

> "Lithological variations are probably the most important cause of contrast between one pavement and another." (p. 187)

She contends that the relevant property is the nature and spacing of the bedding planes, which controls the relative importance of mechanical and solutional erosion. She also found that undissected pavements are a feature of limestones with a high silica content. Sweeting (Oxford University, pers. comm.) has suggested that the differences in the bedding of the various limestones are closely correlated with their petrological character - sparry limestones forming the more massive and biomicrites the much less massive units. A further feature enhancing the solution of the micritic limestones is their greater porosity. Williams (1963) demonstrates that the rate of solution of the sparry limestones of Co. Clare, Ireland, is less than that of the micritic forms of Yorkshire, England, despite all other factors being in favour of more rapid solution in the former area.

In a comprehensive study of the lithologic controls on cavern development in central Pennsylvania, Rauch and White (1970) conclude:

> "Cavity development is enhanced by purity of the bulk rock, small grain size (micrite), and possibly by silty streaks.
>
> Cave development is inhibited by high concentrations of SiO_2, Al_2O_3, dolomite, sparite, and impurities, or by very low dolomite concentrations." (p. 1191)

Their conclusion with respect to the petrologic type of limestone is the same as Sweeting's. They suggest that the inhibiting effect of SiO_2 and Al_2O_3 is due to the fact that these minerals comprise much of the clay found in the carbonate rocks, and that the clay may have a shielding effect on the carbonates. Such shielding effects have been suggested by many karst geomorphologists for the case in which clay particles protect the bed of subterranean streams from continued solution. Rauch and White's comment on the importance of dolimite is interesting in the light of Plummer's (1972) work. Plummer states that the solubility of magnesian calcites reaches a maximum at 24 mole percent magnesium, whilst Rauch and White show that the development of solutional voids appears to reach a maximum in rock with a bulk content of 2% - 5% $MgCO_3$. Both Plummer and Langmuir (1971) consider that dolomite is less soluble than calcite. Figure 2.5 illustrates the variation in solubility and void formation in carbonates as a function of the Mg^{2+} content. Rauch and White suggest that a "partial reason" for the lesser solubility of rock with very low Mg^{2+} content may be that proportionately many such units occur in argillaceous formations. Plummer, however, shows that the petrographic composition of shell fragments is highly variable, and that the most soluble magnesian calcites particles dissolve first, followed by progressively less soluble Mg-calcite particles. In view of the fact that this deduction is based upon microprobe analysis at a far larger scale than the gross chemical analyses performed by Rauch and White, it is possible that the formation of solution voids depends not so much on the overall amount of Mg^{2+} present, as on the manner in which it is combined into Mg-calcite.

The effect of trace metals on the solution of $CaCO_3$ is demonstrated by Terjesen et al. (1961). Figure 2.6 illustrates their findings. It can be seen that a concentration of Ca^{2+} of 10^{-4} M/l, or of Sc of 10^{-5} M/l, is sufficient to reduce calcite solubility by a factor of two. Unfortunately, all experiments were performed under a P_{CO_2} of 1 atm, and so are not immediately applicable to the natural case. Terjesen et al. give the

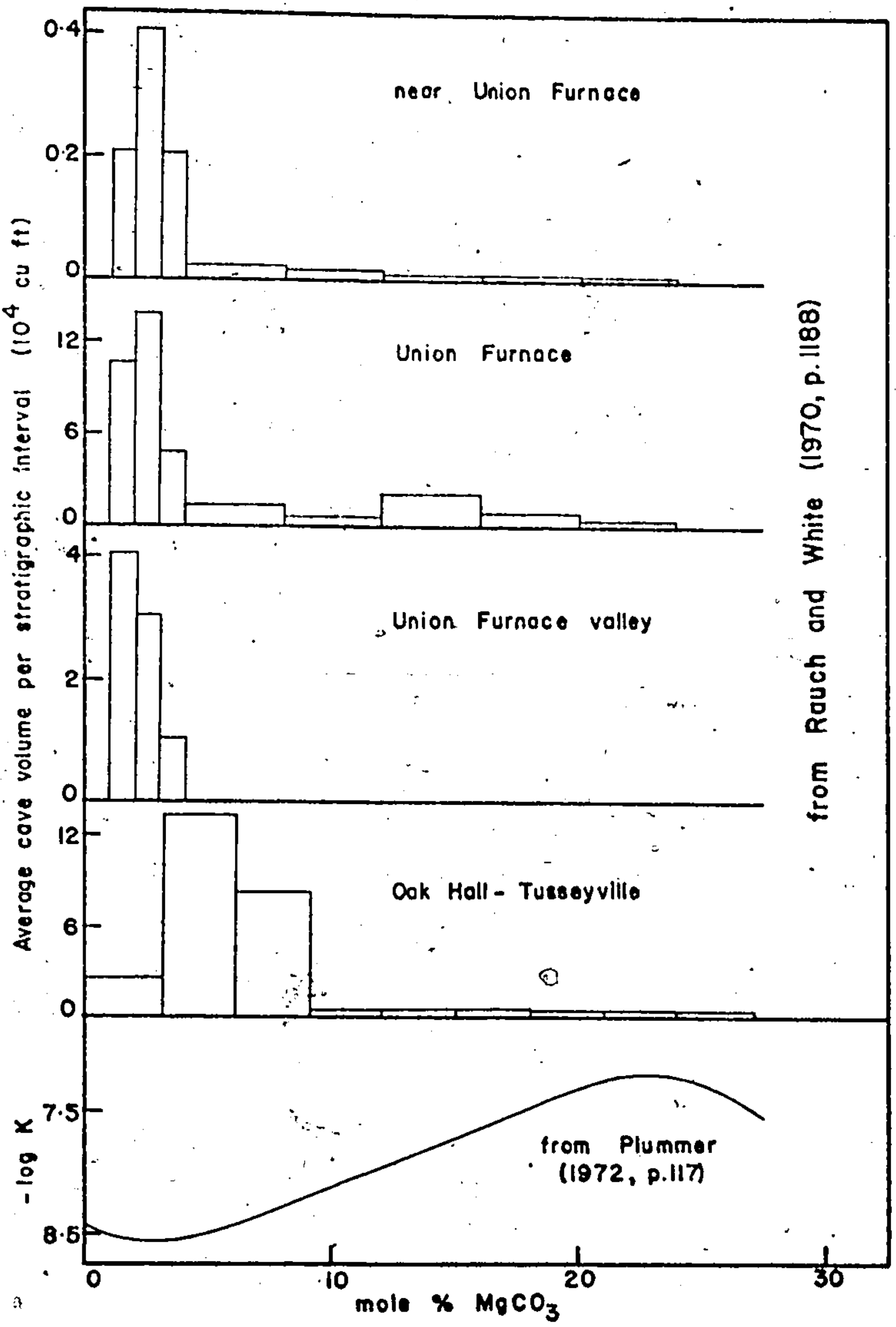


Figure 2.5

Variation in solubility and cave density for various magnesian calcites

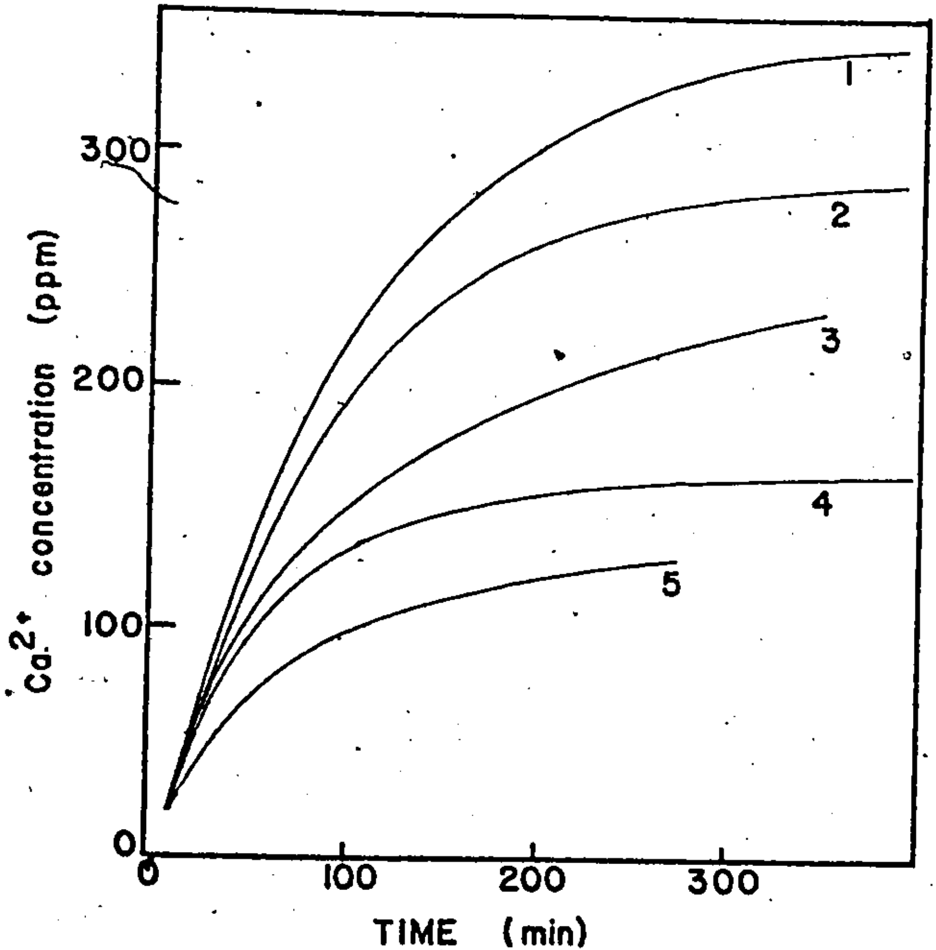


Figure 2.6

Effects of trace metals on calcite solubility under P_{CO_2} = 1 atm. After Terjesen et al. (1961, Fig. 2, p. 281).

	Inhibitors	Concentration (M/l)
1.	None	
2.	Sc	10^{-6}
3.	Cu	10^{-4}
4.	Sc	10^{-5}
5.	Cu	10^{-3}

order of importance of other inhibitors, in decreasing order of effectiveness, as: Pb^{2+}, La^{3+}, Y^{3+}, Sc^{3+}, Cd^{2+}, Cu^{2+}, Au^{3+}, Zn^{2+}, Ge^{4+}, Mn^{2+}, Ni^{2+} = Ba^{2+} = Mg^{2+} = Co^{2+}. They consider that the nature of the inhibition is not the presence of a monomolecular layer at the calcite surface, but rather that the metal carbonates serve to increase the rate of the reverse calcite solution reaction. They also note that the inhibiting effect becomes more pronounced as equilibrium is reached, as evidenced by Figure 2.6, in which the curves do not become distinct until a concentration of Ca^{2+} of 60 ppm is exceeded. This fact tends to suggest that in the very dilute solutions present in a natural carbonate aquifer the effect may be unimportant. Holland et al. (1964) considered the Sr^{2+} : Ca^{2+} ratio in a karst aquifer in Pennsylvania and could detect no inhibitory effect. Whilst Terjesen et al. do not list Sr^{2+} as an inhibitor its position in the periodic table suggests that it would have a similar effect as Ba^{2+} and Mg^{2+}. It seems therefore, that at the present time the possible inhibitory effect of trace metals (with the exception of Mg^{2+}) may be ignored in the natural environment.

2.3.4 Hydrodynamic Controls

The mass-transfer problem of the solution of a solid-fluid interface by a moving fluid has received detailed consideration by Levich (1962). The specific case of the solution of a karst mineral by water flowing through it has been investigated by Weyl (1958), Curl (1968, 1971), Wigley (1971b,c) and Plummer (1972). The rate of solution of a solid may be limited by either the rate of the chemical reaction at the interface, or by the rate of the physical process of the diffusion and/or convection of reactants or products across the laminar boundary layer into the main body of the fluid. In some cases the rate of solution may be limited by a combination of these factors. Both potential rate limiting processes are temperature dependent and the relative importance of each in a specific reaction may change with temperature. Plummer (1972) states that the incongruent solution reactions of some naturally occurring minerals may result in the formation of a porous precipitate on the reaction surface which serves to decrease the rate of diffusion of reactants across the laminar boundary layer. This effect would make the rate of reaction a relatively more important factor in the determination of the rate of solution of the mineral. It is not certain that the rate limiting factor in the solution of the walls of calcite tubes is the diffusion of reactants toward and away from the interface, but Plummer (1972) presents data that support this hypothesis. In the case of the solution of calcite by water the limiting diffusion rate is that of the products of the reaction (Weyl, 1958). Plummer (1972) shows that if the diffusion rate is the rate limiting factor in the calcite solution reaction, then the concentration of the products of that reaction at the interface is the saturation concentration. If, however, the rate limiting factor is the rate of the reaction itself then the concentration of the products at the interface is some lesser value. This approach allows the effects of the motion of the fluid past the interface on the rate of solution to be analysed by the same method whichever the rate limiting factor may be. The difference between the two cases is expressed in the value assigned to the concentration of the reaction products at the solid-liquid interface.

Goodchild (1968) demonstrates the effect of fluid motion in a study of the evolution of erosional scallops, and Coward (1971) measured greater erosion on the upstream side of such features where the fluid velocity is greater and the boundary layer thinner. Plummer (1972) shows that if the diffusion of products into a stationary fluid is the limiting step then the water in pore spaces less than 1 cm in width should be saturated whilst that in spaces wider than 10 cm would take longer than 100 days to reach equilibrium. Evidently in order to account for water in small interstitial spaces being undersaturated (as reported by Back and Hanshaw, 1970) or for water in large voids being saturated after only a very short residence time it is necessary to consider the hydrodynamic effects of the fluid flow.

The type of fluid flow is of great significance since it determines the concentration gradient within the body of the fluid. Kaye (1957) observed experimentally that the rate of solution of the walls of tubes in marble blocks by dilute HCl in a turbulent flow situation is dependent upon the mean fluid velocity through the tubes. His data show an excellent fit to the relationship

$$\frac{\partial a}{\partial t} = 0.2\bar{v}^{0.45} \qquad (2.3.1)$$

where a = tube radius (cm) and $\bar{v}$ = mean velocity (cm/sec). Weyl (1958) provided a detailed theoretical consideration of the effects of flow velocity in narrow conduits such that the flow regime was laminar. Wigley (1971b) derived a theoretical value for the relaxation length of the perturbation of any fluid property under turbulent flow through pipes of constant radius, and later extended the analysis to the laminar condition (Wigley, 1971c). For the case where the initial perturbation of the fluid flow is a deviation from saturation with respect to the pipe material, Wigley shows that the penetration length, defined by Weyl (1958) as the distance at which the deviation of the mean concentration from the equilibrium value has been reduced to 0.1 of its initial value, is a function of the fluid velocity and pipe radius. He quotes the rate of solution of the pipe walls as

$$\frac{\partial a}{\partial t} = \frac{(q_a - q_o)\, a\bar{v}}{2\rho_c x_o} \qquad (2.3.2)$$

where q_a = solute concentration at the pipe wall (the saturation value), q_o = solute concentration of the fluid entering the pipe, a = pipe radius (cm), v = mean fluid velocity (cm/sec), ρ_c = density of pipe material and x_o = relaxation length (cm), given by

$$x_o = \frac{a^2 \bar{v}}{3.658D} \qquad (2.3.3)$$

for laminar flow, or

$$x_o = \frac{2^{0.087} \mu^{0.567} a^{1.087} \bar{v}^{0.087}}{0.0192\ D^{0.654}} \qquad (2.3.4)$$

for turbulent flow, where μ = fluid viscosity (poise) and D = diffusivity of the solute species (sec/cm). Weyl's (1958) analysis of the laminar flow case is shown by Wigley (1971c) to yield a very similar result:

$$x_o = \frac{a^2 \bar{v}}{4.026D} \qquad (2.3.5)$$

2.3.3 and 2.3.4 substituted into 2.3.2 give expressions for the rate of solution as a function of fluid velocity:

$$\frac{\partial a}{\partial t} = \frac{(q_a - q_o)}{\rho_c\, a} \cdot 1.829D \qquad (2.3.6)$$

for laminar flow, and

$$\frac{\partial a}{\partial t} = \frac{0.01\ (q_a - q_o)\ D^{0.654}\ \bar{v}^{0.913}}{\rho_c\ a^{0.087}\ \mu^{0.567}} \qquad (2.3.7)$$

for turbulent flow. It is apparent from these last two equations that in the laminar flow case the rate of solution is independent of flow velocity, whilst in the turbulent flow case it is almost independent of pipe radius.

In the case of a diffusion rate limited solution reaction Levich (1962) is of the opinion that the rate of solution of tube walls by a fluid in turbulent flow is proportional to the fluid velocity to some power between 0.5 and 0.9. He suggests that the determining factor in the exponent is the extent to which the turbulent boundary layer is developed within the fluid. Kaye's (1959) experiment was performed in short lengths of marble wherein the establishment of the turbulent boundary layer may well have been incomplete. Levich (1962) considers that the establishment is not complete within a length of pipe equal to one hundred times its diameter. The exponent of 0.45 which characterises Kaye's experiment is thus in keeping with Levich's suggestions, as is Wigley's (1971c) exponent of 0.913 which was derived from the theoretical analysis of the fully developed turbulent flow situation.

Examples of the determining nature of the hydrodynamic conditions of flow through a carbonate aquifer are, in general, not at the same scale as the theoretical considerations detailed above. Pitty (1966) demonstrated that a relationship between flow-through time and the calcium hardness for waters in Derbyshire, England, existed and in a later paper (Pitty, 1968a) derived the expression

$$C = 152 + 0.667T \qquad (2.3.8)$$

where C = calcium hardness in ppm, and T = flow-through time in days for an area in Yorkshire, England. In an investigation into the formation of domepits in Kentucky, Brucker et al. (1972) suggest that the increase in erosion by water running down the walls of domepits consequent upon a transition of the flow regime from super-critical laminar to sub-critical laminar over irregularities in the walls is responsible for removing the irregularities. A great increase in the rate of erosion at the flow transition (sometimes incorrectly termed the 'hydraulic jump') has also been suggested and explained by Wigley (1971c), Curl (1971), Palmer (1971) and Thrailkill (1968) amongst others.

The hydrodynamic controls affect mainly the rate of solution of, and the rate of saturation of, the water within an aquifer. Except for the case where a stream flows through an aquifer rapidly, water leaving a carbonate aquifer is usually saturated. In this situation the hydrodynamic controls cannot affect the total amount of solution. The rapid flowthrough case does, however, allow for such controls as has been documented in the Canadian Rockies by Ford (1971a,b) for two large springs.

2.4 Spatial Location of Solution

In general it is the environmental factors (particularly the temperature and P_{CO_2} of the water and the geologic nature of the aquifer) that affect the extent of solution in a given situation. The hydrodynamic factors affect the general location of that solution within the aquifer. The effects of the solution kinetics of the aquifer material are also potentially important in determining the location of solution. Investigations by Weyl (1958), Curl (1968), Roques (1969) and Plummer (1972) have, as shown in section 2.3.4, demonstrated that it is the diffusion of species across the solvent - solute interface that is the rate determining factor in solution. Since the hydrodynamic factors determine the rate of this diffusion they are capable of controlling the location of most solution. In areas in the Canadian Arctic that are virtually devoid of soil, Cogley (1972) suggests that the solution of limestone by small streams issuing from snow bodies is substantially completed within the first 100 m of the stream course. Data from the Mt. Castleguard area of the Canadian Rocky Mountains shows that a small snowmelt stream is very nearly saturated after traversing only 100 ft of bare limestone.

In both the laminar flow (Weyl, 1958) and the turbulent flow (Wigley, 1971b) situations the water approaches saturation at an exponentially decreasing rate. Some 90% of the solution per unit volume of water is thus concentrated within two relaxation lengths of the process. Figure 2.7 shows the relaxation lengths for both the laminar and turbulent flow regimes as a function of pipe radius and fluid velocity. The concentration of solution near the point at which water enters (or impinges upon) the aquifer (or rock surface) is consequent upon the small relaxation lengths associated with low velocities and small conduits or sheet flow. Figure 2.7 shows that the relaxation length for the laminar pipe flow case is less than 1 m for flow velocities of less than approximately .3 cm/sec in pipes of radius 0.1 cm. Any water that enters small conduits in the surface of a carbonate aquifer, or which percolates through the pores of a carbonate soil or till, becomes saturated within a few centi-

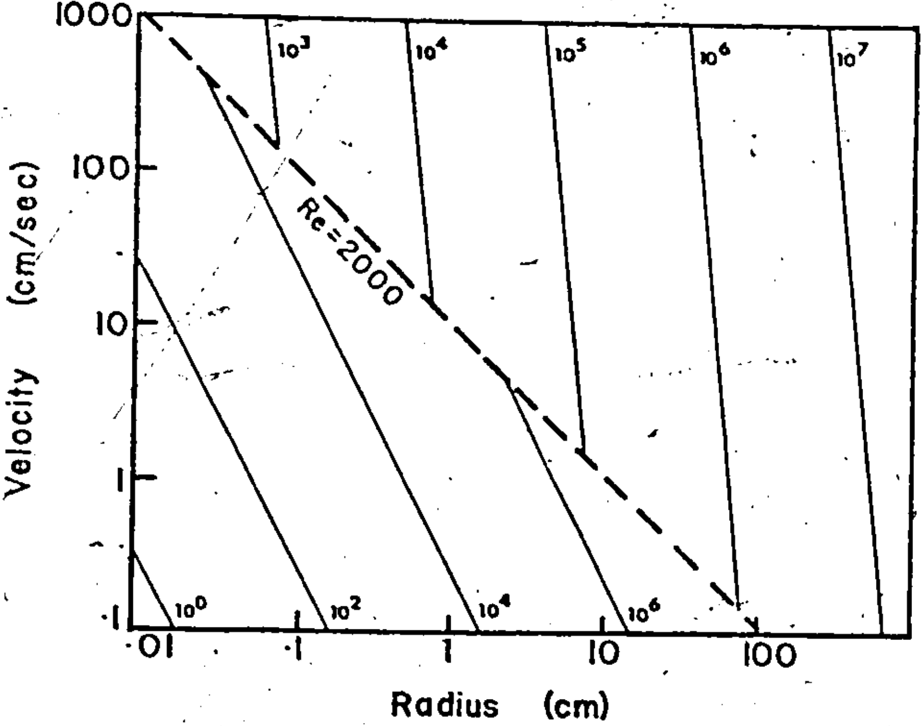


Figure 2.7

Relaxation length (cm) of the calcite solution process under conditions of laminar (Re < 2000) and turbulent (Re > 2000) pipe flow.

metres of the point at which it first encounters carbonate minerals. This fact is responsible for many observed features such as the de-calcification of calcareous tills reported by Williams (1970) in Ireland, and the many varieties of covered karren described by Quinlan (1973).

The presence of large voids in the subsurface testifies to continued solution at depth in many carbonate aquifers. Bögli (1964) invoked his concept of 'mischungskorrosion' in an attempt to explain these voids by the passage of presumably saturated water. Figure 2.8 shows the under-saturation (in ppm Ca^{2+}) resulting from the mixing of two bodies of water saturated with respect to calcite, one in equilibrium with the P_{CO_2} of the atmosphere (0.03% atm) and the other in equilibrium with a different P_{CO_2}. The most dramatic undersaturation occurs when the mixing ratio is between 0.1 and 1.0, but exceeds 10 ppm Ca^{2+} only when the P_{CO_2} of the added water is more than 0.5% atm. The implication of this figure is that 'mischungskorrosion' has the greatest effect near the surface of the aquifer where soil water and surface runoff waters mix in nearly equal volumes. At depth the mixing ratio is very small (the most common situation is the interception of small fractures carrying soil waters by a large conduit conveying surface runoff water). In large conduits of this type the water is likely to be undersaturated in any event because of the exceedingly large relaxation lengths shown in Figure 2.7 for the turbulent flow case in pipes of radius greater than 1 m. An increment of 1 ppm in the Ca^{2+} concentration of a stream discharging 1 cfs results in the

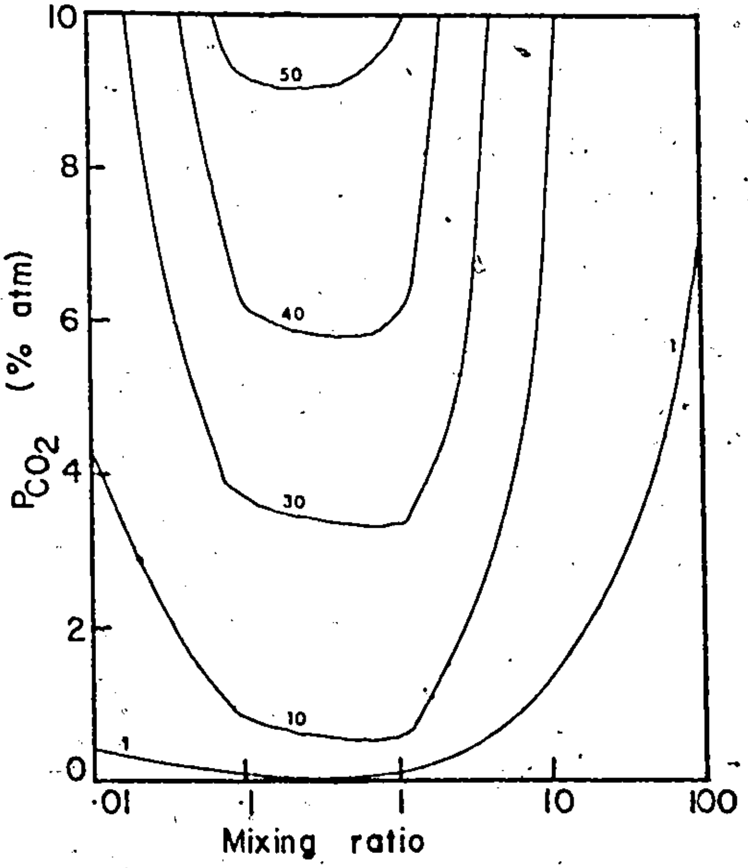


Figure 2.8

Ca^{2+} increment (ppm) due to 'mischungskorrosion' resulting from the mixing of 1 volume of saturated water with P_{CO_2} - $10^{-3.5}$ atm with a saturated water of shown volume and P_{CO_2}.

annual solution of 31.5 cu ft of limestone. It is evident that whilst detailed processes such as 'mischungskorrosion' or changes in the turbulent structure of a stream in response to an obstacle may be necessary to explain the exact morphology of a conduit, the existence of these features can be adequately explained by the fact that even a very small increase in the solute concentration of water flowing through them results in the removal of large quantities of rock from a localised area. These small increases are to be expected in large conduits because of the great relaxation lengths associated with the solution process in this situation.

The formation of large conduits requires that solution be concentrated spatially. Coward (1972) measured an erosion rate of approximately 1000 mm/1000 yr in an underground streamway in West Virginia. The increase in calcium concentration of the flow was only 1 ppm in some 400 m of streamway and the water was essentially saturated. The condition of spatially concentrated solution is met by a large volume of water flowing through a defined conduit within the aquifer. Such conduits are characteristic of karst aquifers and are in contrast to the small inter-granular flow paths found in granular aquifers. The problem of the initiation and location of such conduits is a vexed question. A considerable amount of recent work has, however, suggested that it is the hydrologic conditions within the aquifer that play a large part in determining this aspect of karst development. Ewers (1966, 1973), Curl (1971) and Palmer (1971) all suggest that one path eventually becomes the important conduit through an aquifer, and that the hydrodynamic controls of solution are such that this preferred path develops most rapidly.

CHAPTER III

HYDROCHEMICAL ANALYSIS

3.1 General Considerations

The detailed nature of various environmental controls of the rate and extent of limestone solution has been considered in Chapter II. The manner in which all the controls act determines the ultimate relationship between the discharge and solute concentrations of streams within and leaving a carbonate aquifer, and also the chemical composition of water at various stages of flow within the aquifer. The final interaction is largely dependent upon the hydrologic characteristics of the system. The distribution and extent of precipitation on the basin controls much of the hydrology of a karst aquifer. Climatic parameters also have a direct effect on the solution process in that the temperature can control the P_{CO_2} of the soil air (as shown by Harmon et al., 1973) and the equilibrium state of the reaction.

In most natural karst basins it is not only the water - rock interaction in a single environment that determines the solute concentration - discharge relationships observed at the outlet. The hydrologic regime of the influent area plays an important part in that it determines the proportion of effluent water originating from various segments of the basin.

In areas where there is a well-defined period of base-flow the different characteristics of base-flow and surface runoff have been used to separate strom hydrographs on chemical grounds. This approach has been most strongly advocated by Pinder and Jones (1969). In many instances, however, there may be many chemically distinct sources of discharge which are significant. In such cases neither the hydrograph nor the flow - solute concentration relationship need be of simple enough form to allow an immediate separation of the constituents. Cherry et al. (1972) describe some of the potential difficulties associated with such a hydrochemical system and suggest that the different behaviour of a number of ions considered separately can provide information on the relative importance of various flow types.

In addition to the hydrologic uses of discernible discharge - solute concentration relationships of streams in carbonate aquifers there are a number of geomorphic uses. Corbel (1959) developed the now classic formula:

$$X = \frac{4ET}{100} \qquad (3.1)$$

where X = erosion of the basin (mm/1000 yr), E = mean annual water surplus (dm) and T = mean total hardness of runoff (ppm $CaCO_3$) to estimate the net erosion of the whole basin. Williams (1963) provides a modified version of Corbel's formula to permit the consideration of basins not wholly developed in limestona or those developed in limestones of densities other than 2.5. Formulae of this type cannot estimate accurately the annual load of a stream no matter what refinements may be developed. It is the convolution of two time series (those for discharge and solute concentration) that define the load. This convolution cannot in general be represented adequately by the product of the means of the two series. Williams (1970) and Douglas (1964) realised the geomorphic potential of an analysis of the load carried in solution by streams under various flow conditions. They did not, however, extend their considerations to ions other than Ca^{2+} and Mg^{2+}. Williams' analysis in particular is more concerned with the areal distribution of limestone solution as defined by studies of several tributaries of the Fergus river, Co. Clare, Ireland, than with the spatial distribution of solution between various environments. The difficulties of deriving a meaningful figure for the solutional erosion when faced with the problems of the location of most solution make the successful analysis of hydrochemical relationships an important geomorphic task.

3.2 Hydrochemical Models of Discharge - Concentration Relationships

The relationships of Douglas (1964) and Williams (1970; Williams and Jennings, 1968) are of the nature of empirical statistical descriptions rather than formal models. Williams (1970) does, however, fit a power function to the chemical load - discharge relationship which is in keeping with Wolman and Miller's (1960) conclusions concerning the distribution of the total load between the various flows observed. Pinder and Jones (1968) consider a basic mixing model

$$L = C\,Q' = \sum_i C_i Q_i \qquad (3.2)$$

where L = chemical load, C = solute concentration, Q = discharge and the subscript 'i' refers to the various hydrologic provenances of the components of the total discharge. The relationship between discharge and solute concentration is generally inverse, and in certain cases this can lead to an almost invariant load. Durum (1953) observed such a situation in the Saline River, Kansas, and since that time several other cases have been described. Hendrickson and Krieger (1960) reported one such at the Salt River, Kentucky, but also noted a hysteresis effect. A cyclic deviation from a linear relationship was also found by Gunnerson (1967) and Toler (1965). The general pattern of the relationship given by Gunnerson is shown in Figure 3.1. All these authors ascribe the non-linearity to the action of the increasing discharge in the Spring in flushing highly mineralised water out of the soil zone. In the late summer period of declining flow, when an equivalent discharge is observed, there is no such flushing action.

Gunnerson (1967) states that an exponential model of the form:

$$y = b(1 - e^{-ax}) + K \qquad (3.3)$$

where y = "corrosion rate" and x = "velocity" was also considered, but

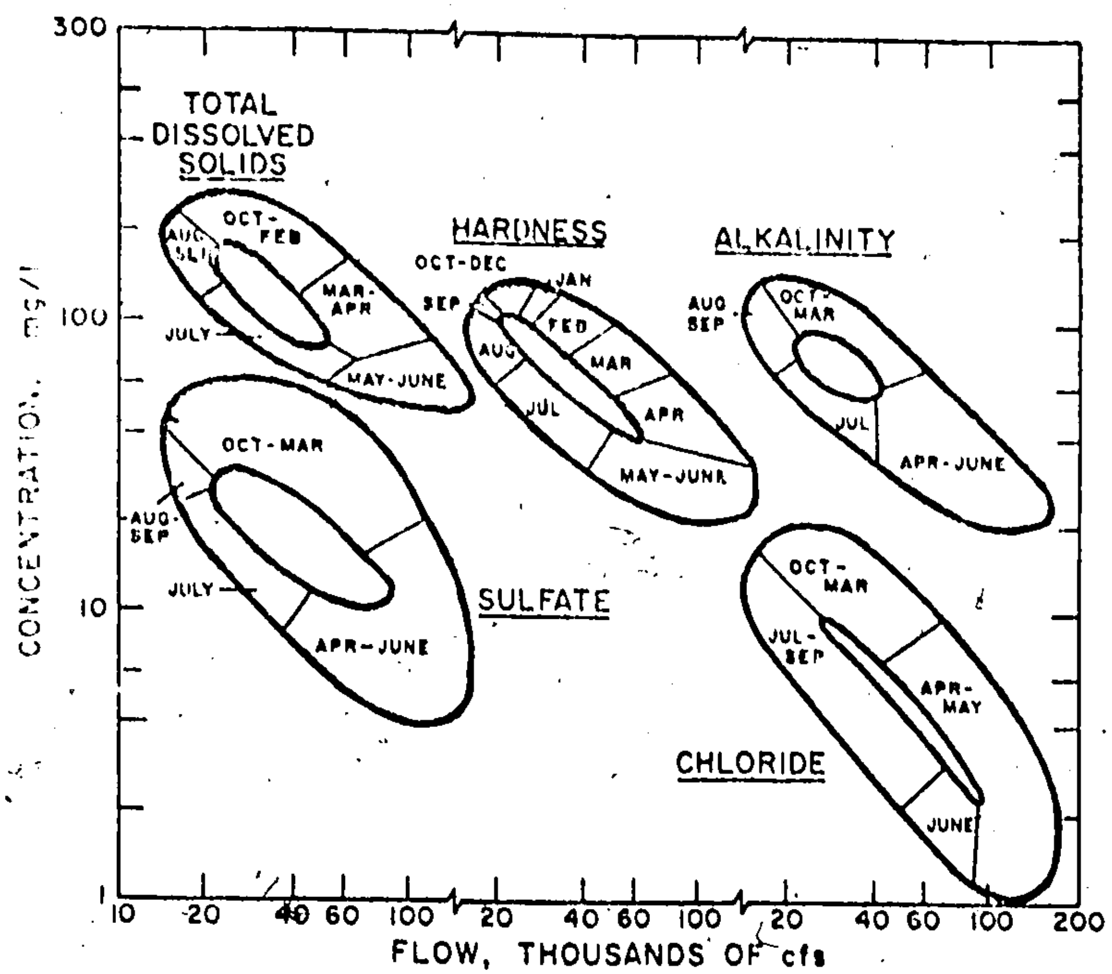


Figure 3.1

Cyclic changes in the discharge-concentration relationships in the Snake River at Wawawai, Oct. 1959 - Sept. 1962. From Gunnerson (1966, Fig. 4, p. 5).

gives no indication of its application. Whilst the exact meaning that Gunnerson intends by "corrosion rate" is unclear, a usual definition would be the rate of transport of dissolved material past a point. In this instance his suggested model reduces to the constant load model shown in equation 3.2 once the "velocity" or discharge exceeds a certain value. The extent to which Gunnerson's model represents an improvement over the constant load model has not been determined.

The model described above applies to a single flow and not to the situation in which there is a mixing of water from more than one source or environment. A theoretical derivation of a two-system mixing model has been given by Johnson et al. (1969). Their starting point is not equation 3.2, but rather:

$$C_oV_o + C_\alpha V_\alpha = C(V_o + V_\alpha) \qquad (3.4)$$

where C_o, C_α, C = solute concentrations of the two mixing waters and their mixture, respectively, and V_o, V_α = volumes of the two mixing water bodies. Under three assumptions:

1) the volume of solvent per unit area in the system approaches a minimum as the discharge approaches zero, i.e. $V \rightarrow 0$, $V_o + V_\alpha \rightarrow V_o$ as $Q \rightarrow 0$

2) the volume of water in the system in excess of V is proportional only to the discharge, i.e. $V_\alpha = \gamma Q$

and 3) associated with V_o is a given concentration of solute, C_o and if $C_o - C_\alpha = C_\delta$ and $\gamma/V_o = \beta$., then

$$C = \frac{C_\delta}{1 + \beta Q} + C_\alpha . \qquad (3.5)$$

Johnson et al. (1969), applying this model to a watershed largely covered by clays found that a positive solute concentration - discharge relationship held for Al^{3+} and H^+ (suggesting that these minerals were being leached from the soil by rainwater), that no relationship could be discerned for SO_4^{2-} and Cl^- (since the only source of these ions was the incident precipitation) or for Mg^{2+} (suggesting a strong Mg^{2+} buffering reaction in the system), and that a negative relationship held for Na^+ and SiO_2 (indicating a dilution effect). The values for C_o, the soil water solute concentration, for Na^+, SiO_2, Mg^{2+}, Al^{3+}, H^+ and K^+ were such that they "most likely represent the equilibrium concentration with co-existing kaolin" (p. 1362). This study provides a good illustration of the potential uses of multiple concentration - discharge analyses on the same stream.

The approach of Johnson et al. (1969) using mixing volumes rather than mixing discharges has been expanded by Hall (1970). The two approaches are formally the same if it can be assumed that there is no (or negligible) effect on the relationship by any change in storage of water in the stream channel. The essential consideration is the second assumption of Johnson et al. (1969) given above. Hall (1970) distinguishes six different mixing models and in a subsequent paper (Hall, 1971) discusses their application to field data. Hall concludes that in many cases it is not possible to choose a 'correct' model from a consideration of the data alone - several may give an equally good statistical fit to the observations. The assumptions used to derive the various models do, however, represent certain chemical and hydrologic constraints on the system which themselves may be used to choose the most applicable. Hem (1970) reviews the concept of mixing models and demonstrates that a simple three-component model provides a reasonable description of the data obtained from the San Francisco River at Clifton, Arizona. A two-component model is shown to be unsatisfactory. Hem quotes Steele (1968) as having applied a mixing model identical to Hall's model 1 (which is in turn the same as that of Durum, 1953) to Pescadero Creek, California.

The causative factors in the cyclic or hysteresis type of concentration - discharge relationships observed by Hendrickson and Krieger (1960), Gunnerson (1967) and Toler (1965) have been used in the specific environment of karst drainage basins in a semi-quantative manner by a number of investigators, Ashton (1966) described the flood response of karst springs and characterised it by the fact that a pulse in solute concentration preceded the flood wave. The explanation offered is the same as that of Hendrickson and Krieger (1960) - that is, that the initial increase in solute concentration represents highly mineralised water being flushed out of the aquifer. Smart (1971) used the flood hydrograph and the corresponding solute concentration curve to assess the time of concentration and the period of flow dominance of different hydrogeologic provinces of a small drainage basin in northern Scotland.

In any given stream there are liable to be a number of specific processes acting which may alter the relationship such that the mixing model becomes inappropriate. The mixing model approach essentially considers the transported material to be conservative in the sense that the only sources of sinks present may be considered to be discreet and of fixed (or simply defined) strengths. This precludes the application of such models to streams wherein the dominant processes are controlled by non-hydrologic factors. Barnes (1965) presents a very detailed analysis of the factors influencing the deposition of travertine by a stream in an arid climate, and concludes that the daily and seasonal variation of the temperature of the surface stream and of the P_{CO_2} of the interflowing groundwater are the most important. In this case the solute concentration - discharge relationship of the stream can only be represented by a detailed model incorporating the geochemical process of travertine deposition. The opposite effect, the solution by material by a stream from its bed, is a potentially important factor in a karst drainage basin. Ford (1971b) shows that a small meltwater stream issuing from a snowfield changes its chemistry radically over a distance of 100 ft. In an earlier paper (Ford, 1966) he showed that the transition of the shale/limestone boundary by streams in the Mendip Hills, England, results in a considerable and rapid change in the dissolved solids concentration. All such situations violate the requirement that the solute be conserved in the stream. Non-conservation of an inorganic solute usually indicates that the stream is not in chemical equilibrium with its environment. For mixing models to apply to a stream the requirement of solute conservation thus implies that the mixing flows and the mixed flow should be in chemical equilibrium with their immediate surroundings.

3.3 Time Variance of Solute Concentrations

An alternative approach to the study of solute concentration - discharge relationships is to regard each as a time series. Time series analysis of natural systems is based upon the assumption that such systems may be represented as the sum of two components - one deterministic and the other random. Matalas (1966) describes the assumption as it applies to hydro-meteorological phenomena:

> "The assumption that hydro-meteorological phenomena are controlled by periodic astronomical events implies that the time series for these phenomena consist of a superposition of periodic functions, with local conditions, in the form of physiographic features and geologic structure, tending to obscure the periodicities." (pp. 277-278)

Time series analysis is based upon the study of the periodogram and the autocorrelation function of a set of data. Schuster (1898) provided an early example of the use of the periodogram, and Anderson (1942) derived the statistical properties of the autocorrelation function. In more recent years much use has been made of power spectrum analysis (e.g. Quimpo, 1968; Rodriguez-Iturbe, 1967). Brown (1972a, 1973) provides an example of its application to karst hydrology. Matelas (1966) gives a useful review of the technique and its applications and limitations when applied to hydrologic data. Ulrych (1972) details a potentially more powerful method of analysing the power spectrum of incomplete or truncated data records. Although this maximum-entropy spectral method has not yet been applied to hydrologic data it seems that the nature of most such data is such that it would have considerable advantages.

The technique of power spectrum analysis has been less applied to water quality data. Gunnerson (1966), analysing a short period of specific conductance records of the Potomac River, Washington, D.C., found only one significant periodicity. This 2 cycle/day component he attributed to the effect of the tidal salt water intrusion from the Potomac estuary. Thomann (1967) used Fourier analysis to investigate the temperature and dissolved oxygen (DO) concentration in the Delaware estuary, Maryland. He demonstrated that the annual cycle accounted for 92% of the annual variance of temperature, and that over 90% of the annual variance of DO was attributable to the first four harmonics. In addition a small variation in DO at non-tidal stations could be discerned, a fact which Thomann attributed to a photosynthetic mechanism. Demayo (1969) provides an interesting comparison of the behaviour of physical (temperature) and chemical (specific conductance) properties of a stream. He shows that the temperature record of the Red River at Emerson, Manitoba, has strong spectral peaks at frequencies of 1 cycle/120 days and 1 cycle/30 days (corresponding to seasonal and monthly cycles) and that there are no 'secular' (in this case cycles with periods of more than 120 days) trends present. Specific conductance also shows the peak at 1 cycle/120 days, but has no monthly component and shows a strong secular trend. The discharge record for the same period shows only a secular variation, indicating that there is no cyclic variation present with a period of less than 120 days and implying that the only cyclic variation is annual. Demayo's analysis demonstrates that, whilst ultimately the ambient temperature partially determines both the flow regime of a stream in a snow-melt situation and the water temperature, the two systems do not have the same response.

One problem of any form of mixing model expressed as a regression equation is that the interaction between discharge and any chemical property is fixed in the sense that it cannot vary with different time scales of fluctuations within the data record. Cross-spectral analysis allows a different interaction between two time series at all frequencies and, as illustrated by Jenkins (1961), the resulting transfer function between the series can define the nature of the system in which they interact. The limiting factor in the application of spectral analysis to water quality data is the exacting data requirements of the technique. Gunnerson (1966) and Demayo (1969) both consider the problem of data collection. The frequency and period of data required is a function of the resolution and range of frequencies needed from the analysis. Since for any period the requirement is basically one of a large number of data equally spaced in time, data collection essentially has to be automated. Whilst this is a common matter for discharge, only recently has the use of automated recording instruments been adopted for quality measurements, and then only for specific purposes.

If both the quality and discharge of a stream are regarded as time series, then the elliptical quality - discharge relationships observed by Hendrickson and Krieger (1960), Toler (1965) and Gunnerson (1967) and discussed above can be seen to be the representation of two out-of-phase series. The angle of the major axis of the ellipse is a function of the phase difference. Both leads and lags of one series on the other can be so represented, and cycles of different periods within both records give rise to minor elliptical traces superimposed on the annual or seasonal pattern. Toler (1965) in particular demonstrates such minor superimpositions.

3.4 Analogies With Studies of Other Stream Properties

If the downstream relationships of the solute concentrations and the discharge of a stream during a flood are regarded as the result of the mixing of two distinct water masses, then an analogy with the behaviour of other water properties is possible. The essential processes are the propagation of the flood wave downstream and the diffusion of the input mass of water in the stream. In the case where a single point input can be identified the resulting solute concentration - discharge relationship is necessarily cyclic since a flood wave propagates more rapidly than the water, and thus the concentration perturbation flows downstream. This problem is essentially the same as that of determining the time-of-travel of water within a river reach. This is a significant problem and has received much recent attention because of the need to be able to predict the downstream movement of pollutants accidentally discharged into a streamway. Buchanan (1964) describes the use of fluorescent dye tracers in time-of-travel studies. Since 1964 many studies of both time-of-travel (e.g. Stall and Hiestand, 1969) and the longitudinal dispersion of pollutant waves (e.g. Fischer, 1968) have been based upon the use of dyes such as Rhodamine WT. Fischer (1968) demonstrates that estimates of longitudinal (one dimensional) diffusion coefficients derived by routing methods agree well with the observed diffusion coefficients for a dye pulse. The general longitudinal and transverse dispersion characteristics of a natural streamway under conditions of uniform discharge are summarised by Yotsukura et al. (1970).

The specific problem of the interaction between the discharge and concentration of a dissolved material downstream from a single input point has been considered by Shull and Gloyna (1969). They examined the rate of transport of radio-nucleides downstream of a hypothetical constant source. With a combination of physical models for radio-active decay, diffusion and benthic storage, and statistical models for streamflow, they predict that the rate of flow of the contaminant past a point 100 mi downstream of the input point can vary between one-sixth and three times the input rate. This paper is important in that it demonstrates that, if storage is possible in the reach, the downstream rate of flow of a dissolved substance can be greater than the input rate - a condition that is not possible with the diffusion and dispersion processes alone.

The stream property that has been studied most intensively is probably the DO or biochemical oxygen demand (BOD). Dresnack and Dobbins (1968) suggest that the problem of defining the downstream DO and BOD profiles in a stream is in many ways the same as defining the rate of heat conduction in solid bars. They state, however, that the presence of additional terms in the equations and the complex boundary conditions for DO and BOD prevent the derivation of analytical solutions except for the case of steady flow in the stream. Falkner (1972) gives a comprehensive review of the processes involved in determining the DO profile of a river and presents a model with reasonable predictive power under conditions of sparse data. The downstream dispersion of thermal plumes in rivers has been considered by Weeks et al. (1971) and Ahlert et al. (1970) amongst others and is similar to the consideration of the dispersion of dye plumes and other contaminants.

All of the studies discussed above deal with the downstream development of discharge - concentration relationships of properties or materials either input at a single point (the thermal and tracer studies) or undergoing absorbtion or generation in the streamway (the radionucleide, DO and BOD studies). As such they are not strictly analogous to the study of the relationships between the discharge and dissolved solids concentration in a karst stream. Certain aspects of the two situations are, however, common. The observed relationship in a stream below the confluence of a large, discreet karst spring may, after a flood pulse input from the spring, mirror the dispersion of a thermal plume. A closer analogue can be made between the DO profile in a stream and the dissolved solids profile of a karst stream. The analogy is closer because in both cases sources and sinks may be found along the length of the stream, and there is a limit (saturation) to the concentrations. The studies of Wigley (1971c) and Weyl (1958) represent the most analytical considerations of the downstream profile of dissolved solids, but they are confined to the pipe-flow situation. A consideration of the dispersal of dissolved solids plumes within a karst aquifer is usually not possible because the characteristics of the conduits cannot be determined. Except for the case where a stream flows into or onto carbonate rocks from a non-carbonate area, the change in the characteristics downstream is usually very minor and difficult to detect. Harmon (1973) considers the profile downstream of a spring, and shows that the controlling factor is the rate of degassing of CO_2 from the water to equilibrate with the atmosphere. In the cases where the analogy with other phenomena is close, as in the consideration of the concentration profile in pipes, the results of the analysis of the karst situation are the same as those of the analogue. In many cases, however, other factors serve to complicate the situation such that no solution may be derived by simple analogy.

3.5 The Identification of Hydrochemical Environments

The chemical composition of groundwaters is in general terms determined by equilibria with the minerals of the aquifer. If in a given region there are several distinct mineral facies, then it is reasonable to expect that hydrochemical facies may also be present. Back (1960, 1961, 1966, and Back and Hanshaw, 1965) has been the principal proponent of this concept, although others have also used it (e.g. Seaber, 1962; Morgan and Winner, 1962). Most of these works have dealt largely with the differentiation of fresh groundwater and incursive seawater in coastal areas. It has been shown that both anions and cations can be mapped into hydrochemical facies. The technique is not immediately applicable to most karst investigations since it requires a great amount of data from wells at different depths in the aquifer. It is also only of limited use in a single mineral environment since it has only shown gross differences in facies such as are observed between areas of different mineral facies or different hydrologic provenances.

The concept of water 'types' has been dealt with extensively by Hem (1970) and is related to that of hydrochemical facies. It is also largely limited to describing gross differences between, for example, calcium bicarbonate and sodium chloride type waters. Dawdy and Feth (1967) used factor analysis to interpret streamwater chemical data from the Mojave River valley, California. They identified three major water types (calcium bicarbonate, sodium sulphate and sodium chloride) but conclude that the technique cannot be used to reveal the areal sources of the various constituent types. Reeder et al. (1972) also used factor analysis for 29 dissolved constituents in the Mackenzie River drainage basin in an attempt to define the source materials and areas for each. They concluded that seven factors accounted for most of the observed variance, but all of the major constituents (Ca^{2+}, Mg^{2+}, HCO_3^- and SO_4^{2-}) are combined into one factor representing the influence of "carbonate materials and gypsum". Evidently such analyses are at too small a scale to be able to differentiate between environments within a carbonate aquifer.

Jacobson et al. (1971) have shown that a Q-mode factor analysis can differentiate between waters from wells in the soil overlying a carbonate aquifer and waters from wells in the aquifer itself. A subsequent R-mode analysis of the aquifer well water samples revealed four factors - carbonate rocks, septic tanks and road salt, depth and elevation, and fertilizers - underlying the variation of the chemical and physical properties. It has long been assumed by many karst geomorphologists that different classes of water within a carbonate aquifer should have a characteristic chemistry. Richardson (1968) summarises these intuitive concepts and gives an example of the use of the different chemical nature of the water from a small number of springs in an area in Yorkshire, England, to identify streams contributing to particular springs. Pitty (1966, 1968b) demonstrated that the variation of the chemical composition of certain spring waters could in part be explained by antecedent climatic conditions, a conclusion also reached by Paterson (1972). Shuster and White (1971, 1972) have since shown that it is only 'conduit' springs (that is, springs which discharge water which has entered the aquifer as a stream and which has flowed through a relatively short, defined conduit within it) that can be so controlled. 'Diffuse' springs (that is, springs which discharge longer resident groundwater from the aquifer) have an essentially constant regime throughout the year. Shuster and White use the geochemical measures SI_c and equilibrium P_{CO_2} to demonstrate that it is the annual cycle of biotic activity rather than of temperature or precipitation as such that is responsible for the variation in chemistry of the water flowing from conduit springs. Ternan (1972) differentiated diffuse and conduit springs on the basis of the coefficient of variation of their calcium hardnesses. Atkinson (Dept. of Geography, Univ. of Bristol, pers. comm.) has used the coefficient of variation of calcium hardness of springs in the Mendip Hills, England, to estimate the relative amounts of percolation or diffuse flow water feeding them.

The differentiation of classes of water within a carbonate aquifer on the basis of the behaviour of one of the dissolved species can only indicate the source of the water in very general terms. In the case of the diffuse and conduit spring differentiation, the behaviour of the solute concentrations are easily explained. Conduit springs show high seasonal variability because the water resides in the aquifer for only a short time and discharges from it with almost the same characteristics as the streamflow recharge. Diffuse springs discharge water which has resided in the aquifer long enough to aquire stable characteristics. The geochemical approach taken by Shuster and White (1971, 1972) is capable of defining the type of recharge water being discharged and also the chemical history of the water within the aquifer. Harmon et al. (1972) have shown that the use of SI_c and P_{CO_2} can differentiate various classes of underground waters in Kentucky, and can indicate the conditions under which the various classes entered and moved through the aquifer. Drake and Harmon (1973) show that the same two geochemical measures can be used to differentiate six different water types within a carbonate aquifer system. Their approach uses linear discriminant function analysis to confirm that SI_c and P_{CO_2} are in fact the most powerful discriminating variables between the six water types considered - soil zone recharge, allogenic streamflow recharge, conduit spring water, diffuse spring water, groundwater (well waters), and the surface outflow from the basin fed by the aquifer. The use of the geochemical measures allows the identification of the processes acting on the water in the different hydrochemical environments. Figure 3.2 illustrates the essential features of the six classes. The fact that the conduit flow waters have a higher P_{CO_2} than the allogenic recharge streams which feed them is evidence that there is some intermixing of soil zone recharge water. A number of other deductions are made from similar reasoning by Drake and Harmon (1972, 1973).

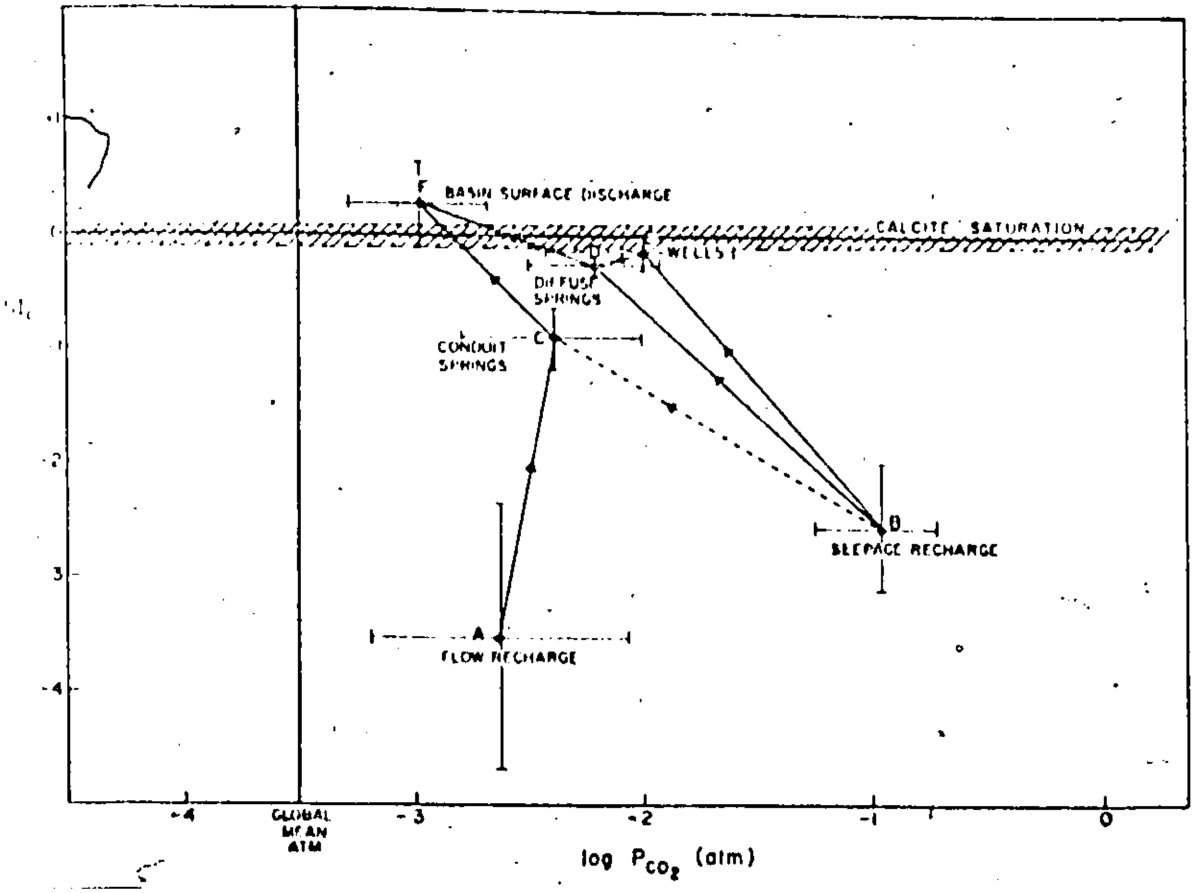


Figure 3.2

Characteristics of karst hydrochemical zones in central Pennsylvania. Symbols indicate mean and bars indicate one standard deviation. From Drake and Harmon (1973, Fig. 4, p. 956).

CHAPTER IV

THE SOUTHERN CANADIAN ROCKIES AREA

4.1 The Area

4.1.1 Introduction

The previous two chapters have described the various controls of the karst solution process and the potential uses to which studies of the discharge - solute concentration relationships of streams may be put. The Canadian Rocky Mountains are in large part composed of carbonate rocks and several papers (Ford, 1971a,b; Brown, 1972a) have illustrated the importance of the solution process in a number of small areas within them. Earlier, Corbel (1956, 1958) had provided an overview of the nature of solutional erosion in the Canadian Cordillera which was in keeping with his climato-morphogenetic ideas. For the eastern Main Ranges he estimated rates of solution of between 37 and 50 mm/1000 yr and for the Selkirk Mountains to the west 90 mm/1000 yr. Corbel attributed the variation solely to the differences in total annual precipitation. There can be little doubt that Corbel's work, while valuable, was a rapid overview since he visited the entire western mountain region (including Alberta, British Columbia, Yukon Territory and the North West Territories) in a single summer. From Corbel's observations on Medicine Lake near

Jasper, Brown (1972a, p. 14) concludes that he was in the area during the spring flood and had no opportunity to investigate the temporal variation of carbonate solution in the area. Similarly Ford (1971a,b) discusses the karstification of the Crowsnest Pass and Mount Castleguard areas from the standpoint of summer observations. The hydrochemical data given by Brown (1972a) span only the summer high discharge period.

Although many of the small karst hydrologic systems appear to cease flowing during the winter months the major rivers draining the area continue to flow. Solution in the contributing aquifers similarly continues year-round. The annual variation of the extent and spatial distribution of solutional erosion is an important consideration in the geomorphology of the area. Since the entire mountain range east of the Continental Divide between Snake Indian River and Bow Summit is drained by the Athabasca and North Saskatchewan Rivers and discharge and dissolved solids data are available for them this study concentrates on their drainage basins. The main purpose is to describe the nature of solutional erosion within the basins and to relate it to the various controls of the process.

4.1.2 The Environment

The general location of the study area is shown in Figure 4.1, together with the locations of previous studies of karst phenomena in

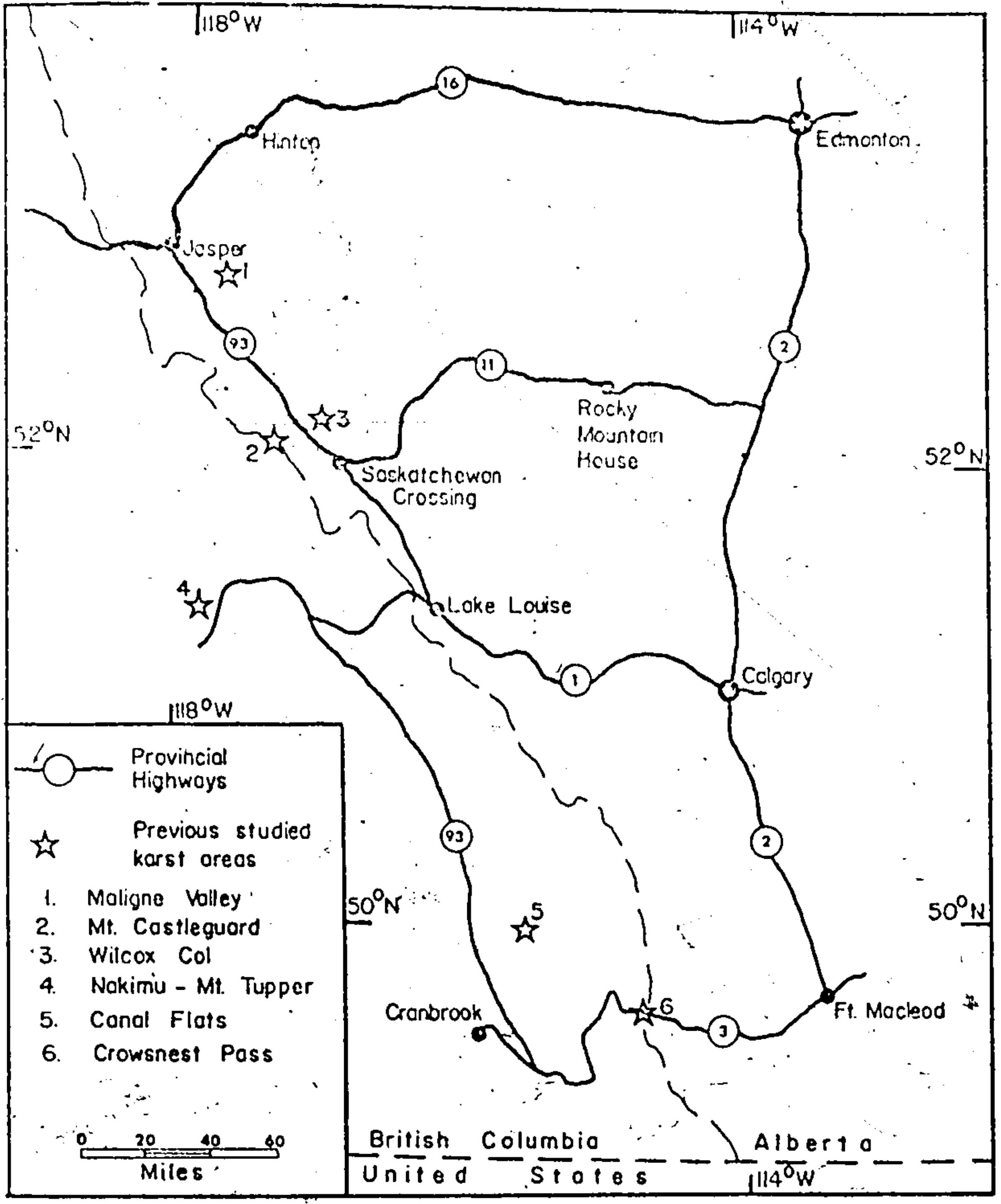


Figure 4.1

Features of the study area.

the vicinity. Many more areas of karst landforms are known in the general area (see, e.g. Ford et al , 1972) but the published accounts are confined to the most well-known and the largest examples. The study area and all of the areas previously studied, with the exception of Makimo-Mt. Tupper and Canal Flats, lie within the Continental Ranges of the Rocky Mountain physiographic division as defined by the Geological Survey of Canada. Its coordinate limits are 49°00' N to 53°49' N and 114°25' W to 118°17' W, although in fact the area is a narrow (30 mi) belt trending NW - SE for a distance of some 350 mi. The western limit to the area is generally the Alberta - B.C. boundary because this is defined in this locale as the Continental Divide. In very small local areas the groundwater divide is not the same as the surface water divide. Any error introduced by this factor into the estimation of drainage basin areas is so small that it is ignored.

Relief in the area is of the order of 8000 ft, with elevations ranging from a little above 3000 ft at the point of emergence of the main rivers from the mountains to more than 11000 ft at many points along the Continental Divide. In general the area is drained by strike line streams which turn eastwards to cut through the Front Ranges and Foothills in large passes. The generalised physiography is shown in Figure 4.2. A consequence of the general increase in crest elevation in the vicinity of the Athabasca - North Saskatchewan and the North Saskatchewan - Bow River system divides is the presence of remnant ice

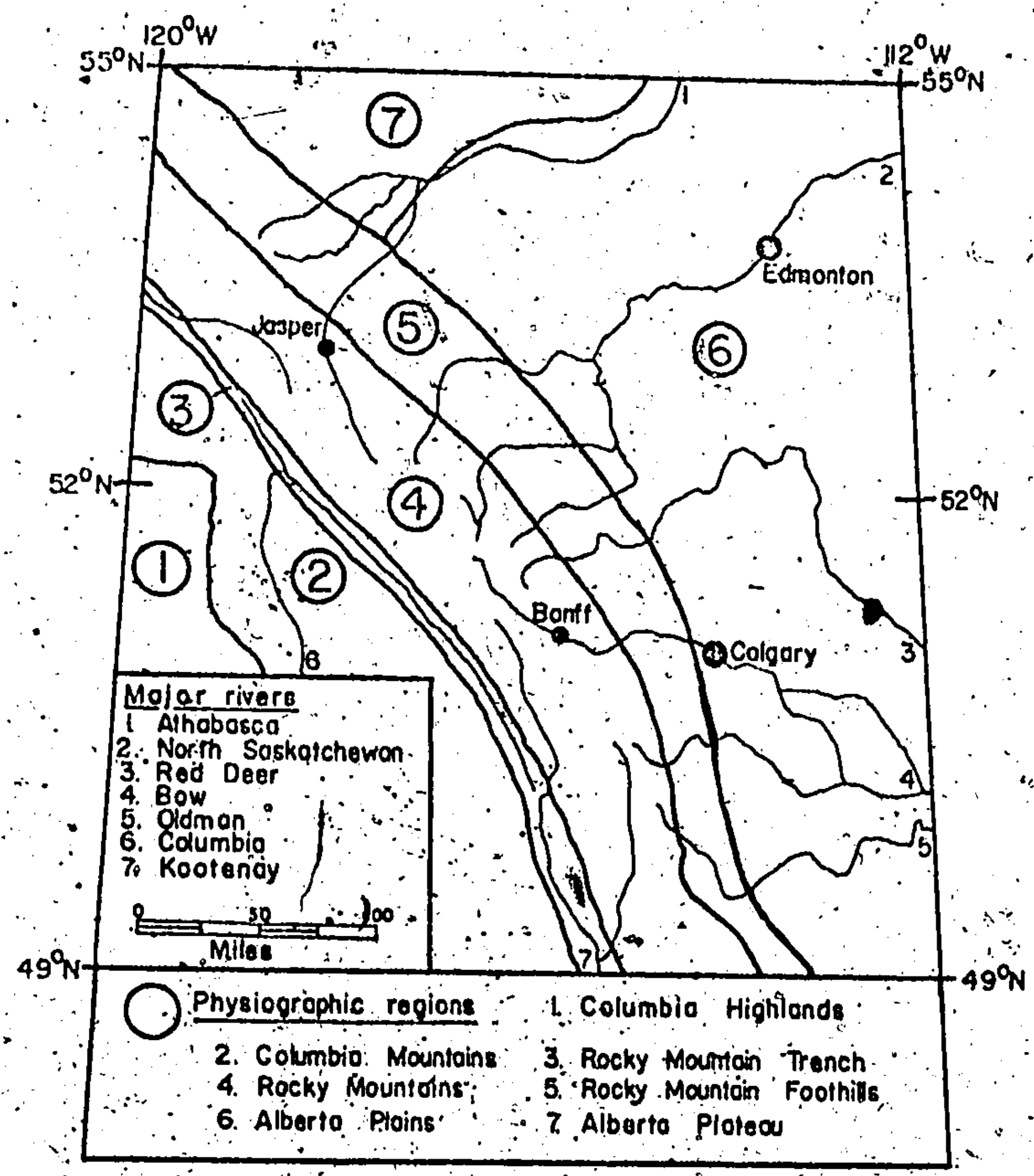


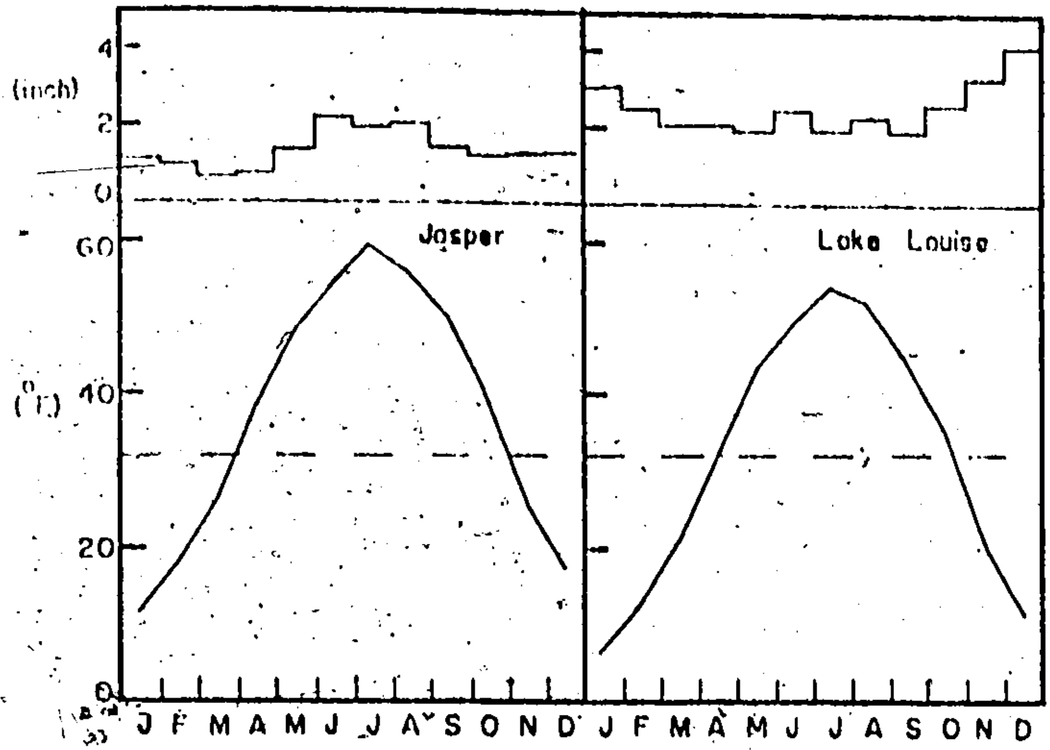
Figure 4.2

Generalised physiography of the study area. After Douglas (1970, Geol. Surv. Can. Map 1254A).

caps, the largest of which are Columbia Icefields and Wapta Icefield. Much of the headwater zone of the Bow, North Saskatchewan and Athabasca Rivers is in an active glacial area. Toward the south peak elevations decline such that none of the tributaries of the Crowsnest River are fed either by ice fields or significant permanent snow fields.

The vegetation in the area is altitudinally distributed. In general the valley bottoms are either bare of vegetation or covered by grasses, depending on the frequency and severity of flooding. Above the valley floors and below the treeline, which is at about 6500 ft to 7000 ft throughout most of the area, dense coniferous forest is established except where local conditions such as excessively steep cliff faces prevent the accumulation of soil and the growth of trees. At the treeline the forest gives way to alpine meadows or tundra with dwarf conifers. The distribution of vegetation above the treeline is largely controlled by shelter. Most of the area above about 8000 ft is devoid of any vegetation. Ford (1971a) has discussed the importance of the altitudinal vegetation zonation to the karst development of the area.

A direct consequence of the relief structure of the area and its location within the Cordilleran physiographic region is the type of climate. Thermographs and hyetographs for Banff, Lake Louise and Jasper are shown in Figure 4.3. These are the only stations in the area that are operated throughout the year. The climate is continental and is dominated in winter by the presence of Polar air masses and in summer by Pacific weather



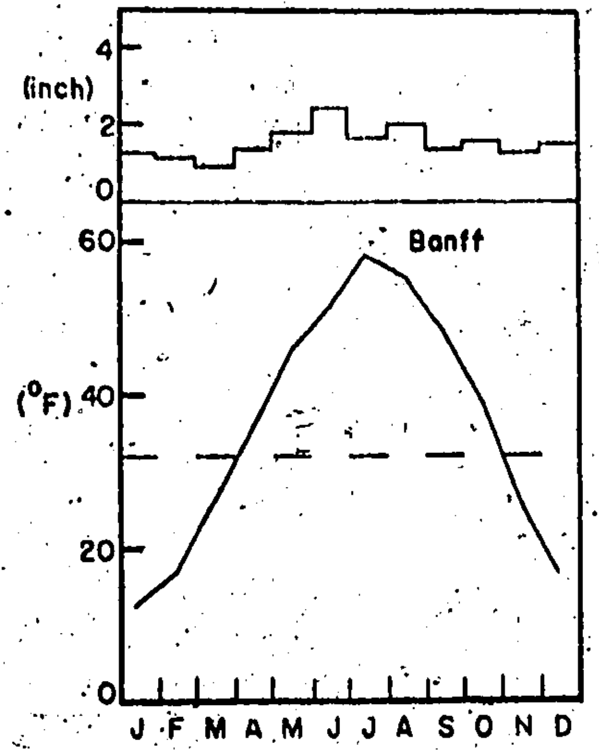


Figure 4.3

Mean annual monthly temperatures and precipitation for Jasper, Lake Louise and Banff.

systems. The Thornwaite (1948) classification of the Banff station is $C_2C_2'rb_1'$ (moist subhumid, microthermal, with little or no water deficit). Annual precipitation is 18.5" at Banff and 16.0" at Jasper, with a slight summer maximum. Approximately 20% of the total annual precipitation falls as snow. Records have been kept intermittently during the summer at Columbia Icefields. The higher areas receive considerably greater amounts of precipitation than the valley floor stations, and that there is a tendency toward a winter maximum. All meteorological data used are compiled by the Atmospheric Environment Service. The relevant stations record only daily minimum and maximum temperatures and precipitation on a regular basis. The nature of any mountain climate is such that there are not only considerable altitudinal differences, but also great spatial variations. The mean figures shown in Figure 4.3 can therefore only represent the general situation. Even in late July and early August freezing temperatures and snow are not uncommon in the vicinity of the Columbia Icefields.

4.1.3 Geology

The study area lies within the Rocky Mountain Thrust Belt which is described by Douglas (1970):

> "The southernmost sector of the Canadian Cordillera, the Rocky Mountain Thrust Belt, was produced by the Columbian and Laramide Orogenies during the Cretaceous and early Tertiary. The dominant structures are subparallel, west dipping thrusts that produce a series of narrow, linear mountain ranges formed of resistant Paleozoic carbonates." (p. 367).

This statement of the general structure of the area belies the actual complexity of the thrusting. Overthrusts and overturns are common. Price and Mountjoy (1970) describe in detail the most recent assessment of part of the area. This study is concerned either with large drainage basins (the Athabasca and North Saskatchewan) where the general structure controls the main features of the geohydrology or with small local area (such as Mount Castleguard and Crowsnest Pass) in which the geology is relatively simple. The pertinent features of the geology of the small areas has been described - Mount Castleguard by Ford (1971b) and Crowsnest Pass by Ford et al. (1972).

The most significant feature with respect to the development of karst landforms is the positioning of aquifers and aquicludes. Figure 4.4 shows parts of two geological columns relevant to this study. Generally, as stated by Douglas (1970; v.s.) the Paleozoic carbonates are resistant and massive. Throughout the southern Main Ranges three units, the Rundle Group (corresponding to the Livingstone in the Front Ranges), the Palliser Formation and the Fairholme Group are the main aquifers and are also the main cliff-forming units (see e.g. Luckman, 1973). The Mississippian Rundle Group is separated from the Devonian Palliser by the Banff and Exshaw shales which are effective aquicludes. Locally in the Mount Castleguard area the main aquifer is the Cambrian Cathedral dolomite, but the Pika limestone and Eldon dolomite, separated from the Cathedral by the Stephen shales, also show considerable karstification.

Figure 4.4 (over)

Geologic columns for the study area. From Douglas (1970, Chart III).

Contacts

— — conformable
┴┬┴┬ disconformable
∿∿ unconformable

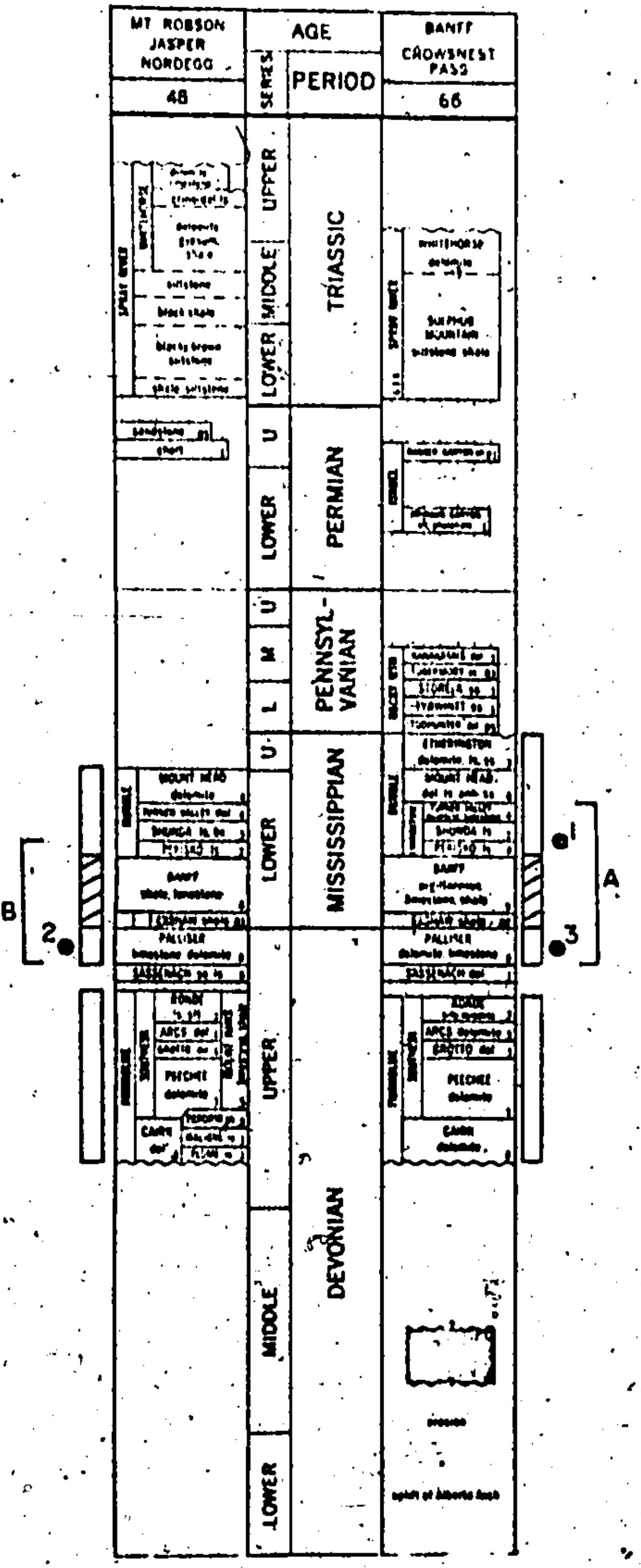
1.5 thickness (1000 ft)

Major cave systems
1 Ptolemy-Andy Good Caves
2 Old Man River Rising
3 Maligne Cave
4 Castleguard Cave

] Major karst areas previously studied
A Crowsnest Pass
B Maligne Valley
C Mt. Castleguard

▯ Major karst aquifers

▨ Major aquicludes


MT ROBSON
JASPER
NORDEGG
48
AGE
SERIES
PERIOD
BANFF
CROWSNEST PASS
66
UPPER
MIDDLE
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TRIASSIC
U
LOWER
PERMIAN
U
M
L
PENNSYL-
VANIAN
U
LOWER
MISSISSIPPIAN
UPPER
MIDDLE
LOWER
DEVONIAN
siltstone
black shale
shale siltstone
sandstone
chert
WHITEHORSE
dolomite
SULPHUR
MOUNTAIN
siltstone shale
ETHERINGTON
MOUNT HEAD
dolomite
SHUNDA
PEKISKO
BANFF
shale, limestone
EXSHAW shale
PALLISER
limestone dolomite
SASSENACH
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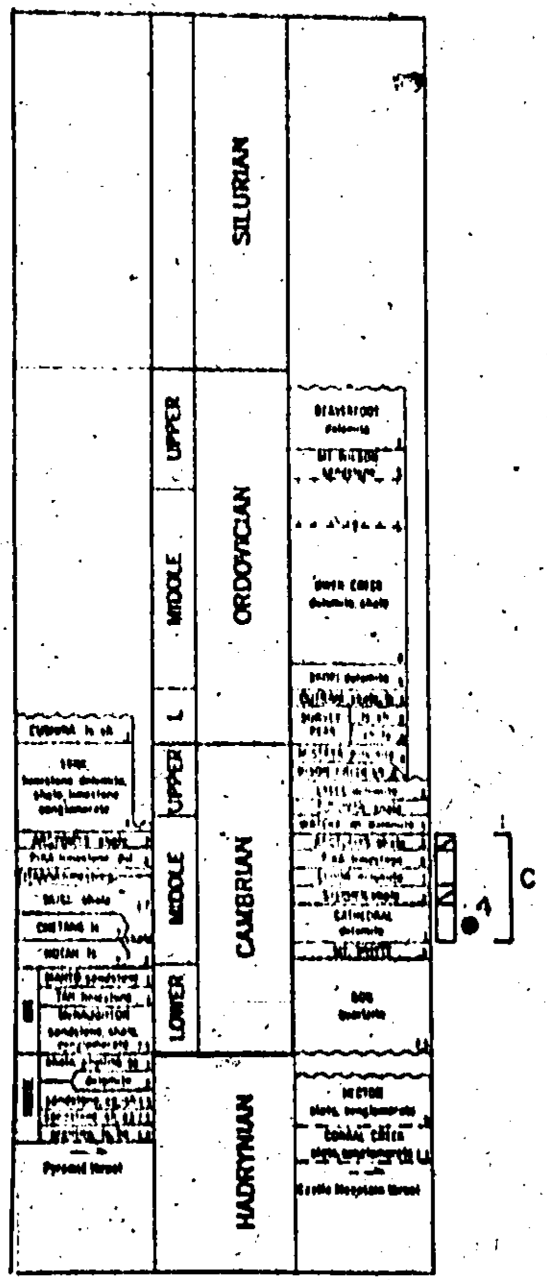

SILURIAN
ORDOVICIAN
CAMBRIAN
HADRYNIAN
UPPER
MIDDLE
L
UPPER
MIDDLE
LOWER
C
A

All units above the Gog (effectively the lowest unit) are shales, limestones, dolomites or sandstones with two exceptions. In the south the Mount Head unit of the Rundle Group contains some anhydrite, and in the north the Whitehorse member of the Triassic Spray River Formation shows some gypsum. In both cases the sulphates appear to be limited to the eastern margin of the units. The Mount Head is described by Douglas (1953, 1959) and the Whitehorse by Gibson (1968). Between the North Saskatchewan and Athabasca Rivers the Lower Starlight Evaporite Member of the Whitehorse Formation contains limestones, gypsum and collapse breccias which are, according to Quinlan (1973), indicators of interstratal karstification.

The essentials of the hydrogeology of the area are relatively simple. Most of the thrust ridges are formed of limestones and dolomites which are capable of acting as aquifers. The intervening aquicludes serve to eject groundwater from the aquifers at spring points. In much of the area the transmissivity of the carbonate units is sufficiently low that meltwater from the snow cover during the spring freshet drains from them on the surface. Only a small amount of the spring meltwater drains through the aquifers but in certain local situations they can transmit large quantities of water in defined paths, as is the case in, for example, the Maligne River valley.

4.1.4 Geomorphic Processes and Karstification

The geomorphic processes acting within the study area are many, but may be broadly classified into gravitational mass-movements, glacial, periglacial, fluvial and karst processes. Instances can be found in local areas of any one being predominant. Massive rockfalls can have catastrophic effects on the development of stream valleys as in the case of the Maligne valley (Brown, 1972a) and Surprise valley (Luckman, 1973) where the rockfalls have blocked the original stream course and halted further fluvial action. More regular but smaller rockfalls and debris avalanches play an important role in the development of the many talus slopes in the area (Gardner, 1970; Luckman, 1971, 1973). The effects of glacial erosion can be seen throughout the area. Ford et al. (1971), however, tentatively suggest that the last two glacial periods (since 200,000 B.P.) lowered the floor of Crowsnest Pass by no more than 400 ft. The discrepancy between the apparently overwhelming effects of glacial erosion and the relatively small rate of erosion in the late Pleistocene and Recent suggest the early Pleistocene glacials may have been more significant. Ford et al. (1971) suggest that at least 63% of the present relief in Crowsnest Pass existed 275,000 years B.P. In light of this fact it would seem that present geomorphic processes are modifying the landforms created during the Pleistocene glacials. Present glacial erosion is limited to areas around the major icefields and other small glaciers. There is considerable evidence for a Neoglacial event during the late 18th and early 19th centuries (Richmond et al., 1965) and in the areas adjacent to the larger glaciers the effects can be seen in scoured rock faces devoid of vegetation or periglacial activity.

As in any area uncovered by deglaciation, glacial deposition has contributed to the development of the landforms. McPherson (1970) describes many depositional features in the Upper North Saskatchewan River valley, as does Rutter (1966) in the Bow River valley near Banff. Present glacial depositional processes are limited to the small areas adjacent to the remaining glaciers, but substantial moraines are accumulating in such areas. The Neoglacial event left moraines which can be seen in the valleys containing glaciers draining from the Columbia and Wapta Icefields. Periglacial features are largely limited to the areas above the treeline. Corbel (1958) considered that there was an absence of periglacial activity in the area, but certainly it is widespread in the vicinity of Mount Castleguard (Ford, 1971b). At higher elevations near Crowsnest Pass rock glaciers and solifluction lobes are common. In parts of the Front Ranges and on peaks near Jasper patterned ground phenomena exist.

The local effect of gravitational mass-movements, glacial and periglacial acting at present can be considerable. Ultimately, however, any erosion products must be transported out of the area by streams. The streams themselves show a considerable ability to modify their channels. In the upper reaches most exhibit complex braiding, with extensive erosion and re-deposition occurring during the snow-melt period. Data from a study on the North Saskatchewan River suggest, however, that this process may have been overestimated. Some of the braid islands have been stable for more than twenty years (D.G. Smith, Univ. of Calgary, pers. comm.).

Langbein and Schumm's (1958) figures suggest that the annual suspended sediment yield for stream basins in the area should be of the order of 600 tons/sq mi. Data from the Water Survey of Canada (1972) based upon the use of depth-integrated samples and shown in Table 4.1 indicate a great variability in the annual suspended sediment yield. Of the five stations shown (the only ones in the vicinity of the study area with complete data for at least one year) only one, Marmot Creek, lies within the Rocky Mountains. It flows in a rocky channel with little alluvium. The other four stations are either in the Foothills or on the edge of the Prairies and flow in channels cut in alluvium. This is reflected in the generally higher sediment yield. The variability of fluvial erosion is demonstrated by the extreme loads carried by all the streams in 1967. The five year mean for Marmot Creek, extrapolated to an erosion rate (assuming a sediment bulk density of 2.5) gives a figure of 1.8 mm/1000 yr. The maximum observed annual rate is 84.6 mm/1000 yr for the Oldman River near Brocket in 1967. On the basis of these measurements it is impossible to estimate the annual sediment yield for any of the streams in this study. It is, however, reasonable to assume that it lies within the range between the values for Marmot Creek and the other four stations because the streams

Table 4.1

Sediment Transport Data for Southwest Alberta

Site	WSC No.	Area (sq.mi)	Year	Mean Daily Sediment Yield (Tons)	Specific Yield (tons/sq.mi/yr)	Erosion Rate[1] mm/1000 yr
Marmot Ck., Main Stem	05BF016	3.63	1964	0.40	40	5.6
			1965	0.11	11	1.5
			1966	0.05	5	0.7
			1967	0.04	4	0.6
			1968	0.03	3	0.4
			Mean	0.13	12.6	1.8
Oldman R., near Brocket	05AA024	1700	1967	2730	586	82.1
			1968	234	50	7.0
			Mean	1482	318	44.6
Streeter Ck.	05AB030	2.30	1967	0.23	36	5.0
			1968	0.04	6	0.8
			Mean	0.14	21	2.9
Willow Ck.	05AB028	62.8	1967	93.4	542	76.0
			1968	1.8	10	1.4
			Mean	47.6	276	38.7
Willow Ck.	05AB021	446	1965	81.6	66	9.3
			1966	71.9	59	8.3
			1967	419	343	48.1
			1968	10.9	9	1.3
			Mean	146	119	16.7
Mean[2]					93.5	13.1

Notes: [1] Calculated assuming a bulk specific gravity of 2.5
[2] Excluding Willow Creek 05AB028

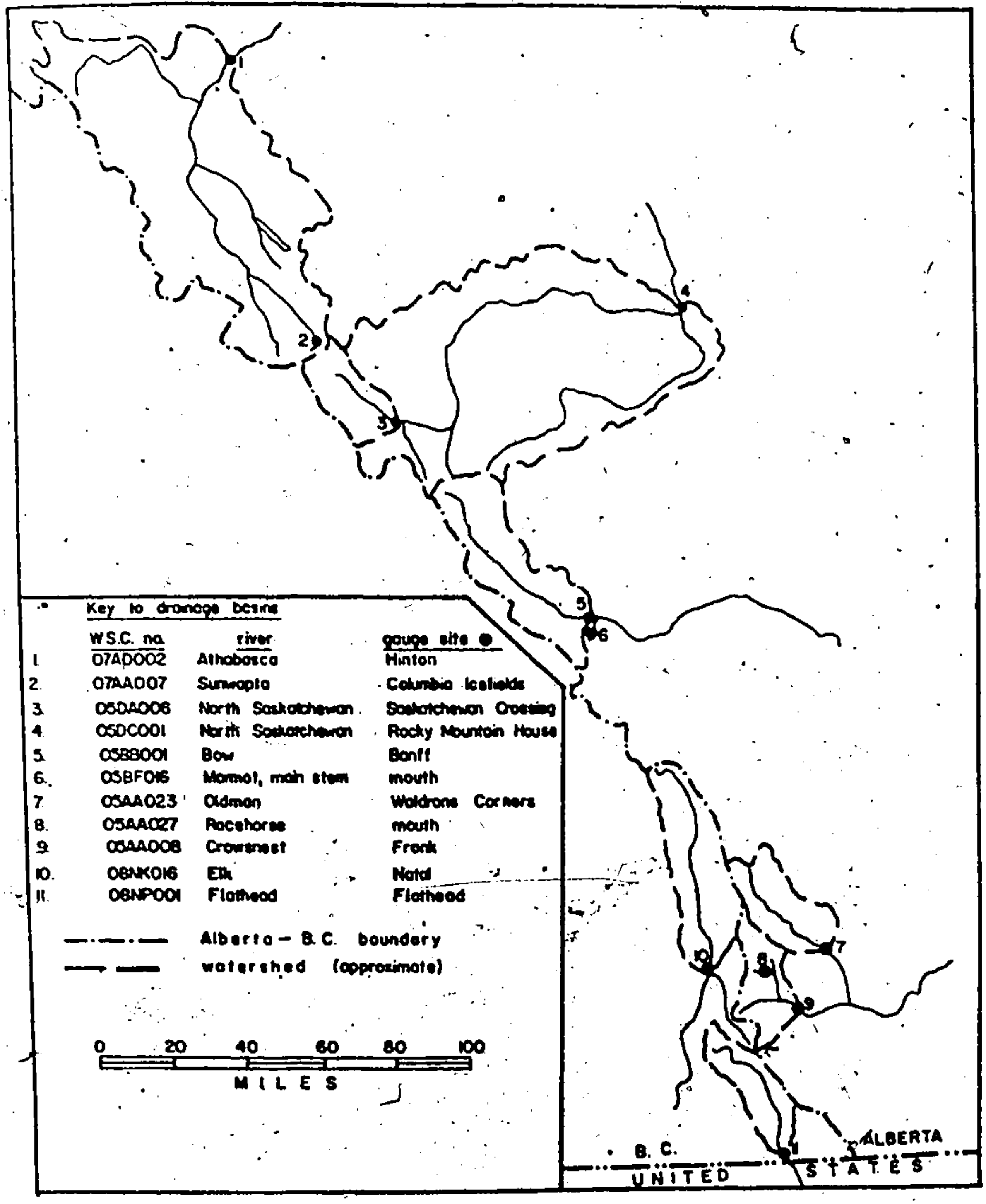
have headwaters similar to Marmot Creek and lower reaches more like the alluvial Foothill streams. In this case the values are likely to be between 12.6 and 170.6 tons/sq mi/yr, or 1.8 and 24.1 mm/1000 yr. These values are considerably less than those which would be expected from Langbein and Schumm's (1958) work.

The Main and Front Ranges of the Rocky Mountains are mainly composed of carbonate materials. The carbonate solution process is therefore widespread and is potentially the most significant geomorphic process in terms of net annual erosion. Corbel (1958) quotes rates of erosion by solution of between 37 and 50 mm/1000 yr in the eastern Main Ranges, a range somewhat higher than the tentative range derived above for the erosion represented by the removal of solid material. Although relatively few areas of karst topography have been described in the southern Rocky Mountains it is thought by Ford et al. (1972) that it is a common phenomenon and that the lack of documented occurrences is due to the fact that access to much of the region is difficult. The areas that have been studied are Wilcox Col (Corbel, 1958), Maligne and Surprise valleys (Brown, 1972; Ford et al., 1972), Mount Castleguard (Ford, 1971b; Ford et al., 1972) and Crowsnest Pass (Ford, 1971a; Ford et al., 1972). All show extensive karstification. Sinkholes of several different types (shafts, uvalas, alluvial filled) are common. Many caves are reported, including Maligne cave (10 mi in length) and Castleguard cave (7 mi). At least three rivers (Maligne, Castleguard and Crowsnest) are fed by large springs which contribute over 60% of the flow during the summer months. All rivers draining from the region are of the calcium bicarbonate type. Products of carbonate solution form the main component of the dissolved load carried by the streams.

Minor karst forms are present on bare rock surfaces in many locations. Rillenkarren and pit-karren are particularly well-developed in the Surprise Valley and Mount Castleguard areas. Whilst there are few areas containing very large karst surface features some massive rockfalls may have been precipitated by the solutional undermining of the basal members of a cliff face. Ford (1967) considers that the Maligne valley rockfall was so caused. Although the area is not considered a 'typical' karst as are, for example, central Kentucky and southern Yugoslavia, it is a large Alpine karst area wherein the karst process is everywhere active.

4.2 Hydrologic Study Basins

The Inland Waters Division of the Canadian Department of the Environment maintains a number of discharge gauging stations in the Rocky Mountains south of the Athabasca River. Eleven of these were selected for a hydrological study to define the main discharge controlling factors. The basins are shown in Figure 4.5. Table 4.2 shows their location, altitude, area and mean annual runoff. They include a small mountain



Key to drainage basins

	W.S.C. no.	river	gauge site ●
1.	07AD002	Athabasca	Hinton
2.	07AA007	Sunwapta	Columbia Icefields
3.	05DA006	North Saskatchewan	Saskatchewan Crossing
4.	05DC001	North Saskatchewan	Rocky Mountain House
5.	05BB001	Bow	Banff
6.	05BF016	Marmot, main stem	mouth
7.	05AA023	Oldman	Waldrons Corners
8.	05AA027	Racehorse	mouth
9.	05AA008	Crowsnest	Frank
10.	08NK016	Elk	Natal
11.	08NP001	Flathead	Flathead

Figure 4.5

Location of the study basins.

Table 4.2

Drainage Basins in Study

Stream	Gauge Location	WSC No.	Gauge Elevation	Area (sq.mi)	Zone[1]	Mean Annual Runoff (ins)	Lat (°N)	Long (°W)
Athabasca	Hinton	07AD002	3195	4000	6	22.32	53.41	117.59
Sunwapta	Columbia Ice-fields	07AA007	6370	11.4	5	42.52	52.22	117.23
N. Saskatchewan	Saskatchewan Crossing	05DA006	4590	492	5	42.61	51.97	116.73
N. Saskatchewan	Rocky Mountain House	05DC001	3148	4220	-[2]	15.87	52.38	114.94
Bow	Banff	05BB001	4520	858	5	22.82	51.18	115.57
Marmot, main stem	Mouth	05BF016	3.63	3.63	6	17.15	50.95	115.15
Oldman	Waldrons Corner	05AA023	4145	551	3	12.22	49.81	114.18
Racehorse	Mouth	05AA027	4550	83.9	2	15.45	49.84	116.62
Crowsnest	Frank	05AA008	4200	162	2	16.40	49.59	114.41
Elk	Natal, B.C.	08NK016	3890	760	-[2]	17.82	49.87	114.89
Flathead	Flathead, B.C.	08NP001	3980	450	-[2]	29.64	49.00	114.48

Notes: [1] After Davis and Coulson (1967)

[2] Outside zoned area

Zones:
2 Highwood and Oldman Tributaries
3 Southern Foothills
5 Northern Intermountain
6 Northern Mountain

basin in the Front Ranges (Marmot Creek), a glacial basin (Sunwapta River) and the three streams which drain the reported karst areas (Athabasca, North Saskatchewan and Crowsnest Rivers). Two, Elk and Flathead Rivers, drain the western side of the Main Range in British Columbia.

Davis and Coulson (1967), using discharge records for 77 stations, divided the Alberta Rocky Mountains south of the Athabasca River into seven zones on the basis of similarity of flow characteristics. The criterion for defining a zone was that the smallest correlation coefficient of logarithmic monthly flow for any pair of streams in one zone should be higher than 0.60. The zones of each of the eleven stations used in this study are shown in Table 4.2. Davis and Coulson concluded that the zones north of Crowsnest Pass correspond to topographic units and that topographic effects are the most important in determining the hydrologic regime of a basin. Zone 4 is distinguished from zone 3 by the influence glacial meltwaters have on the discharge of the basins within it.

Hypsometric analysis of the eleven basins using a random point count method with 100 points in each shows that all except two are comparable. The hypsometric curves are shown in Figure 4.6. Generally the basins have a disproportionate fraction of their area (approximately 80%) below the 50% relief point. This is consequent upon the presence of wide valleys in the lower sections of the basins and steep mountain slopes and peaks in their headwaters. The two exceptions, Marmot Creek and Sunwapta River, both have a more uniform distribution of area. They do not show the

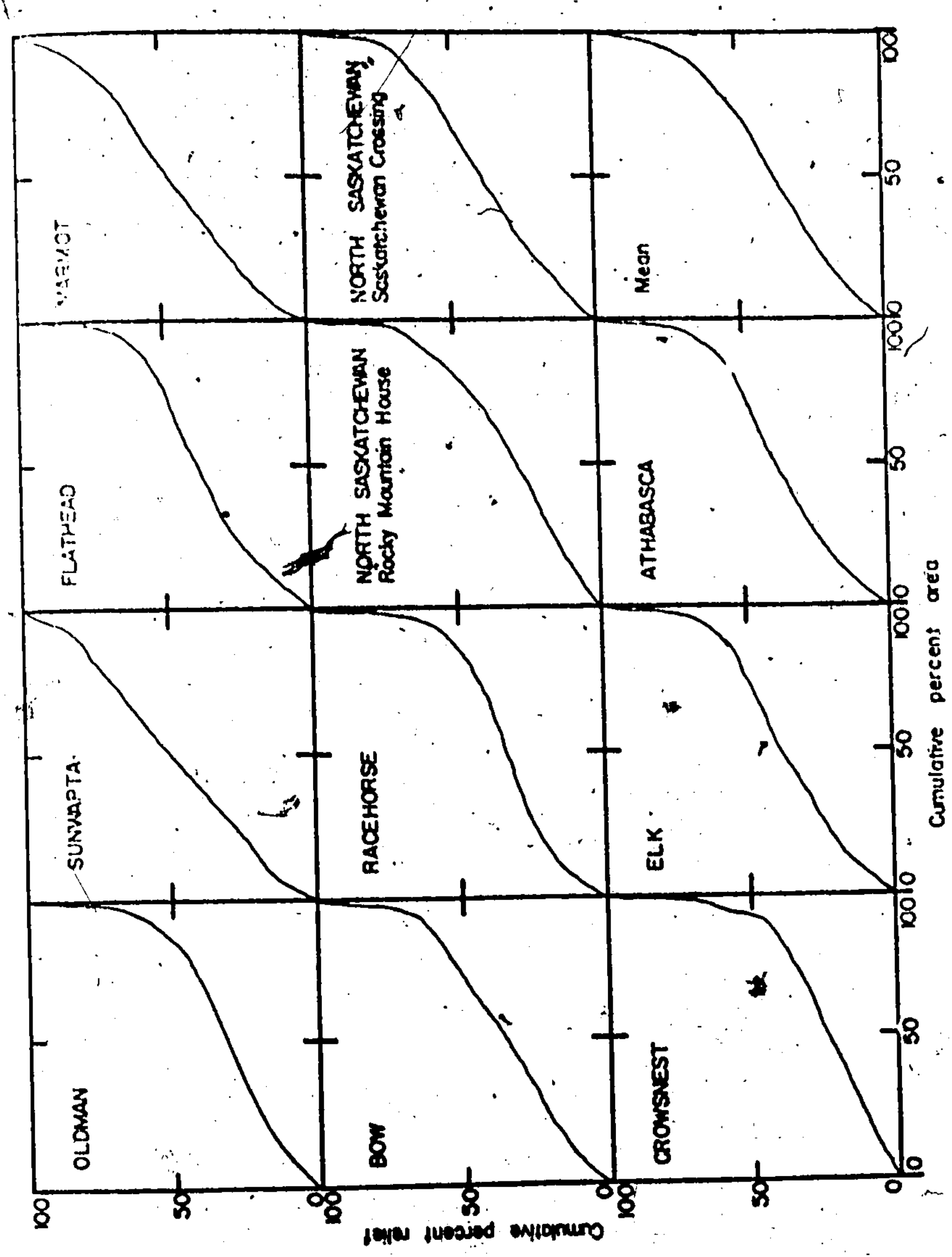


Figure 4.6

Hypsometric curves of the study basins.

broad lower valley common to the other nine basins. Crowsnest River is an extreme example with over 90% of its area below the 50th percentile of relief. Much of the basin above the gauging station at Frank lies in a broad trough between the Main and Front Ranges. This trough is much narrower north of the Crowsnest Pass area. A Kolmogorov-Smirnov two sample test of the hypsometric frequency distributions gives the results shown in Table 4.3. It shows that, at the 0.01 confidence level, Crowsnest River basin is unique and that Marmot Creek and Sunwapta River basins form a unique group. The other eight basins are all similar to one another.

Davis and Coulson (1967) showed that hydrologic zones could be distinguished and that they were differentiated by topography. Hypsometric analysis of a considerably smaller sample of basins shows that the relief characteristics of basins within some of the zones do reflect the topography. The characteristics of a particular basin are of course dependent upon the position of the gauging station. Although Sunwapta River (and other headwaters of Athabasca River) has a particular relief configuration the overall configuration of the Athabasca basin above Hinton is dominated by the lower sections. Many of the stations in zones in Davis and Coulson's (1967) study away from the Continental Divide derive a portion of their flow from the headwater zones. The distinguishing feature between the hypsometric types suggested above is not topographic position but the nature of the bulk of the streamway.

Table 4.3

Comparison of Hypsometric Curves

Upper: Maximum differences between cumulative hypsometric frequency curves for the study basins (%).

Lower: Probability of exceedence by Kolmogorov-Smirnov two-sample test ($n = 100$) where $p < 0.1$.

	Crowsnest R.	Racehorse Ck.	Flathead R.	Oldman R.	Elk R.	N.Sask.R., R.M.H.[1]	Marmot Ck.	Sunwapta R.	Athabasca R.	N.Sask.R., S.X.[2]	Bow R.
Crowsnest R.		26	33	26	30	16	41	43	32	31	26
Racehorse Ck.	<.01		11	7	12	14	32	37	11	18	15
Flathead R.	<.01			18	3	17	22	27	1	8	7
Oldman R.	<.01		<.01		16	11	31	36	18	20	14
Elk R.	<.01	.1		.01		14	20	28	2	7	6
N.S.R., R.M.H.[1]	<.01	.04	<.01	/	.04		26	30	16	16	10
Marmot Ck.	<.01	<.01	<.01	<.01	<.01	<.01		10	21	14	17
Sunwapta R.	<.01	<.01	<.01	<.01	<.01	<.01			27	21	26
Athabasca R.	<.01			<.01		.01	<.01	<.01		7	6
N.S.R., S.X.[2]	<.01	<.01		<.01		.01	.04	<.01			6
Bow R.	<.01	<.01		.04			<.01	<.01			

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[1] North Saskatchewan River at Rocky Mountain House

[2] North Saskatchewan River at Saskatchewan Crossing

Large streams flowing in major glaciated and infilled valleys are necessarily different from small mountain streams regardless of their topographic position.

4.3 Athabasca and North Saskatchewan Rivers

4.3.1 The Athabasca River Basin

For the purposes of this study the Athabasca basin is defined as the area drained by Athabasca River and all its tributaries above Hinton, Alberta. The gauging station at this point is maintained by the Inland Waters Division of the Water Survey of Canada (WSC No. 07AD002) and is the highest continuous station. Continuous records are available from 1961 and their accuracy is considered to be 'good' during periods of open water and 'fair' during ice conditions. The Water Quality Division of the Water Survey of Canada established a regular monitoring program at the same site in September, 1967, and since that time monthly analyses are available from the Division's Calgary office. Details of the analytical methods used are given by Traversy (1971).

Figure 4.7 shows the major streams and icefields within the Athabasca River basin. The alignment of the tributary streams is largely controlled by the geologic structure of the area. The Athabasca above Jasper, the Sunwapta, Maligne, Rocky, Snaring and Snake Indian Rivers are

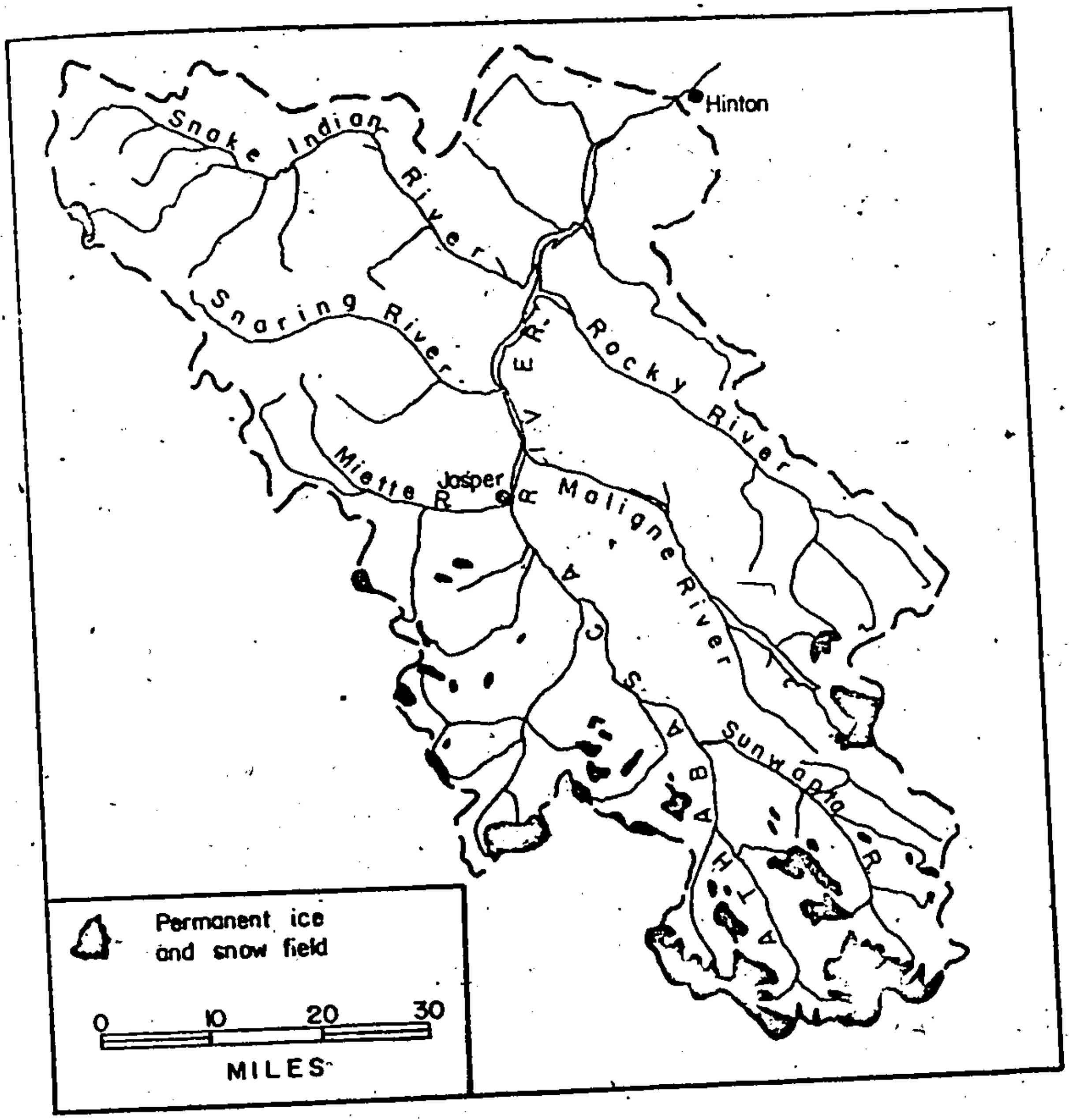


Figure 4.7

The Athabasca River basin.

all strike-line streams flowing in valleys positioned by sub-parallel, west dipping thrusts. The Miette and Athabasca below Jasper flow through the broad, transverse Yellowhead Pass. Except for the uppermost reaches all streams flow in wide valleys containing considerable amounts of glacial material. The Athabasca below the confluence of the Sunwapta shows extensive terracing up to 350 ft above the present floodplain. Below Jasper it flows through a series of wide, shallow lakes developed in glacial deposits.

The basin is 4000 sq mi in area and is approximately 115 mi NW - SE (parallel to the mountain ranges) by 55 mi SW - NE. Almost all the basin lies within Jasper National Park and is essentially free of development. Jasper is the only settlement within the basin and uses the river for waste disposal. Waste water is treated before being returned to the river by seepage through the gravel aquifer in the main valley. The Athabasca at Hinton is devoid of large amount of any dissolved material that could be attributed to human intervention.

Although detailed geologic map coverage of the whole area is not available Quinlan (U.S. Parks Service, pers. comm.) has estimated the basin to be 31.4% carbonate rock by area. Much of the precipitation falling on the carbonate area sinks into the aquifer and is subsequently discharged into the rivers. Few published accounts deal with the carbonate aquifer systems but Brown (1972a) describes the Maligne River underground drainage system. In a later paper (Brown, 1972b) he describes the use of infrared imagery to locate a spring in Medicine Lake in the Maligne valley. The present resurgence of the Maligne River cave system is a number of small, constricted springs in a limestone canyon in the flanks of the Athabasca valley. Ford (1967) hypothesizes that these springs are relatively recent and that the system originally discharged through a large spring which is now buried and infilled by glacial deposits. This hypothesis would account for the apparent scarcity of springs in the carbonate areas of the basin.

Elevations in the basin range from 11847 ft near the headwaters of Sunwapta River to 3195 ft at the gauging station at Hinton. The streams lose much of this relief in their upper sections before flowing into the relatively gentle main stem Athabasca. A long profile of the Athabasca River and the mean gradients over various segments are shown in Figure 4.8. There are a number of waterfalls on the various streams within the basin, including Sunwapta, Athabasca and Snake Indian Falls. Baird (1966) considers that these are unrelated phenomena, each having a specific geologic cause, rather than being a general indication of any geomorphic disturbance.

4.3.2 The North Saskatchewan River Basin

The highest gauging station on the North Saskatchewan to measure all the discharge from the Rocky Mountain area is near Rocky Mountain.

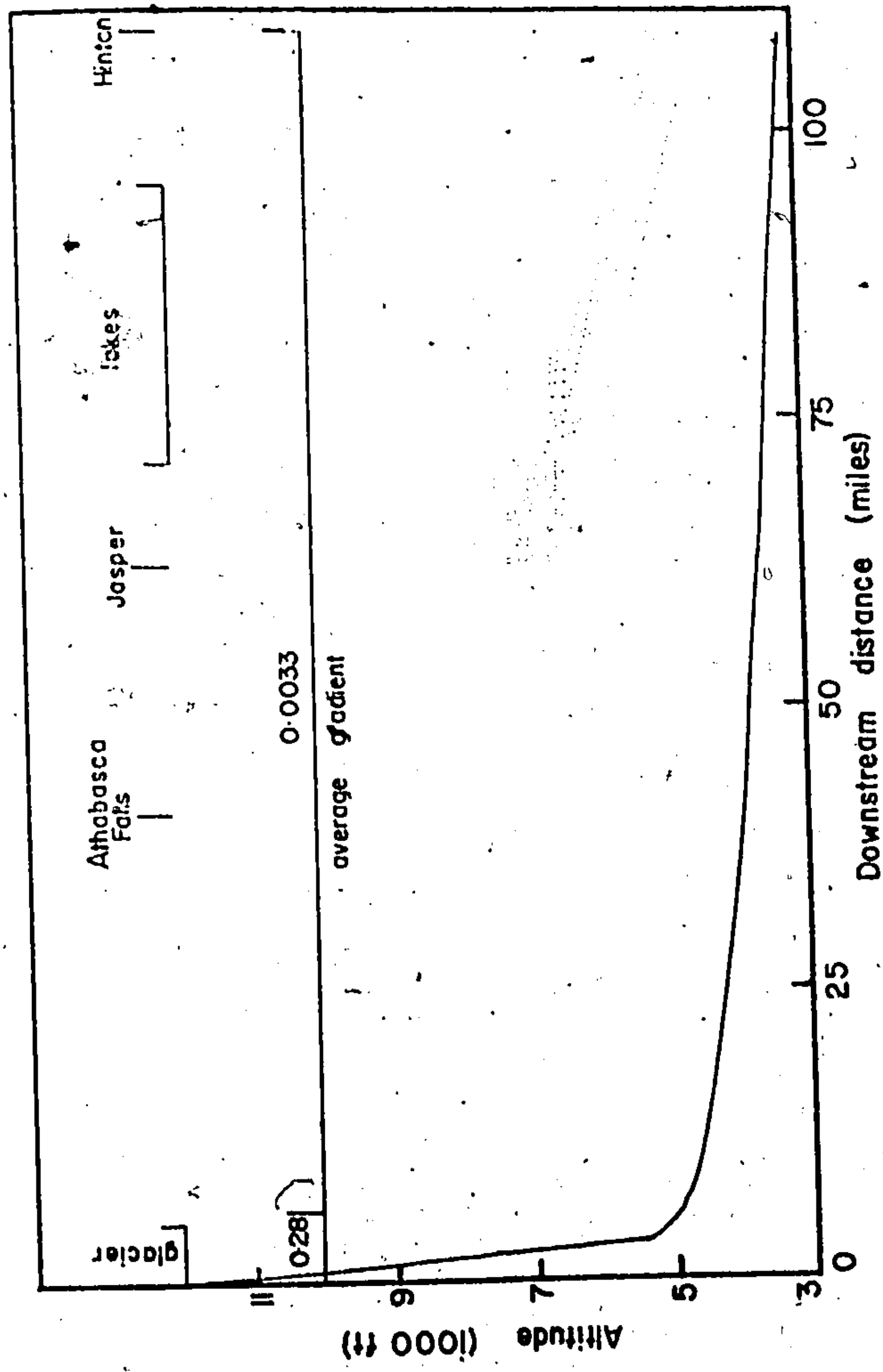


Figure 4.8

Long profile of the Athabasca River.

House, Alberta. The gauge is operated by the Water Survey of Canada (WSC No. 05DC001) and monitors the flow from a 4220 sq mi basin. Continuous records of discharge are available from 1953 and their accuracy is estimated to be 'good' under all conditions. The Water Quality Division has maintained a monthly monitoring program at the same site since March, 1967.

Figure 4.9 shows the North Saskatchewan basin above Rocky Mountain House. Although the section above the confluence of the Mistaya (at Saskatchewan Crossing) is similar to the pattern of the Athabasca, much more of the basin lies in the Front Ranges and Foothills. The Upper North Saskatchewan (above Saskatchewan Crossing) and Mistaya Rivers are oriented along the strike along thrusts. Below the confluence the river turns eastward and flows out toward the Alberta Plains. Two large tributaries, the Ram and Clearwater, join the main stream upstream of the gauging station and drain tributary basins largely in the Front Ranges. Most of the North Saskatchewan valley is a broad, glacial infilled feature. The upper sections contain a braided stream and below Saskatchewan Crossing there are a number of interspersed lakes. The streamway is in many respects similar to that of the Athabasca River.

Quinlan (U.S. Parks Service, pers. comm.) has estimated the area of the basin to be 33.4% carbonate rocks. As in the Athabasca basin much of the carbonate rock acts as a karst aquifer. There are accounts dealing with the carbonate hydrology of the headwater area (Ford, 1971b; Ford et al., 1972) and as Baird (1967) reports many small springs can be seen in

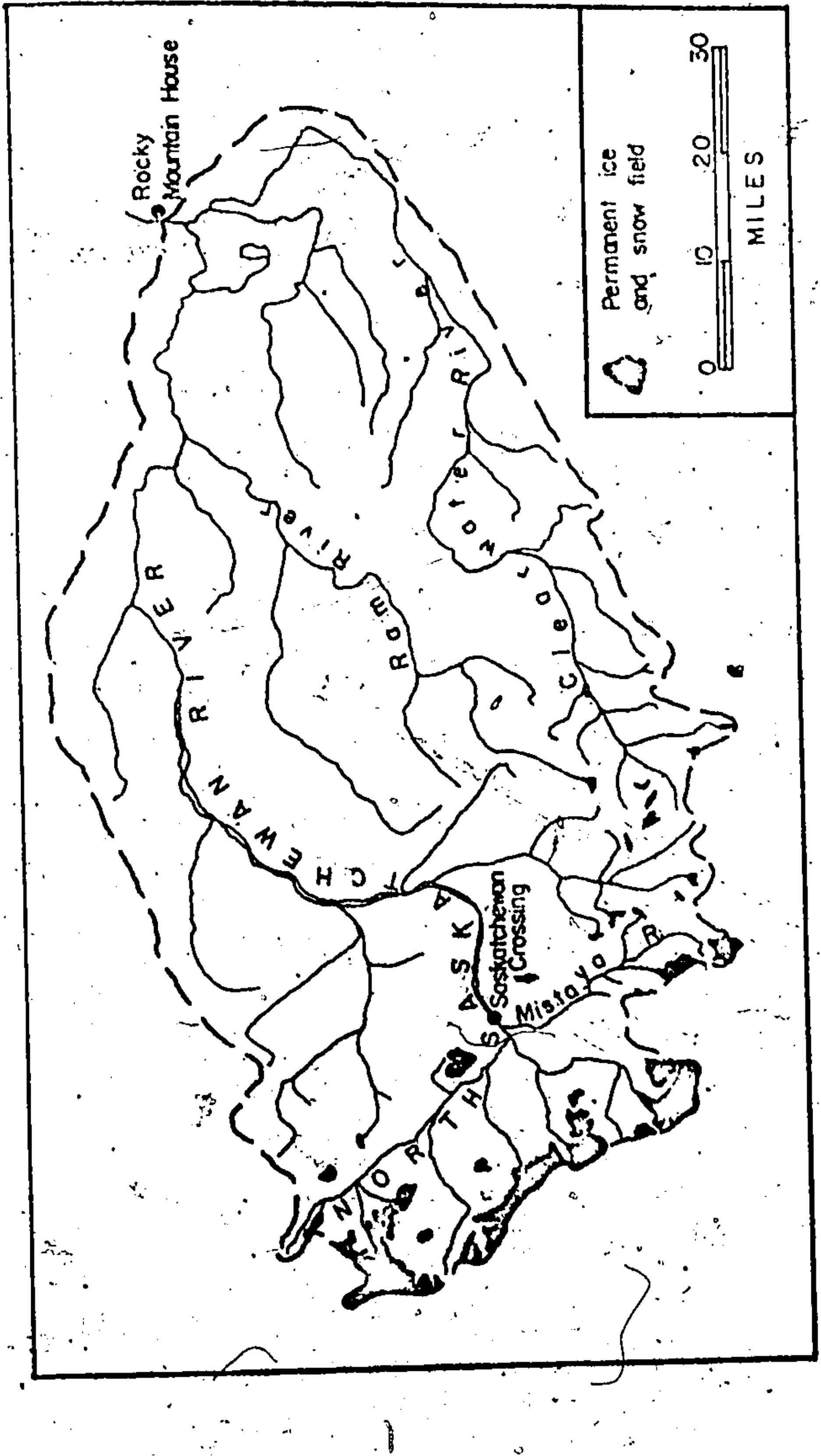


Figure 4.9

The North Saskatchewan River basin.

the area above Saskatchewan Crossing. One of the tributaries of the Upper North Saskatchewan is Castleguard River. This stream is fed in part by a large karst spring which discharges meltwater from the Columbia Icefields (Ford, 1971b). In August, 1969, the discharge of the spring was approximately 400 cfs, one-tenth of the flow of the North Saskatchewan at Saskatchewan Crossing (WSC Station No. 05DA006). Because there are numerous smaller springs in the area and it can be assumed that much of the carbonate aquifer discharges directly into the bed of the major streams (as is the case in the Athabasca basin) the flow of the North Saskatchewan consists largely of water that has passed through carbonate rocks and/or carbonate-rich tills.

Elevation in the basin ranges from 11852 ft near the headwaters of the North Saskatchewan River to 3148 ft at the Rocky Mountain House gauging station. Total relief is thus some 8700 ft. A long profile of the North Saskatchewan River is shown in Figure 4.10. A comparison of Figures 4.8 and 4.10 shows that although the two rivers have similar profiles the North Saskatchewan has less steep headwaters and a less abrupt transition to the valley floor situation. The Upper North Saskatchewan and Mistaya Rivers both have waterfalls in their courses but as is the case in the Athabasca basin these are attributed to particular local causes and not to any geomorphic event affecting the whole basin (Baird, 1967). The smaller proportion of the North Saskatchewan basin lying within the Main and Front Ranges is shown by the hypsometric

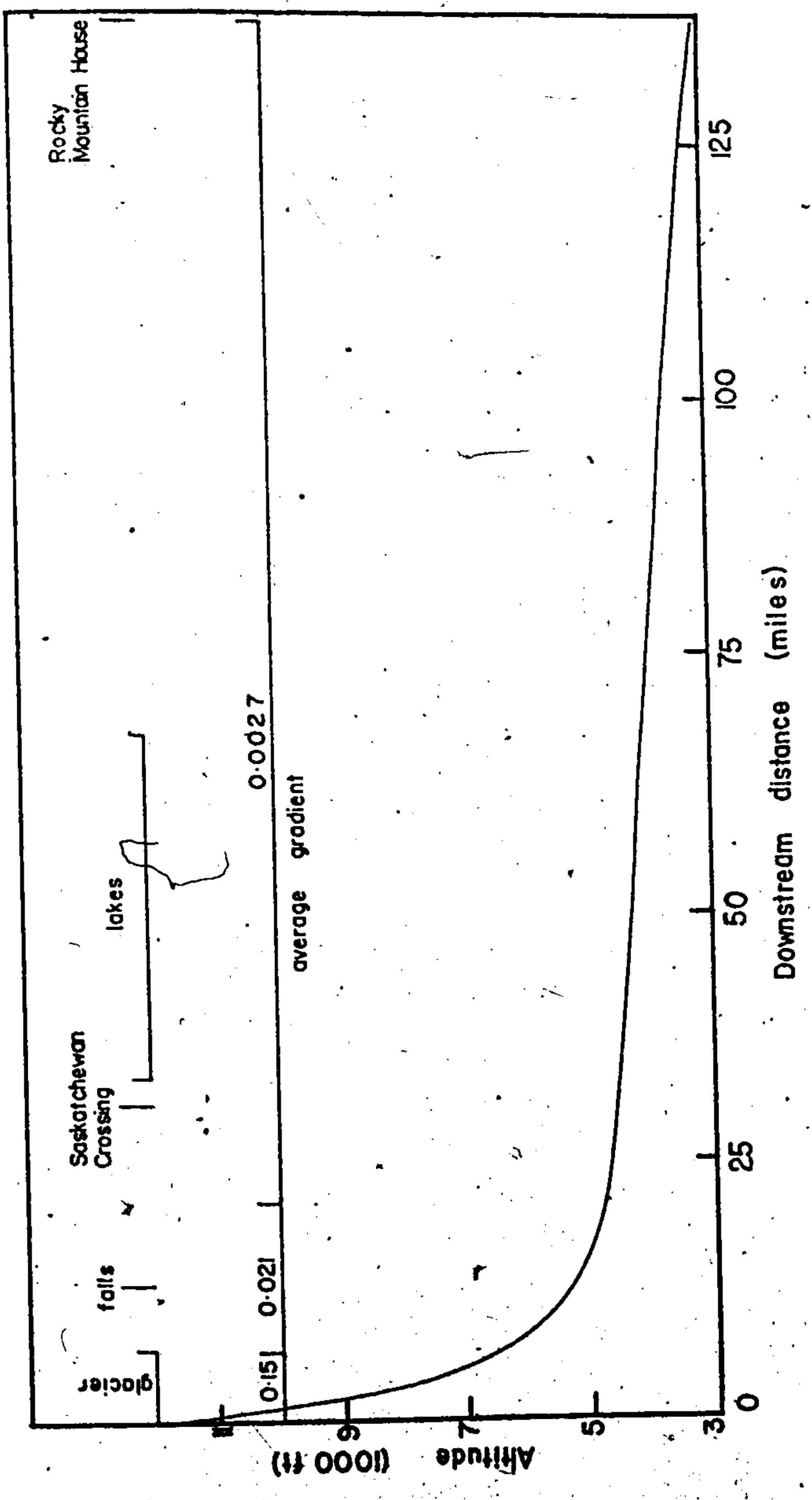


Figure 4.10 - Long profile of the North Saskatchewan River.

curves in Figure 4.6. Thirty per cent of the area of the North Saskatchewan basin lies below the 20th percentile of relief as contrasted to only 20% of the Athabasca basin.

CHAPTER V

HYDROLOGY OF THE RIVERS

5.1 Introduction

The general hydrologic regime of the streams in this study is illustrated in Figure 5.1 which shows the daily mean discharges for the Athabasca River in 1967 and 1968. This hydrograph exhibits two of the characteristics of mountain streams - a rapid increase in discharge when the winter's accumulation of snow begins to melt in the spring and considerable year to year variability of the discharge pattern. The hydrograph for 1967 approximates a flood hydrograph with superimposed fluctuations whilst that for 1968 is dominated to a greater extent by short-term events which mask the seasonal flood trend. The variability of the discharge during the summer months of both years is in contrast to the relative constancy during the winter periods.

The winter flow of the basins is considered to be 'base flow' in the sense that Pinder and Jones (1969) define the term. It is the residual flow from groundwater bodies which is maintained at a constant or slowly declining rate throughout a period of little or no groundwater recharge or surface runoff. The excess of discharge over the base flow during other

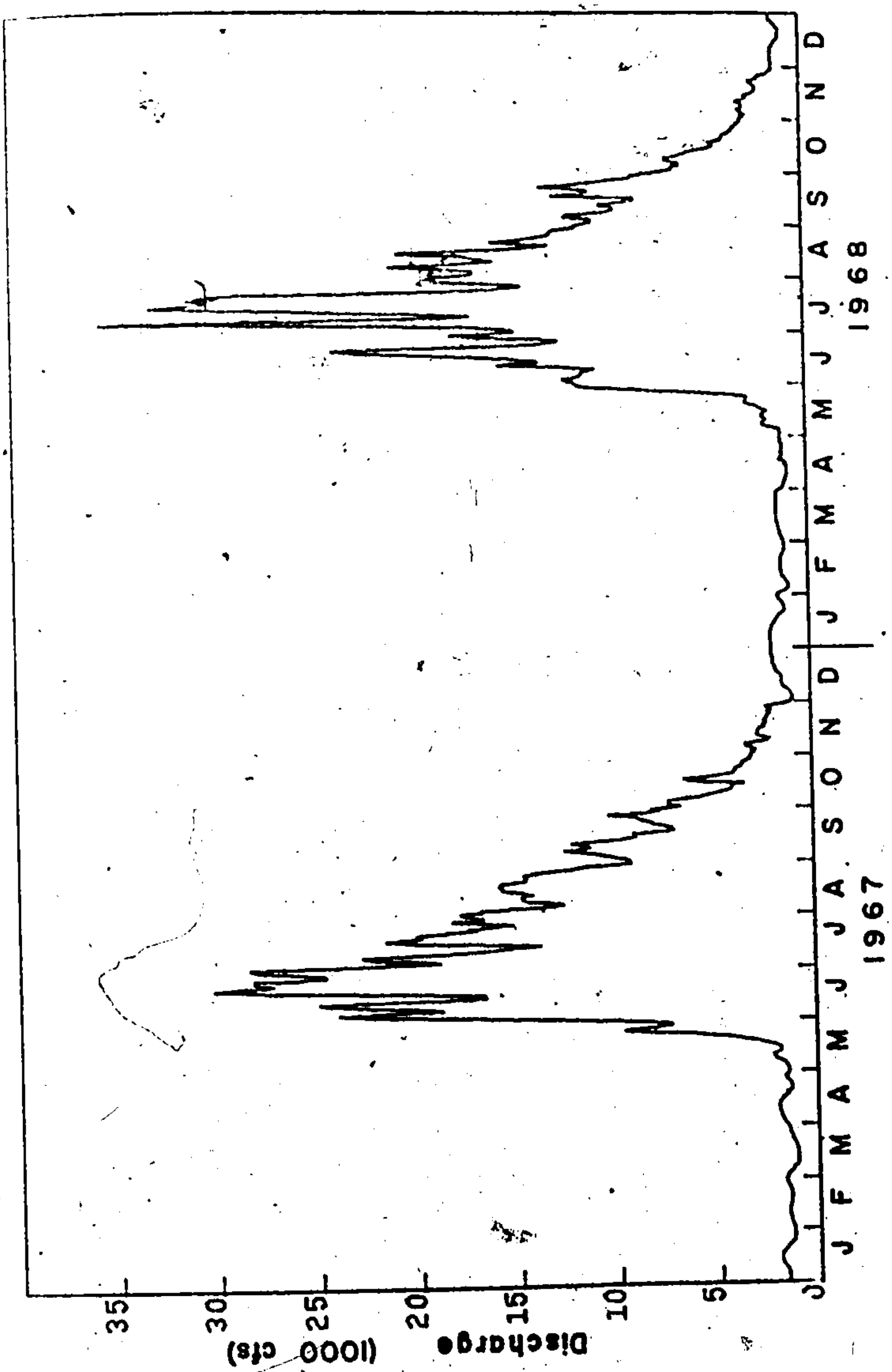


Figure 5.1 - Hydrograph of the Athabasca River at Hinton, 1967-68.

seasons is derived from the melting of accumulated snow and from precipitation incident on the basin. The pattern of snowmelt in the spring is the most important process determining the nature of the hydrographs of the basins in this study. Pipes et al. (1970) reach the same conclusion in a simulation study of the Fraser River in the Rocky Mountains of British Columbia. They also assume that the rate of snowmelt is proportional to the excess of the mean daily temperature over some threshold value and that there is a constant lapse rate. The physical interpretation of these assumptions is that snowmelt begins first in the lower parts of the basin and progresses upwards. The lower parts of the basin also become snow free first.

The implication of the upward retreating snowline concept is that as the melt season progresses the higher parts of a drainage basin will contribute proportionately more flow to the basin discharge than will the lower parts. Figure 5.2 shows the daily mean discharges of the North Saskatchewan River at Saskatchewan Crossing as a percentage of the same river's discharge at Rocky Mountain House for 1967 and 1968. The hydrograph of the river at Rocky Mountain House for the same period is shown in Figure 5.3. The area of the basin above Saskatchewan Crossing is 492 sq mi, or approximately 11% of the 4000 sq mi area above Rocky Mountain House. It is evident that the flow at Saskatchewan Crossing is disproportionately high except for short periods in January and April 1967 and March - April 1968. The pattern during 1967 shows that the proportion of the total dis-

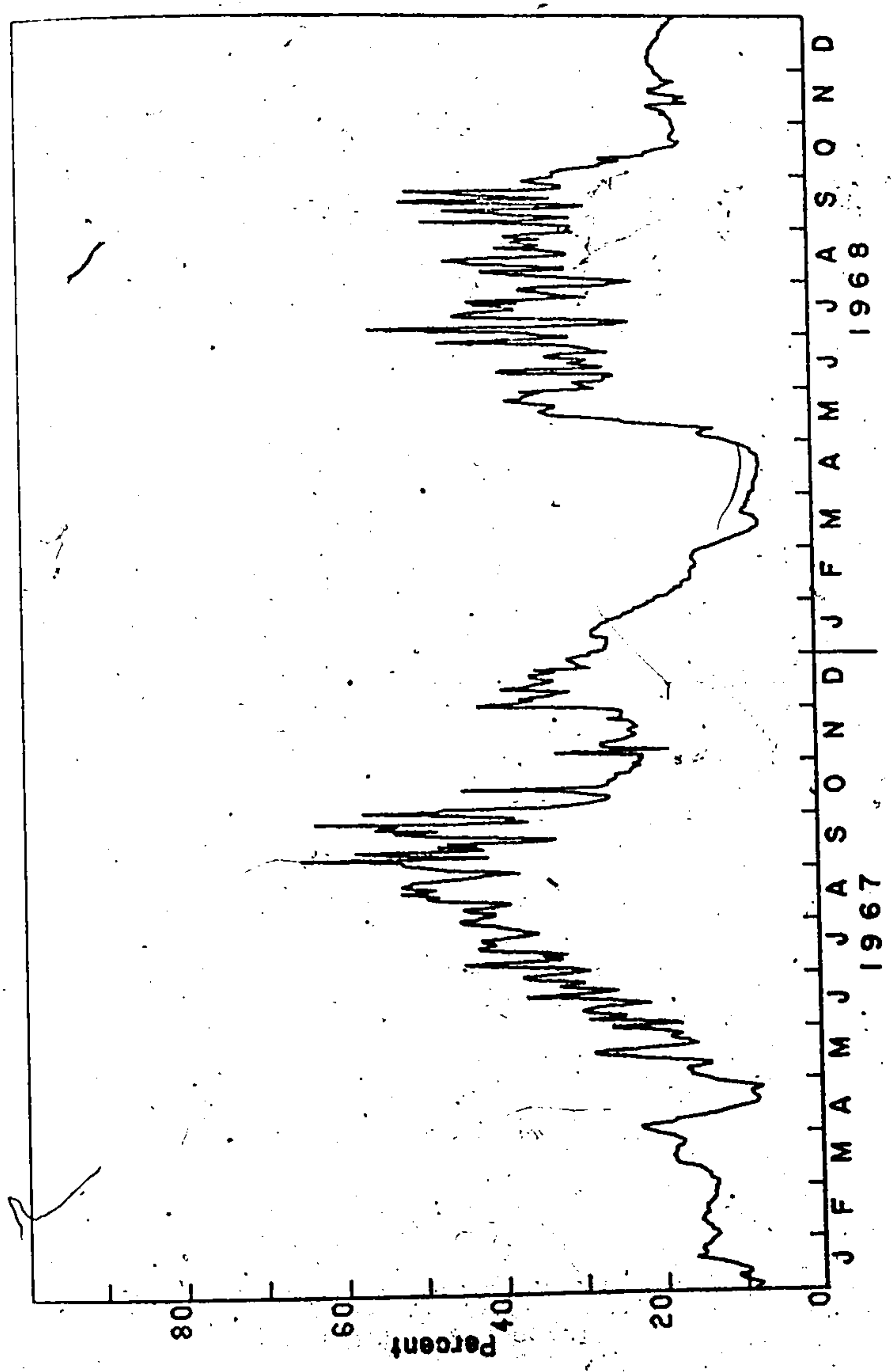


Figure 5.2 - Proportion of the discharge of the North Saskatchewan River at Rocky Mountain House contributed by the basin above Saskatchewan Crossing.

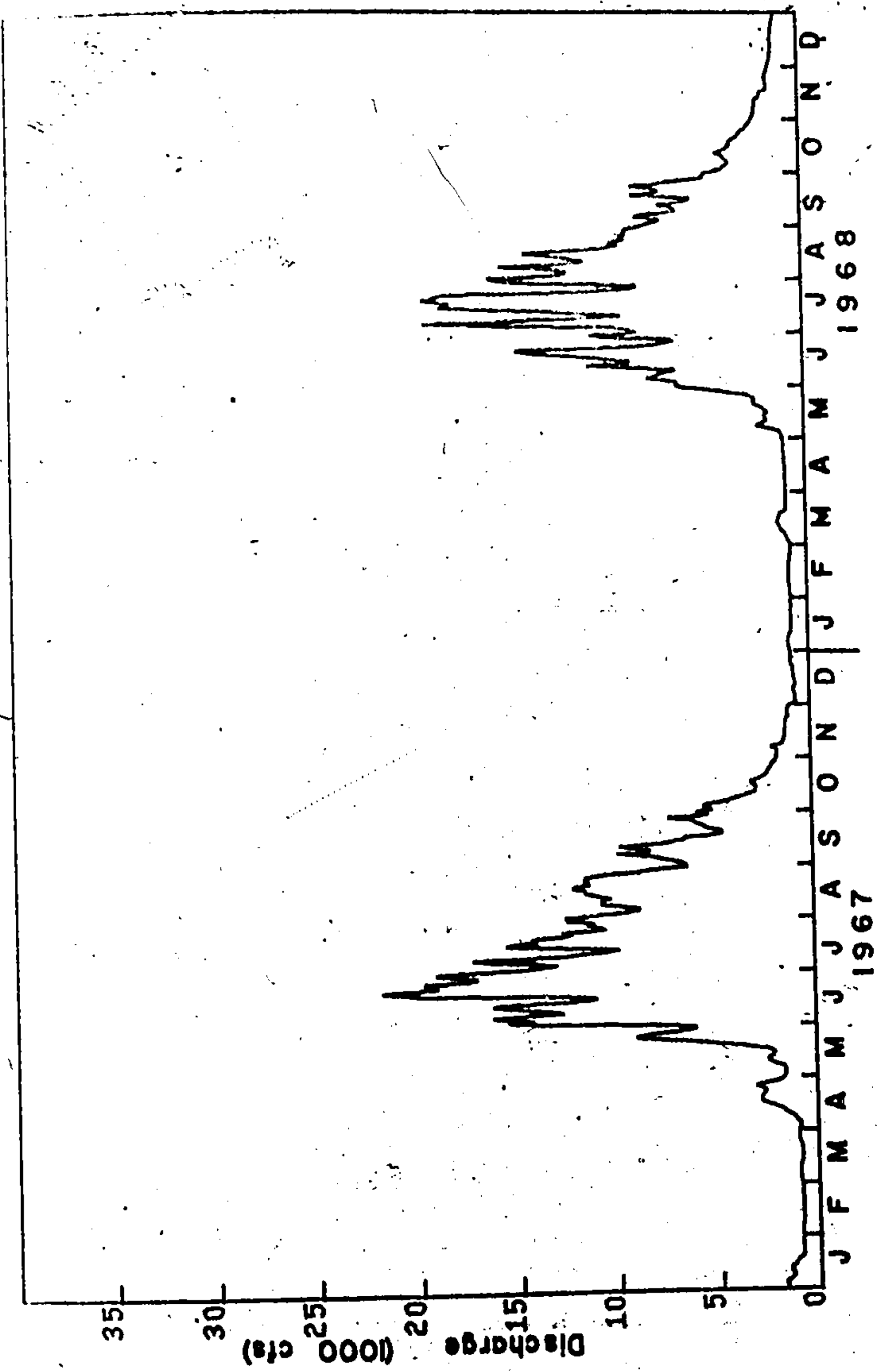


Figure 5.3 - Hydrograph of the North Saskatchewan River at Rocky Mountain House, 1967-68.

charge contributed by the upper section of the North Saskatchewan River basin increases steadily during the melt season. It peaks at approximately 60% of the total flow during September and October, a period of declining flow in the basin as a whole. During 1968, however, there is no such simple pattern. Throughout the melt season the upper section of the basin contributes some 35% of the total discharge. As is the case for the Athabasca River (see Figure 5.1) the discharge of the North Saskatchewan River in 1968 fluctuates considerably and does not have the characteristic flood hydrograph shape that it does in 1967. Figures 5.2 and 5.3 together suggest that while the upward retreating snowmelt process may well have been operating in 1967, it was not in 1968. The general pattern of melting in 1968 appears from Figures 5.2 and 5.3 to have been one of a steady, generalised melt over the entire basin for an extended time. Temperature differences from normal for the Rocky Mountain area as a whole are given in the General Synopsis of the Monthly Records (Meteorological Observations in Canada, Atmospheric Environment Service, Dept. of the Environment, Ottawa; monthly) and are shown for the melt seasons of 1967 and 1968 in Table 5.1.

Table 5.1

Differences of Temperature from Normal in the Rocky Mountains (°F)

	April	May	June	July	Aug.	Sept.	Oct.
1967	-5	-3	+1	+1	+5	+8	+1
1968	-2	-2	-1	-1	-1	0	-1

Although the difference between the two years is small the weather patterns of the two years were different. The rapid warming in May - June 1967 corresponds to the rising sections of the hydrographs of both the Athabasca and North Saskatchewan Rivers. Because this rise in temperature occurs during the time when the lower parts of the basin are already above the freezing point (see Figure 4.3) the effect is to greatly increase the rate of melt in these areas. Melting in the upper parts of the basins is not initiated by the rise in temperature in May and June, but begins later when the lower parts are snow free. In 1968 the rise in temperature was more gradual and the melt progressed in a more uniform manner over the entire basin.

Much of the runoff of the North Saskatchewan River basin in the latter part of the melt season is derived from the melting of glacier ice in the headwater areas around the Columbia and Wapta Icefields. The unusually high proportion of flow contributed by the North Saskatchewan basin above Saskatchewan Crossing in September 1967 is attributed to this source during a month when the mean temperature of the area was 8^{O}F above normal. The same period in 1968 shows neither abnormally high temperatures nor an abnormally high runoff. The effect of glacier melt on the hydrograph of the river at Saskatchewan Crossing can be considerable. The basin above Rocky Mountain House is sufficiently large that glacial meltwater is only a very small proportion of the discharge even during periods of rapid melting and the hydrograph at this station shows no marked effects caused by glacial melting.

The mean and standard deviation of the annual runoff for each of the eleven basins described in Chapter IV is shown in Table 5.2. This table also shows the years for which partial and complete discharge records are available for these basins. Although the periods of record are not equal for all stations it is apparent that the smaller basins have greater variability of runoff than do the Athabasca and North Saskatchewan River basins. This is to be expected because small local vagaries of climate affect the large basins to a proportionately much lesser extent. In general, however, the variation of annual runoff is largely due to general differences in climatic conditions from year to year. Figure 5.4 shows the annual runoff for the years 1961 - 1968 for the six stations which have continuous records available for this period. Years of high and low runoff from basins between Crowsnest Pass and the Yellowhead Pass are generally well correlated.

The annual runoff from any river basin is a function of both precipitation and evaporation. No estimates of annual evaporation are available for the Rocky Mountain area, and the lack of radiation data precludes any physical modelling of the process. Although evaporation and radiation measurements and studies have been undertaken in the Marmot Creek basin, which is an I.H.D. Research Watershed, the data are very limited (Storr, 1968; Water Survey of Canada, 1969). In an earlier study of the headwaters of the Saskatchewan River system Laycock (1957) concluded that the annual evaporation does not vary greatly along the

Table 5.2

Mean and Standard Deviation for the 6 Study Basins (inches) and the Period of Record Used

	Mean	Standard Deviation	Period of Record[3]
Crowsnest R.	16.40	1.77	(1949-1964), 1965-1968
Racehorse Ck.	15.45	-	(1966-1968)
Flathead R.	29.64	4.96	(1949-1951), 1952-1968
Oldman R.	12.22	2.94	(1949), 1950-1968
Elk R.	17.82	2.86	(1950-1952), 1953-1957, (1958-1959), 1960-1968
N.S.R., R.M.H.[1]	15.87	2.78	(1949-1953), 1954-1968
Marmot Ck.	17.15	2.61	(1962), 1963-1968
Sunwapta R.	42.52	-	(1949-1968)
Athabasca R.	22.32	2.01	(1961), 1962-1968
N.S.R., S.X.[2]	42.61	6.58	(1950-1966), 1967-1968
Bow R.	22.82	2.93	1949-1968

[1] North Saskatchewan River at Rocky Mountain House

[2] North Saskatchewan River at Saskatchewan Crossing

[3] Parentheses indicate partial records

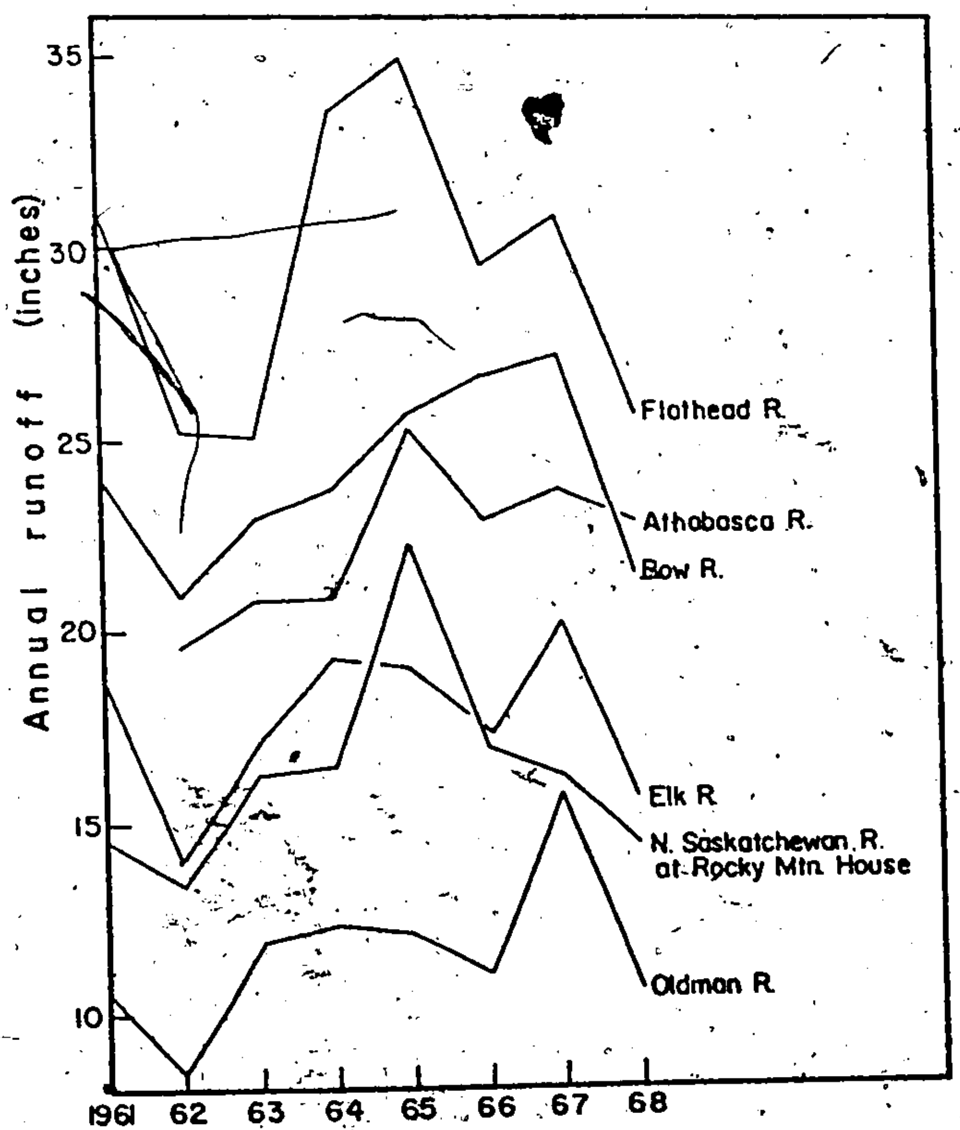


Figure 5.4 - Annual runoff from six basins, 1961-68.

mountain axis. Storr et al. (1970) measured the daily evaporation rate in the Marmot Creek basin by energy budget methods during July 1967 and they provide a mean daily evaporation of 4.5 mm. They extrapolate this value to an annual evaporation of 560 mm (22") by assuming that the July rate is a maximum and that the mean monthly evaporation through the year is distributed normally. Whilst there appears to be little justification for this last assumption, Storr et al. (1970) quote an earlier estimate of the annual evaporation calculated from water budget methods of 18". The Thornthwaite (1948) calculations for Banff give a figure for the annual actual evapotranspiration of 15". These three estimates, obtained by different methods, are not widely disparate. The mean annual precipitation at Banff is 18.5", only 0.5" in excess of the water balance estimation of the evapotranspiration at Marmot Creek. The Thornthwaite calculations for Jasper show that there is a slight water deficit in that area. These figures suggest that little of the streamflow of the basins traversing the Front Ranges originates in their lower sections. The Oldman, Bow, North Saskatchewan and Athabasca Rivers drain the Main and Front Ranges between the Snake Indian River and Crowsnest Pass, and there are continuous discharge records for them available since at least 1961. The mean annual runoff for these river basins is shown in Table 5.3. The precipitation must exceed the evaporation in the upper parts of these basins by a considerable amount in order to yield this runoff because little water is contributed by the parts of the basins in the Alberta Plains rainshadow. Table 5.3 also shows the proportion of each basin lying to the east of the Front Ranges. It is evident that most of the runoff of these streams comes from the mountainous sections of their basins because there is an inverse correlation between mean runoff and the proportion of the basin in the non-contributing zone. The proportion of the area of the basins occupied by lakes or by icefields or permanent snowfields (with the exception of the Sunwapta River) is less than 1%.

Table 5.3

River basin	Oldman	Bow	North Sask.	Atha.
Mean runoff (ins)	12.2	22.8	15.9	22.3
Area in Alberta Plains (%)	17	0	16	3

The characteristics of the runoff of the eleven basins described in Chapter IV are considered more fully in the sections following. The important runoff generating processes and the contributing areas of the basins at various times of the year have significant effects on the nature of the geomorphic phenomena in the area.

5.2 Spatial Variations in Runoff Patterns

Table 5.2 shows the years between 1949 and 1968 for which complete or partial discharge records for the eleven basins in this study are available. The correlation matrix of daily discharges is shown in Table 5.4. All correlations are statistically significant ($p < 0.001$) because of the large number of data pairs in each. The smallest number of pairs is 683 between Racehorse Creek and each other stream. All other correlations are based upon more than 1000 pairs. Very high correlations exist between streams in the same vicinity. This trend is especially noticeable in the Crowsnest Pass area which includes the Crowsnest, Oldman, Elk and Flathead Rivers and Racehorse Creek. Three groups can be established on the basis used by Davis and Coulson (1967), that is that all streams within a zone be intercorrelated with coefficients greater than 0.60. The three groups are:

1) the Crowsnest Pass group,

2) a group of larger streams draining the Main and Front Ranges which includes the Bow, North Saskatchewan (at both Saskatchewan Crossing and Rocky Mountain House) and Athabasca Rivers,

and 3) the Sunwapta River which is a high altitude glacier melt stream.

This grouping excludes Marmot Creek, which is small (3.63 sq mi) and

Table 5.4

Correlation of Daily Flows for Eleven Basins

	Crowsnest R.	Oldman R.	Racehorse Ck.	Bow R.	Marmot Ck.	N.S.R., S.X.[1]	N.S.R., R.M.H.[2]	Sunwapta R.	Athabasca R.	Elk R.	Flathead R.
Crowsnest R., Frank	1.0 1.0	.937 (5203)	.979 (683)	.610 (5343)	.807 (2214)	.262 (3527)	.500 (4713)	-.094 (3029)	.563 (2476)	.865 (4682)	.938 (4713)
Oldman R., Waldrons Cross.		1.0	.962 (683)	.662 (7032)	.849 (2455)	.268 (3529)	.554 (6030)	-.081 (2918)	.570 (2832)	.860 (6138)	.877 (6210)
Racehorse Ck, south			1.0	.592 (683)	.796 (683)	.241 (683)	.400 (683)	-.258 (520)	.409 (683)	.831 (683)	.948 (683)
Bow R., Banff				1.0	.861 (2455)	.790 (3529)	.895 (6030)	.387 (3029)	.948 (2832)	.863 (6138)	.612 (6210)
Marmot Ck.					1.0	.519 (1711)	.749 (2455)	.095 (1124)	.768 (2455)	.926 (2455)	.740 (2455)
N.S.R., S.X.[1]						1.0	.821 (3324)	.838 (2778)	.894 (1896)	.475 (3313)	.177 (3324)
N.S.R., R.M.H.[2]							1.0	.503 (2695)	.954 (2832)	.698 (5665)	.467 (6030)
Sunwapta R.								1.0	.596 (1308)	.064 (2667)	-.175 (2695)
Athabasca R., Hinton									1.0	.768 (2832)	.489 (2832)
Elk R., Natal										1.0	.858 (5789)
Flathead R., Flathead											1.0

Number of data pairs for each correlation are given in parentheses.

[1] North Saskatchewan River at Saskatchewan Crossing.

[2] North Saskatchewan River at Rocky Mountain House.

which is located in the Foothills to the south of the Bow River. Its discharge correlates well with that of streams in both of the first two groups above because it is located in the area between the first, more southerly and the second, more northerly. The other basins with the exception of Sunwapta River are all sufficiently large that the correlation of discharges between them is a result of general climatic conditions in their respective areas and small, local weather variations do not have a profound effect on their discharges. Widespread climatic conditions affecting either of the first two groups of basins affect Marmot Creek basin also and give rise to the observed correlations. The Sunwapta River at Columbia Icefield is fed almost entirely by the melting of snow and ice from the Athabasca Glacier and is in a different hydrologic situation from the other ten streams.

The mean annual runoff for each of the eleven basins is influenced by the position of the basin within the Rocky Mountains. Meteorological records in the area suggest that altitude is the most important factor in the variation of precipitation and temperature within the mountains (v.s., Section 4.1.2). The correlation matrix of ten variables relating to the spatial location and relief configuration of each basin and its mean annual runoff is shown in Table 5.5. The last four variables in the matrix, H_{100}, H_{75}, H_{50}, and H_{25} are the altitudes below which 100%, 75%, 50% and 25% of the basin area lies respectively. H_{100} is thus the

Table 5.5

Correlation Matrix of Runoff and Spatial Variables

	Mean Annual Runoff	Gauge Altitude	Latitude	Longitude	Area	Fraction of Forest Cover	H_{100}	H_{75}	H_{50}	H_{25}
Mean Annual Runoff	1	0.64	0.38	0.69	-0.22	-0.71	0.35	0.77	0.79	0.74
Gauge Altitude		1	-0.22	0.25	-0.72	-0.80	-0.08	0.67	0.79	0.91
Latitude			1	0.85	0.65	-0.38	0.83	0.63	0.50	0.26
Longitude				1	0.31	-0.54	0.70	0.75	0.71	0.55
Area					1	0.35	0.60	-0.06	-0.24	-0.49
Fraction of Forest Cover						1	-0.47	-0.90	-0.92	-0.89
H_{100}							1	0.64	0.50	0.22
H_{75}								1	0.97	0.86
H_{50}									1	0.95
H_{25}										1

$n = 11$

maximum altitude within a basin. Several features of the spatial distribution of the basins are apparent. The general SE - NW trend of the southern Rocky Mountains is reflected in the high positive correlation ($r = 0.85$) between the latitude and the longitude of the gauging stations. All basins with the exception of Marmot Creek extend upward to the Continental Divide. Stations at lower altitudes are further from the Divide and thus gauge larger basins. This fact explains the inverse correlation ($r = -0.72$) between gauge altitude and basin area. The Continental Divide generally increases in altitude northward away from the 49th Parallel and thus the latitude and maximum altitude are correlated ($r = 0.83$). The high correlations ($r > 0.86$) between the altitudes of the basin area quartiles (H_{75} etc.) is a consequence of the fact that the altitudinal distributions of all of the basins are similar as shown by the hypsometric analysis in Section 4.2.

The variable with the highest correlation with the mean annual runoff of the basins is the altitude of the 50th percentile of the basin area, H_{50} ($r = 0.79$). Stepwise multiple linear regression shows that the partial correlation coefficients of all other variables and the mean annual runoff are insignificant ($|r| < 0.30$). The variation in H_{50} thus explains some 63% of the variation in mean annual runoff and the associated standard error of the estimate is 8.1". Table 5.5 also shows that the percentage of the basin area that is forest covered is inversely correlated ($r = -0.92$) with H_{50} as is to be expected in an area throughout which the treeline is at approximately the same altitude. The dependence of the mean annual runoff on this measure of the altitudinal position of a basin is thus not only a function of the increase of precipitation with altitude but also of the decreasing potential for evapotranspiration caused by a decreasing amount of forest vegetation.

5.3 Temporal Variations of Runoff

In the previous section it was demonstrated that the altitude of a drainage basin is the most important spatial variable in determining its mean annual runoff in the study area, and that climatic influences predominate the physical processes of runoff generation. The effects of climatic conditions on the hydrology of the Athabasca and North Saskatchewan River basins will be examined in more detail. These two basins were chosen because there is a meteorological station located in the vicinity of the gauging station and because there are water quality records available for them. Any conclusions concerning the temporal variation of discharge in these basins can therefore be incorporated in a discussion of their role in the solutional erosion of the Rocky Mountain region.

The hydrologic regime of the streams in the study area is dominated by the annual snowmelt event. Figure 5.5 shows the power spectrum of the daily discharges of the Athabasca River at Hinton for the 1968

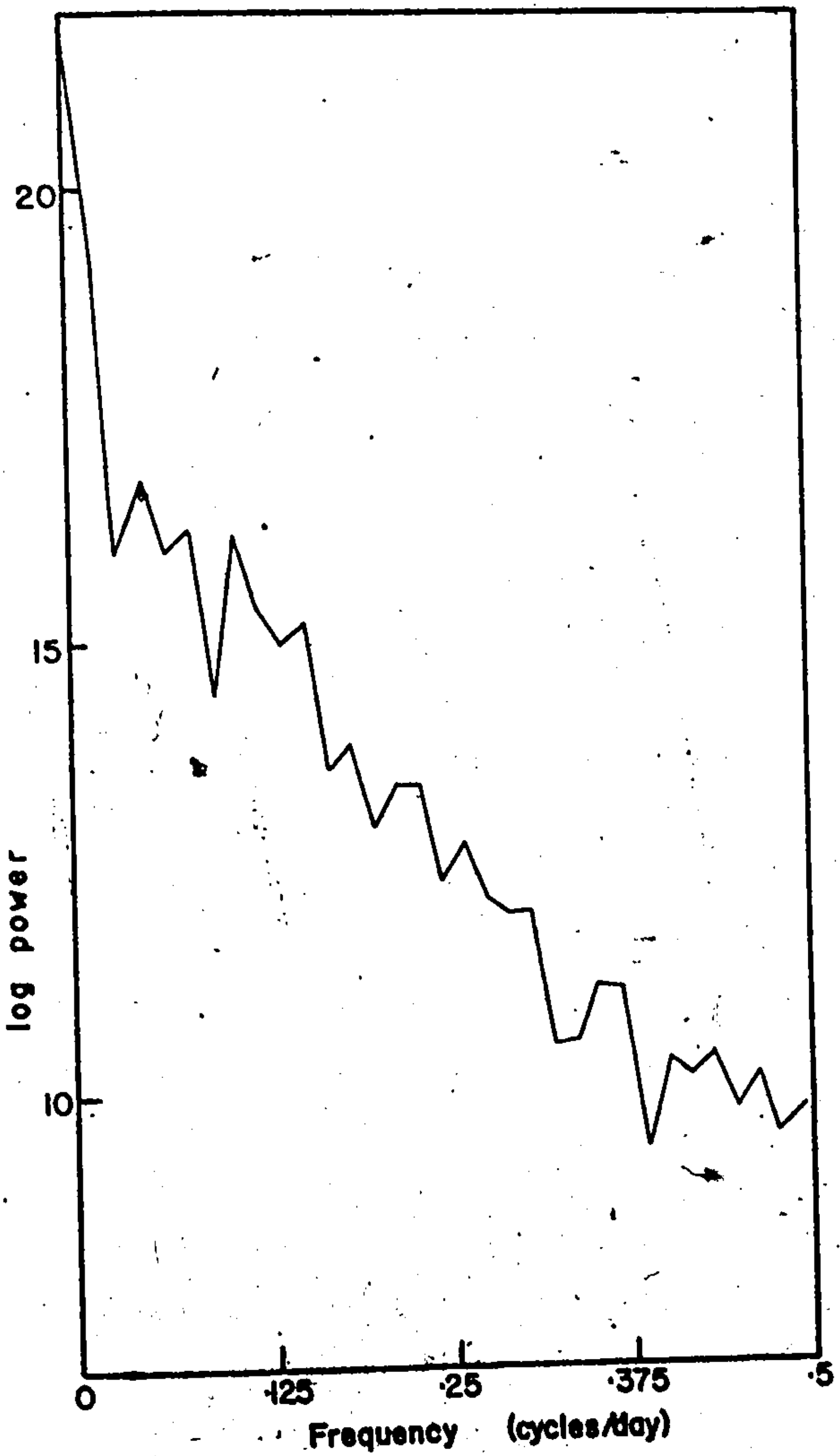


Figure 5.5 - Power spectrum of daily discharges of the Athabasca River at Hinton, 1968.

calendar year computed with the BMDX92 program (Dixon, 1972). Only the zero frequency peak is distinct which shows that over the yearly period the only significant periodic component is that caused by annual snowmelt. If an Ormsby prefilter is constructed to pass only those periodic components with wavelengths of between approximately 7 and 60 days the power spectrum of the filtered series shows the presence of cyclic components of all such wavelengths (Figure 5.6). There are no distinct peaks. M.-k. Woo (Dept. of Geography, McMaster Univ., pers. comm.) has noted the same phenomena in the spectra of daily temperatures in the Coast Ranges of British Columbia. Inspection of the hydrograph of the Athabasca River (Figure 5.1) shows that there are short-term fluctuations superimposed on the annual cycle. These fluctuations appear to have periods of between some 6 and 15 days. Because the BMDX92 estimation of power spectra is discrete and because the range of frequencies of these short-term cycles spans several of the frequency classes constructed by the program this particular technique is ill suited to the purpose of assessing the relative importance of such components.

The flow of the North Saskatchewan River at Saskatchewan Crossing in 1968 comprises between 6% and 55% of the flow of the river at Rocky Mountain House. Cross-spectral analysis can be used to estimate the amount of the variance of each cyclic component at the latter station attributable to that at the former. Figure 5.7 shows the coherence and lag between the discharge series at the two stations. For all except

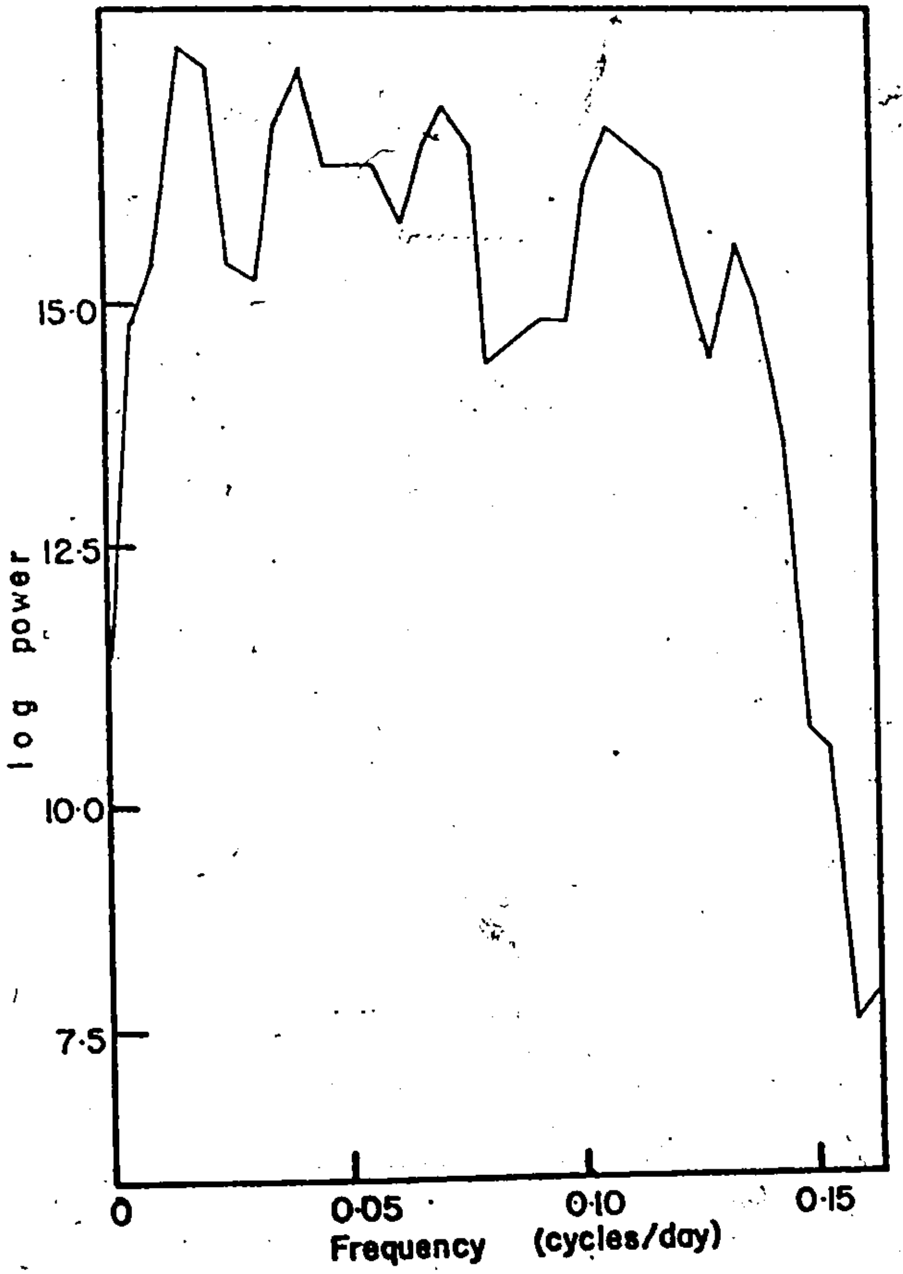
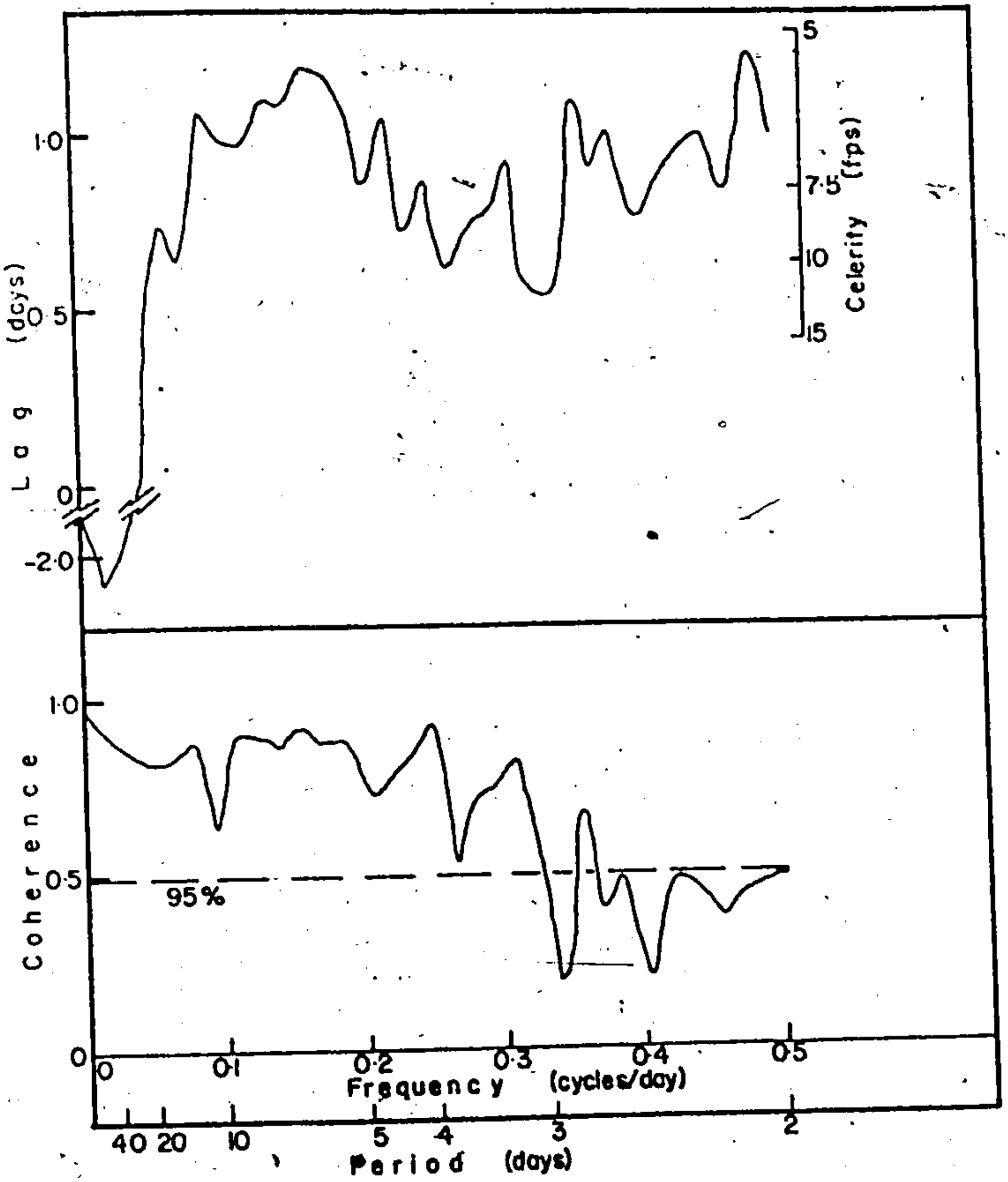


Figure 5.6 - Filtered power spectrum of daily discharges of the Athabasca River at Hinton, 1968.



<u>Figure 5.7</u> - Coherence and lag of cross spectrum of daily discharges of the North Saskatchewan River at Rocky Mountain House and at Saskatchewan Crossing, 1968. Confidence limit from Granger and Hatanaka (1964, p. 79).

the very short cyclic components of discharge (with periods of less than 4 days) over 50% of the variance at Rocky Mountain House can be 'explained' by the variance of flow at Saskatchewan Crossing. The lag between the two gauging stations is generally of the order of one day, representing wave velocities over the 105 mi distance of between 6 and 12 fps. This range of velocities is in keeping with those commonly measured at both stations (K. Davis, District Engineer, Inland Waters Directorate, Calgary, pers. comm.). The negative lag at frequencies of under 0.05 cycles/day (corresponding to periods of 20 days or more) represent the fact that low frequency components arise from the annual snowmelt event which increases flow in the lower parts of the basin first. Frequencies above 0.05 cycles/day represent short term fluctuations of discharge arising from the passage of weather systems across the entire basin. Woo (1972) has observed that such systems cause short term fluctuations in the thermographs of stations in British Columbia.

The discharge of streams in the Rocky Mountain area is a response to climatic conditions which can be regarded as a 'forcing function' in time series models. There are, however, two separate components of such models in this instance. The first of these is the general, annual snowmelt event controlled by the annual cycle of temperature within the basin and the second is the presence of short term fluctuations of no well defined period which are controlled by the passage of separate weather systems across the basin. The two components should be analysed separately. The annual cycle of temperature can be represented well by a sine (or cosine) function with a period of one year. The Athabasca River basin provides an example, with both meteorological and discharge data available for the Hinton station. The daily minimum temperature and the fitted sine function for 1967 are shown in Figure 5.8. The parameters of the function

$$T = \overline{T} + a\sin(t+\phi) \qquad (5.1)$$

where T is daily temperature, the overbar denotes the annual mean, t is time and a and ϕ are the amplitude and phase parameters of the sine curve are shown in Table 5.6 for the daily minimum, maximum and mean temperatures for 1961 to 1968. This table also shows the percentage of the variance of the yearly record explained by the fitted curve and the time at which the yearly cycle crosses the freezing point.

The annual discharge cycle cannot be adequately described by a trigonometric function. Because the cycle has the characteristic shape of a flood event the function

$$Q = Q_b + (t-\phi)^n e^{-k(t-\phi)} \qquad (5.2)$$

where Q is the daily discharge, Q_b represents an assumed constant base flow, t is time and ϕ, n and k are fitted parameters is used. The parameters represent various features of a flood hydrograph. ϕ is the time from the time origin at which the flood rise begins, n describes the nature of the rising limb of the hydrograph and k is the recession constant of of the falling limb. Q_b, ϕ, n and k were estimated by the use of a

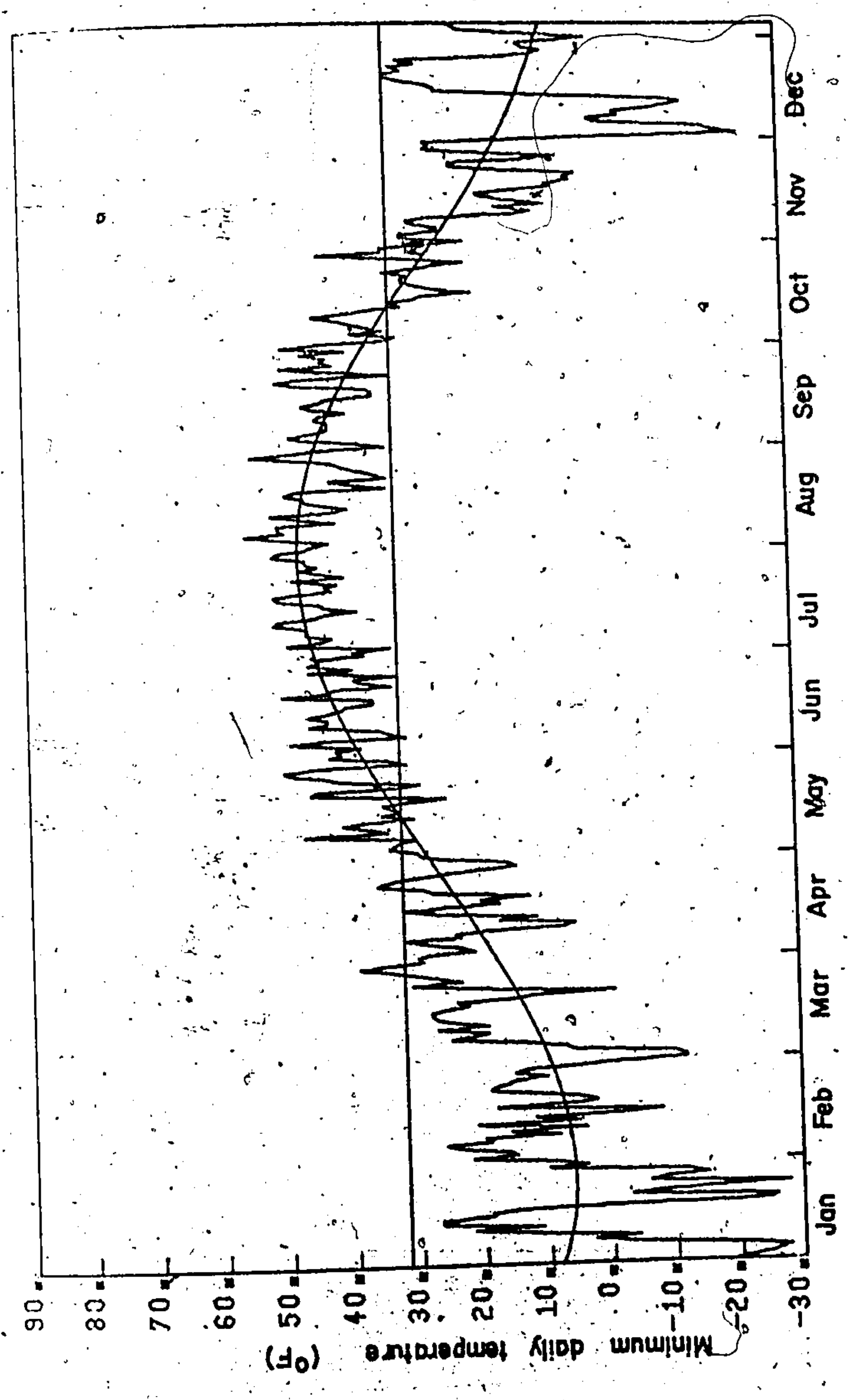


Figure 5.8 - Daily minimum air temperatures and fitted sine curve for Hinton, 1967.

Table 5.6

Parameters of Annual Temperature Sine Function

	Daily Maximum					Daily Minimum					Daily Mean				
	$\overline{T}$ °F	a	Ø rad.	Day of Crossing Freezing Pt.	Exp. Var. %	$\overline{T}$ °F	a	Ø rad.	Day of Crossing Freezing Pt.	Exp. Var. %	$\overline{T}$ °F.	a	Ø rad.	Day of Crossing Freezing Pt.	Exp. Var. %
1961	51.0	25.4	4.57	50.5	67.8	25.4	20.7	4.56	119.4	63.5	38.2	23.1	4.56	84.2	70.8
1962	50.1	22.9	4.31	61.3	65.9	25.3	20.7	4.24	138.2	60.7	37.7	21.8	4.28	101.2	68.4
1963	50.2	24.9	4.45	58.6	65.2	26.4	20.4	4.40	125.6	59.6	38.3	22.7	4.43	91.4	66.7
1964	47.5	24.7	4.54	62.2	64.9	24.4	17.9	4.50	129.7	49.7	35.9	21.3	4.52	91.8	61.7
1965	47.2	25.6	4.45	69.6	60.7	25.4	22.5	4.33	130.8	58.5	36.3	24.0	4.40	99.3	63.1
1966	45.7	25.7	4.50	71.0	64.0	23.9	23.3	4.43	128.3	64.9	34.8	24.5	4.47	98.9	68.8
1967	49.4	26.3	4.27	75.2	73.4	26.5	20.7	4.27	132.6	65.3	37.9	23.2	4.27	102.0	74.6
1968	47.5	23.6	4.53	60.2	60.3	24.2	20.5	4.45	129.6	60.4	35.9	22.0	4.49	94.0	63.9

non-linear curve fitting program using the Marquardt (Marquardt et al., 1961) algorithm. The objective function minimised was chosen to be the sum of squared deviations in order to obtain the best possible fit to the high discharge section of the hydrograph. Figure 5.9 provides an illustration of the fitted curve and daily hydrograph for the Athabasca River in 1967. Table 5.7 shows the parameters and percentage of explained annual variance for this river for the period 1961 to 1968. The mean value for n is 3.09 and the 95% confidence limits of this estimate are $2.79 < n < 3.39$. Wooding (1965) shows that the depth of the outflow stream of a simple catchment is proportional to the elapsed time over the period between the time of concentration of the basin and the cessation of input for the case of uniform precipitation. Analysis of measured stage and discharge data for the Athabasca River from Water Survey of Canada records shows that $Q \alpha H^{2.66}$ where Q is discharge. In this case the Wooding model implies that the discharge should be proportional to the 2.66 power of the time elapsed since the beginning of the input. This estimate is similar to that derived above. The form $Q \alpha e^{-kt}$ is often used to describe the falling limb of a hydrograph under conditions of a depleting 'reservoir' - either groundwater or soil zone storage. The curve described by equation 5.2 is thus a reasonable approximation to the expected form of a flood hydrograph and the correspondance of the parameter n with Wooding's theoretical prediction suggests that the annual snowmelt event can be regarded as an analog of a steady precipitation over the basin maintained

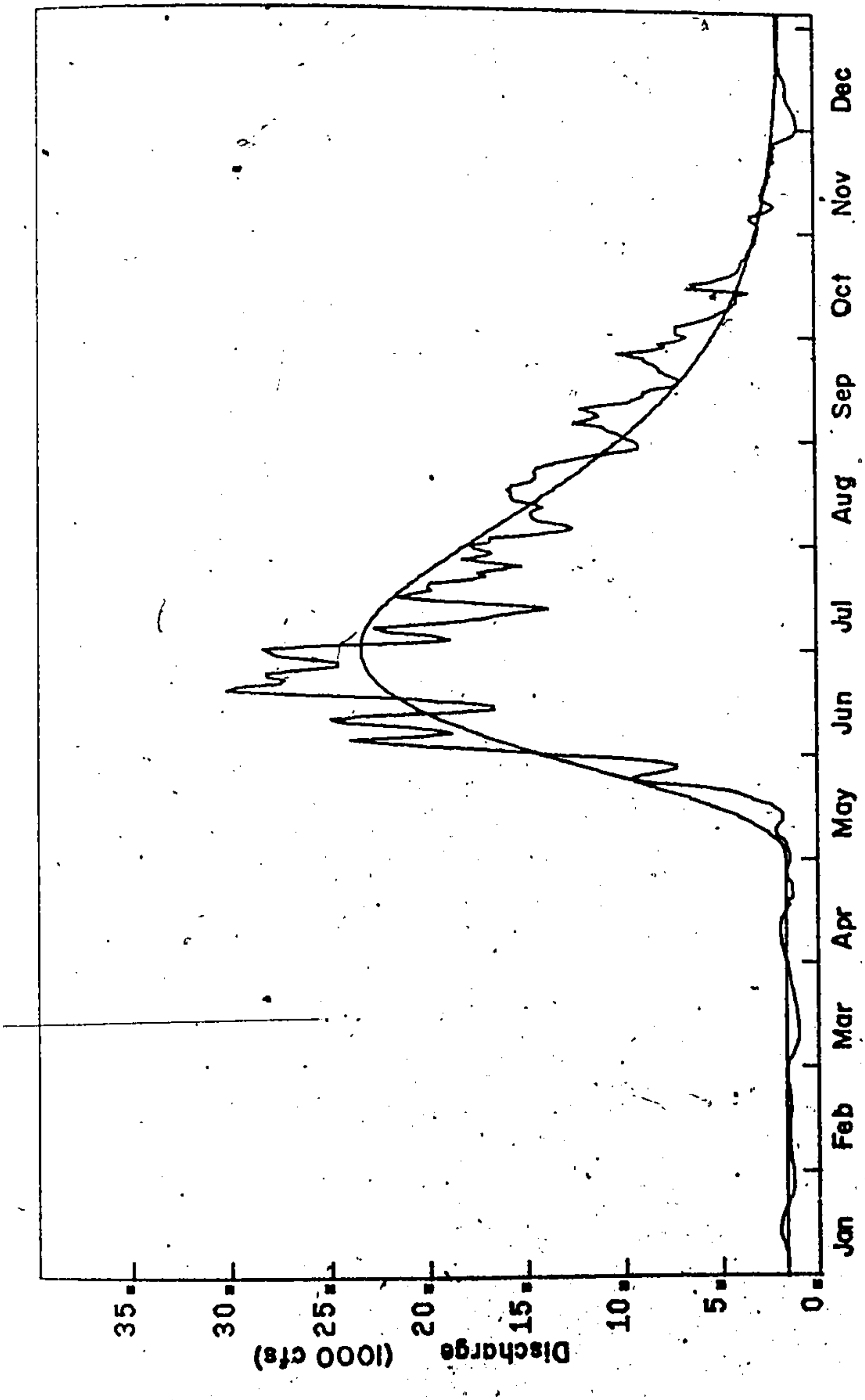


Figure 5.9 - **Hydrograph and fitted function for the Athabasca River at Hinton, 1967.**

Table 5.7

Parameters of Annual Discharge Function

Year	Q_b cfs	n	k	ϕ days	Day of Maximum	Q_{max} cfs	Exp. Variance
1961	1662	3.07	-.047	108.6	173.9	18995	76.9
1962	1034	3.06	-.046	117.2	183.7	18789	92.8
1963	1456	3.03	-.045	113.8	181.1	18191	90.6
1964	1965	3.33	-.062	125.7	179.4	22604	86.2
1965	1734	3.12	-.047	118.2	184.6	23106	91.8
1966	915	2.91	-.037	105.2	183.8	18208	89.2
1967	1644	3.20	-.052	118.8	180.3	23297	92.8
1968	1483	3.01	-.041	116.0	189.4	21843	89.6

for a time longer than the time of concentration of the basin.

For both the discharge and temperature records the annual cycle generally accounts for some 50% to 75% of the total annual variance. The correlations between the parameters of the annual temperature functions and those of the annual discharge functions are generally not significant (Table 5.8) and are too low for the relation between them to have any great predictive power. The correlation between the amplitude of the annual cycle of daily minimum temperature and the time of the beginning of the rise of the snowmelt hydrograph is significant ($r = -0.71$). This suggests that it is indeed the initiation of steady above-freezing temperatures that begins the general melting of the accumulated snow cover of these mountain basins.

The short-term variations of flow are less easily analysed. There are fluctuations with periods of between approximately 6 and 20 days. Although they and the annual cycles have a common cause - the passage of weather systems over the basin - they do not necessarily arise from basin-wide events. Spectral analysis of the discharge records for the two gauging stations on the North Saskatchewan River has shown that, in general, such fluctuations of discharge flow downstream at approximately the same velocity as the water. In this case the fluctuations must largely arise above Saskatchewan Crossing. Meteorological records at one site at the mouth of the basin cannot be expected to yield a high level of statistical explanation of the discharge variance. Lagged

Table 5.8

Correlation Matrix of Parameters for Annual Cycles of Daily Temperature and Discharge

(see equations 5.1 and 5.2 for definition of parameters)

		Q_b	n	k	Ø
Maximum	$\bar{T}$	.13	.12	-.19	.00
	a	.30	.14	-.10	-.22
	Ø	.26	-.12	.07	-.25
	t_{32}[1]	-.14	.10	.01	.16
Minimum	$\bar{T}$	.24	.22	-.22	.15
	a	-.60	-.74	.80	-.71
	Ø	.34	-.00	-.07	-.26
	t_{32}[1]	-.30	.17	-.10	.50
Mean	$\bar{T}$	.17	.15	-.20	.05
	a	-.30	-.50	.55	-.66
	Ø	.30	-.07	.01	-.26
	t_{32}[1]	-.41	-.05	.14	.19

[1] t_{32} refers to the day of the year on which the annual trend of temperature reaches 32°F.

$r_{5\%} = .707$

$r_{1\%} = .834$

cross-correlations of the residuals from the annual temperature and discharge cycles show that the coefficients are generally very small. Figure 5.10 illustrates this for the Athabasca River in 1966. The best correlation (r = 0.23) is obtained at a lag of 3 to 4 days, but only some 5% of the residual variance is explained. The annual cycle for this year explains 89.2% of the annual variance and the extra reduction achieved by the cross-correlation is only 0.5%. Seasonal or short term variations in precipitation do not explain a significant fraction of the variance of the discharge record.

If short-term cycles of different periods show different lags on the meteorological data, cross-correlation is not a good technique to investigate the lag structure because it can only estimate the best lag for all periodicities. Spectral analysis can consider each frequency component (or each of a number of classes thereof) separately. Figure 5.11 shows the coherence and lag spectrum for the discharge and mean temperature residuals for the Athabasca River in 1966. The coherence is generally low, exceeding the 95% confidence limit for only two frequency bands. These bands correspond to periodicities of approximately 18 and 4.5 days. The lag spectrum follows no simple pattern and the estimates are not significantly different from zero. Because of the non-significant coherences the lag spectrum cannot be regarded as a good estimate. The sign reversals may be an expression of the fact that weather systems can cross the basin in different directions and affect

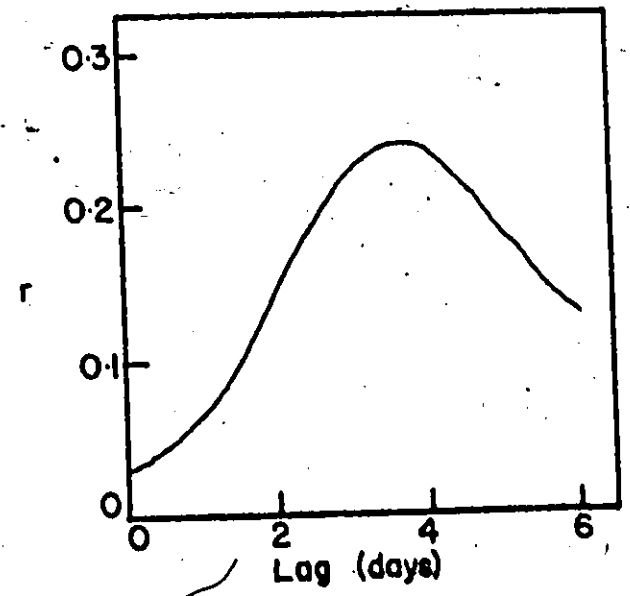


Figure 5.10 - Lag correlation of daily minimum air temperature residuals and daily discharge residuals for the Athabasca River at Hinton, 1967.

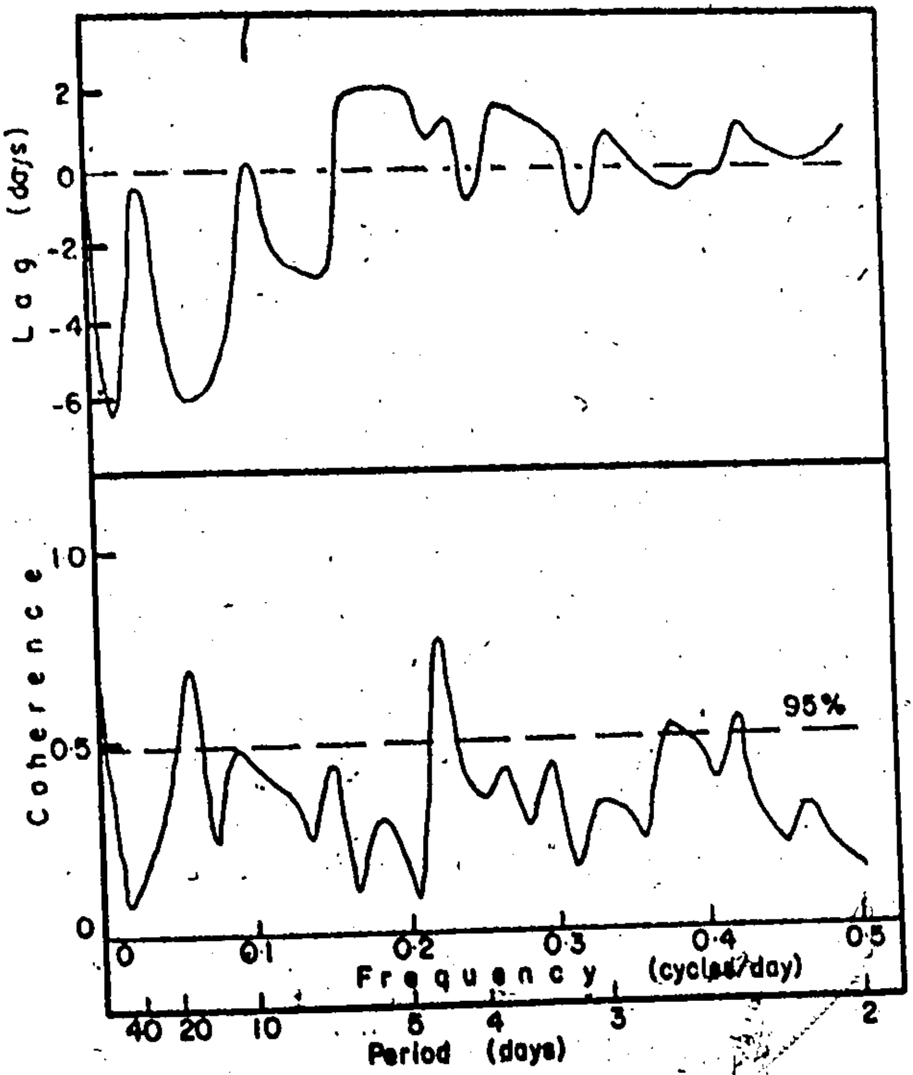


Figure 5.11 - Coherence and lag of cross spectrum of daily mean air temperature residuals and daily discharge residuals for the Athabasca River at Hinton, 1967. Confidence limit from Granger and Hatanaka (1964, p. 79).

the meteorological station at the mouth either before or after the upper zones which contribute much of the runoff during the summer months. It is also likely that small, local disturbances affect higher parts of the drainage system without affecting the meteorological station at the mouth of the basin which is to the east of the mountain ranges.

5.4 Summary

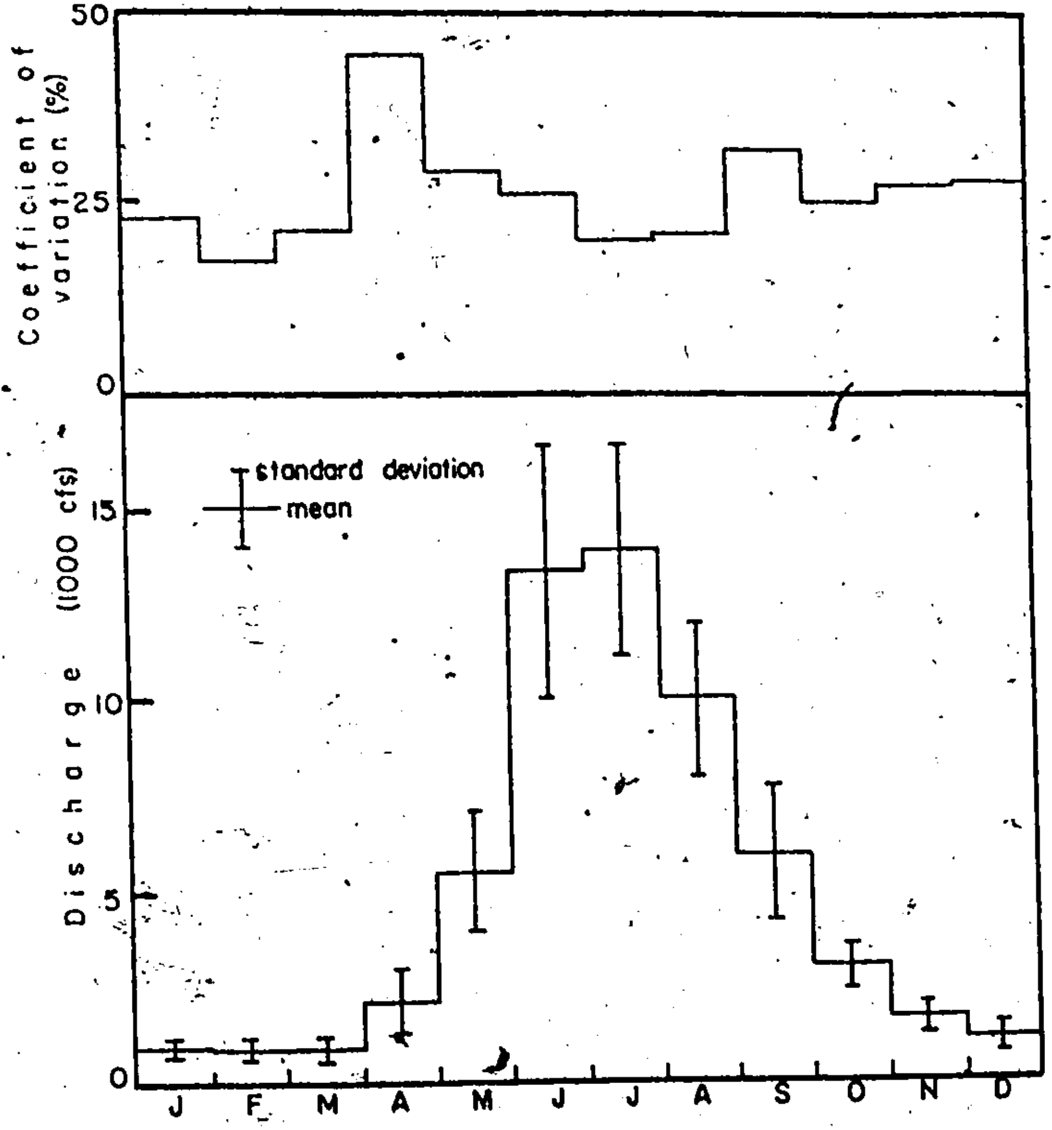
The discharges of the streams in the Rocky Mountain area is a response to the prevailing climatic and weather systems of the area. The annual cycle of snowmelt runoff is the most significant feature of the hydrographs and accounts for between 77% and 93% of the annual variance. The fluctuations of discharge superimposed on the annual trend are evidently a response to small, localised weather systems within the larger basins. Meteorological data are too sparse to provide any basis for physical modelling of the discharge patterns, and the climatic effects described in the previous sections cannot be rigourously quantified. For the same reason the major basins cannot be disaggregated into smaller units. The analysis of basins of the size of the Athabasca and North Saskatchewan is at too small a scale to estimate the effects of such factors as aspect, exposure and vegetal cover on the pattern of snowmelt in the southern Canadian Rockies.

The statistical prediction of discharges based upon known climatic events is therefore not possible with the present data base. At attempt at statistical modelling of the daily discharges of the Sunwapta River at Columbia Icefields has been made by Mathews (1962), using meteorological data for Jasper, Alberta. The model used by Mathews was

$$Q = b(\sum_{n=0}^{n} T_n k + a/b), \quad T \geq 45^{\circ}F \qquad (5.3)$$

where Q_o is the discharge for the day in question, T_n is the mean temperature of the n^{th} preceding day, k is an empirical recession constant found by trial and error, and a and b are regression coefficients. The model is essentially a heating degree-day function compounded with a flow recession term and is similar in concept to the model for the Fraser River given by Pipes et al. (1970). Although Mathews states that the correlation coefficient between the predicted and actual discharge commonly exceeds +0.80 for individual monthly periods, the values for a, b and k vary with season and between years. This variation is sufficiently great and unrelated to any other physical process that the model cannot be used for prediction.

Although the statistical prediction of discharges is not feasible it is possible to obtain estimates of the usual trend of discharge through the year. Figure 5.12 shows the monthly mean discharge and the associated standard deviation and coefficient of variation for the North Saskatchewan River at Rocky Mountain House for the period 1949-1968. The coefficient of variation reaches a primary peak of 43% in April and a



<u>Figure 5.12</u> - Mean, standard deviation and coefficient of variation of monthly discharges of the North Saskatchewan River at Rocky Mountain House, 1949-68.

secondary peak of 32% in September. The implication is that the time of the beginning of the spring flood is more variable than its magnitude because the high coefficients of variations at the times of the beginning and end of the flood period are consequent upon these times varying between April and May and September and October respectively. The mean discharge for the months of December through March is approximately 1000 cfs and shows a small decline. The standard deviations in this period are small. These facts are evidence for the assumption that the winter flow is base flow, derived from ground- and soil-water storage, rather than any form of surface runoff. If the summer runoff is always sufficient to fill these storage zones their discharge during the base-flow period is a function of their physical properties and does not depend on climatic conditions.

A further feature of the hydrology of the streams in this study which may be estimated independently of any physical model is the flood excedence probability distribution. Figure 5.13 shows this distribution for the North Saskatchewan River at Rocky Mountain House estimated by the procedure given by Coulson (1966) for fitting observed annual maxima to the Gumbel distribution. The extrapolation of the curve which is based upon 20 years' data to the 100 year flood is extreme and it is probably only reliable up to the 50 year recurrence interval. The 50 year flood is only three times the maximum mean monthly discharge as shown in Figure 5.12. Mandelbrot and Wallis (1969a) suggest that most

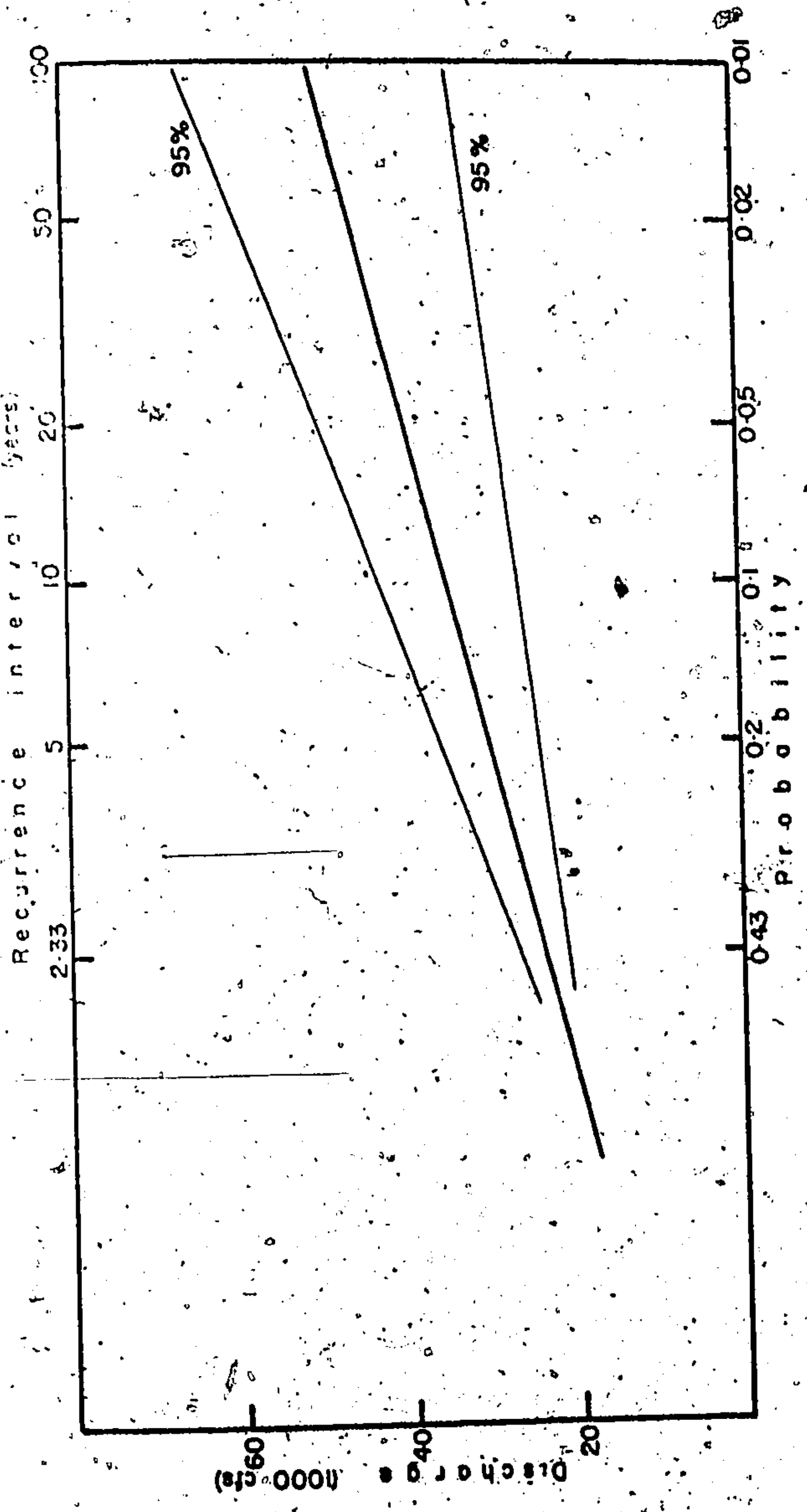


Figure 5.13 - Flood exceedance probabilities for the North Saskatchewan River at Rocky Mountain House.

geophysical data show a very long-term self-dependence, and that the Gumbel distribution may not be appropriate to the problem of flood exceedances. In a series of papers (Mandelbrot and Wallis 1968, 1969a,b) they argue that the rescaled range technique developed by Hurst (1951) shows that geophysical data cannot therefore be described adequately by models falling within the 'Brownian domain of attraction'. Two essential features of such statistical models (of which the Gumbel distribution is one) are that they assume that the mean of a sample approaches a limit (the population mean) and the distribution becomes approximately Gaussian as the sample increases in size. A test for long-term self-dependence in a data record that violates these assumptions is provided by a rescaled range analysis. The parameter 'H' which expresses the dependence of the rescaled range (R) on the standard deviation (S) by $R \propto S^H$ is 0.5 for models in the Brownian domain. Figure 5.14 shows the so-called "pox diagram" of Mandelbrot and Wallis applied to 20 day discharges of the Crowsnest River. It is evident that the parameter H has a value (0.92) much greater than 0.5. Although there is a cyclic trend of length 18 data intervals (which corresponds to the annual cycle) present, Mandelbrot and Wallis (1969a) state

> "... the presence of a periodic element complicates the picture but does not hide the Hurst phenomenon." (p. 327)

The low rate of increase of the size of flood with the recurrence interval shown in Figure 5.13 may therefore be a reflection of the fact that the

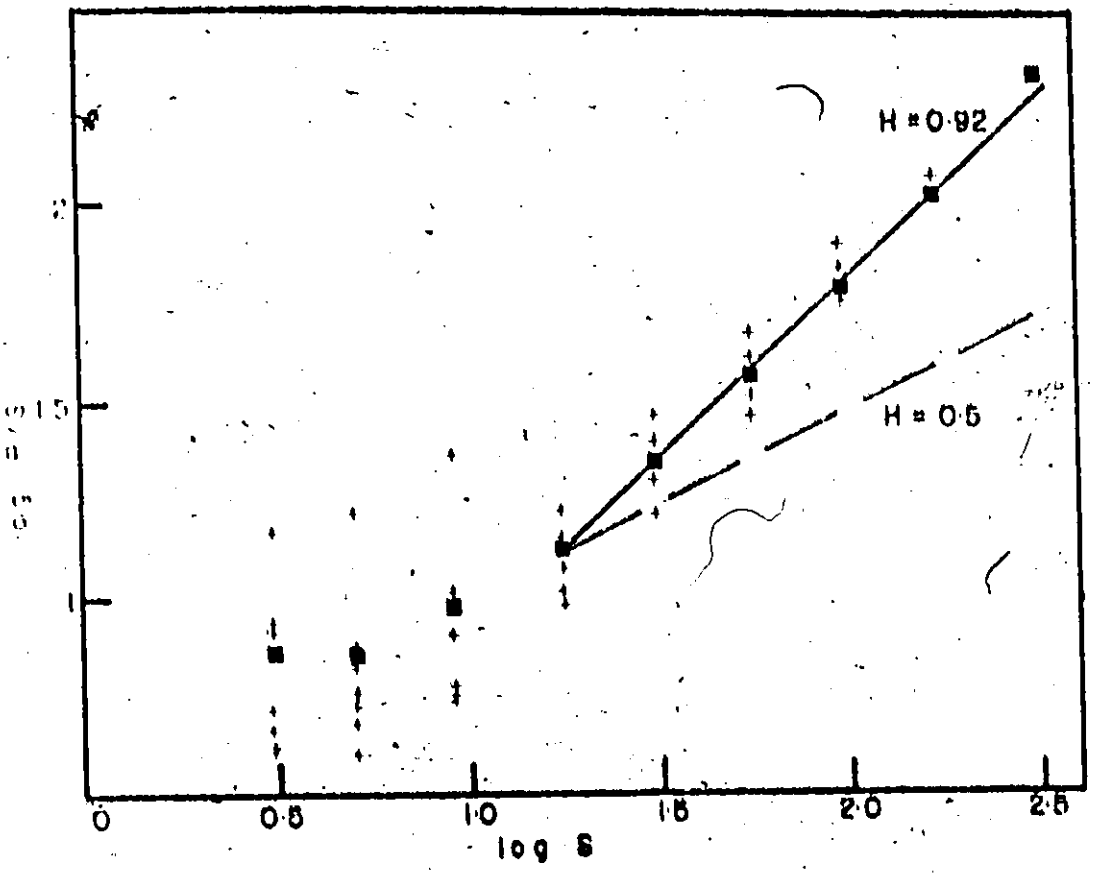


Figure 5.14 - 'Pox diagram' for the discharge of Crowsnest River.

20 years of record are insufficient to define the low-probability events because of their long-term self-dependence.

CHAPTER VI

HYDROCHEMISTRY OF THE ATHABASCA AND NORTH SASKATCHEWAN RIVERS

6.1 Introduction

The Water Quality Division of the Inland Waters Directorate has regularly monitored the quality of the Athabasca River at Hinton since July, 1967, and that of the North Saskatchewan River at Rocky Mountain House since May, 1967. The chemical constituents determined are dissolved CO_2, pH, total alkalinity, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, SO_4^{2-}, Cl^{-}, F^{-}, PO_4^{2-}, NO_3^{-}, and SiO_2. The methods used and the estimated accuracy of the determinations are given in Traversy (1971). In addition to these chemical constituents the physical characteristics of temperature, colour, turbidity and specific conductance are also monitored. For each river the sampling interval since the initiation of the program has been roughly monthly. In this study the records up to February, 1970, are used, giving a total number of samples of 28 for the Athabasca River and 34 for the North Saskatchewan River. There are certain months for which data are not available and in some instances there are two samples in the same month. The distribution of the available samples over the range of stream discharges commonly

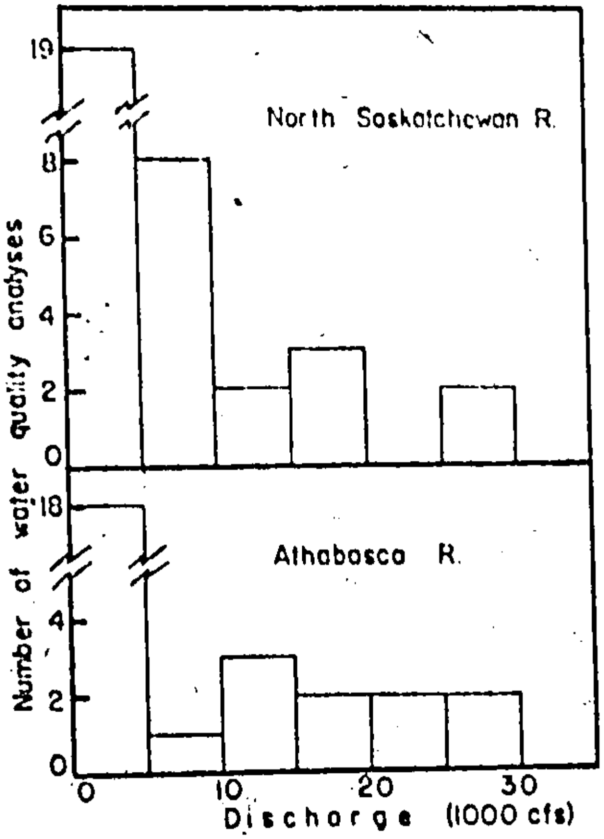


Figure 6.1 - Distribution of water quality samples with respect to discharge.

encountered is biassed by the distribution of those discharges. Figure 6.1 shows the frequency of sampling within discharge classes of 5000 cfs for each river. Because the discharges of the winter months fall within the first class and those of the summer months are distributed between the other five classes there is a preponderance of water quality information for discharges of between 0 and 5000 cfs. In general, however, there is coverage over the range of discharges observed for the rivers.

An estimate of the overall accuracy of the determination of the composition of a given sample is provided by the ion balance error, calculated as

$$\text{Error} = \frac{\sum Nc_i - \sum Na_i}{\sum Nc_i + \sum Na_i} \times 100\% \qquad (6.1)$$

where Nc_i and Na_i represent the normality of the i^{th} cation and the i^{th} anion respectively and the summation is performed over the range of ions determined. The maximum error for the Athabasca River is +2.5% and for the North Saskatchewan River is +4.0% (one sample with an error of +6.8% is not used in this study). The errors are not distributed with a mean of zero and a runs test shows that there is a marked tendency for them to occur in positive sequences ($p < .0001$) for each river. The sequences of runs do not follow the sequence of high and low discharges. The implication of this behaviour of the ion balance errors is that the Calgary laboratory of the Water Quality Division tends to overestimate the cations present and/or underestimate the anions. In all cases the ion balance error is within the range of probable analytical error. The positive bias suggests, however, that the most likely source of error is in the estimation of anions that are present in very small concentrations. Table 6.1 shows the maximum concentration of the minor ions Na^+, K^+, Cl^-, F^-, NO_3^-, and PO_4^{2-} reported in the period under consideration.

Table 6.1

Maximum Concentrations of Minor Ions (ppm)

	Na^+	K^+	Cl^-	F^-	NO_3^-	PO_4^{2-}
Athabasca R.	2.9	0.7	1.1	0.22	0.66	0.17
North Saskatchewan R.	5.0	1.0	0.6	0.29	0.40	0.29

The data for the major ions in solution (Ca^{2+}, Mg^{2+}, HCO_3^- and SO_4^{2-}) in the two rivers during the period from May, 1967, to February, 1970, is presented in Figure 6.2a and 6.3a, together with the stream discharge for the sampling dates. The values of two geochemical measures of interest in the study of limestone solution, SI_c and P_{CO_2} (v.s., Section 2.2) are shown in Figure 6.2b and 6.3b together with the temperature and pH data. Figures 6.2a and 6.3a clearly show an annual cycle in the major ion concentration which is in opposition to the annual cycle of discharge. The concentrations reach a maximum during the winter months when the streamflow represents base flow and a minimum at the time of maximum discharge (or, as in the case of the Athabasca River in 1969, at the time of the first peak of discharge). Water temperature, shown in

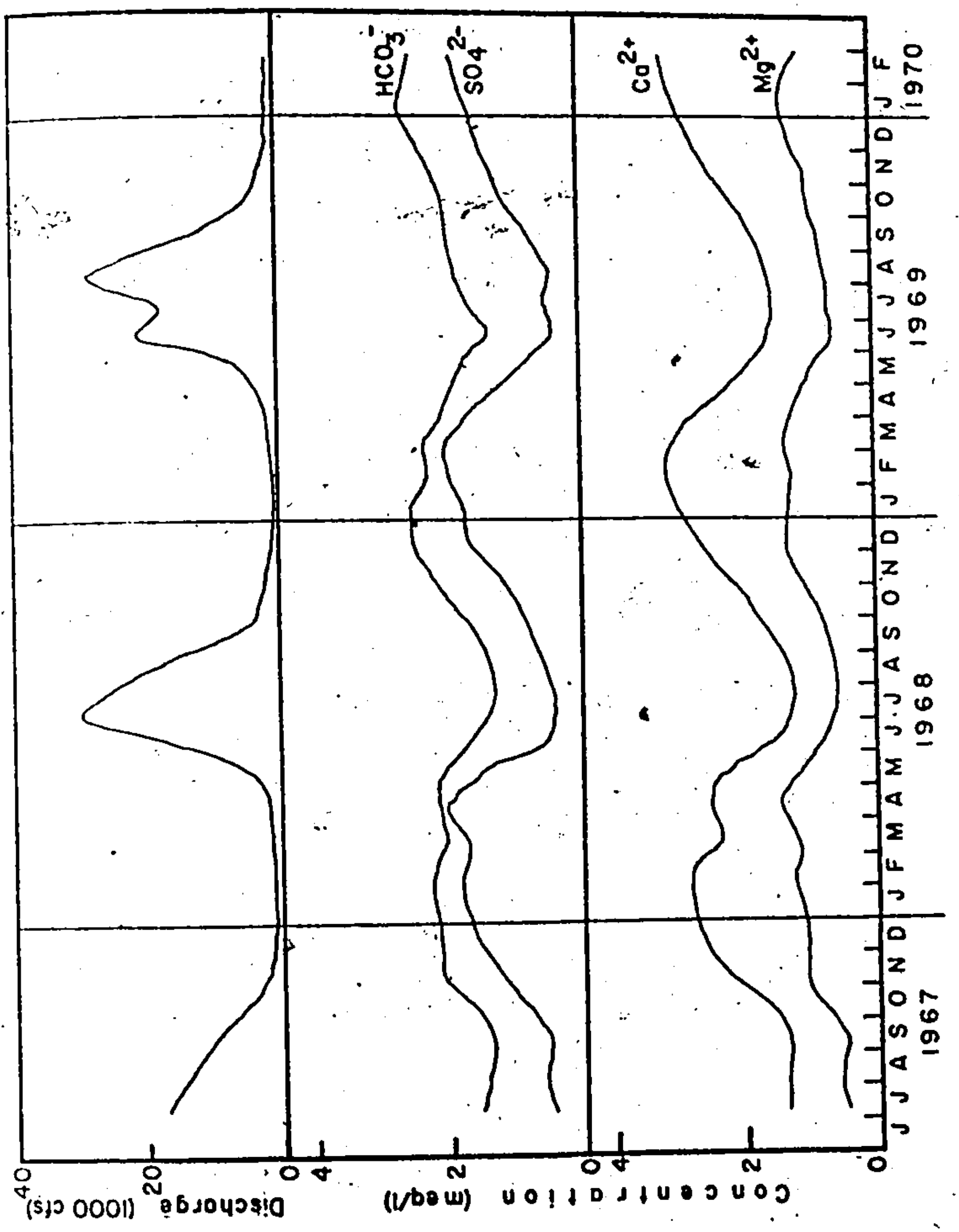


Figure 6.2a - Discharge and major ion concentrations of the Athabasca River at Hinton, 1967-70.

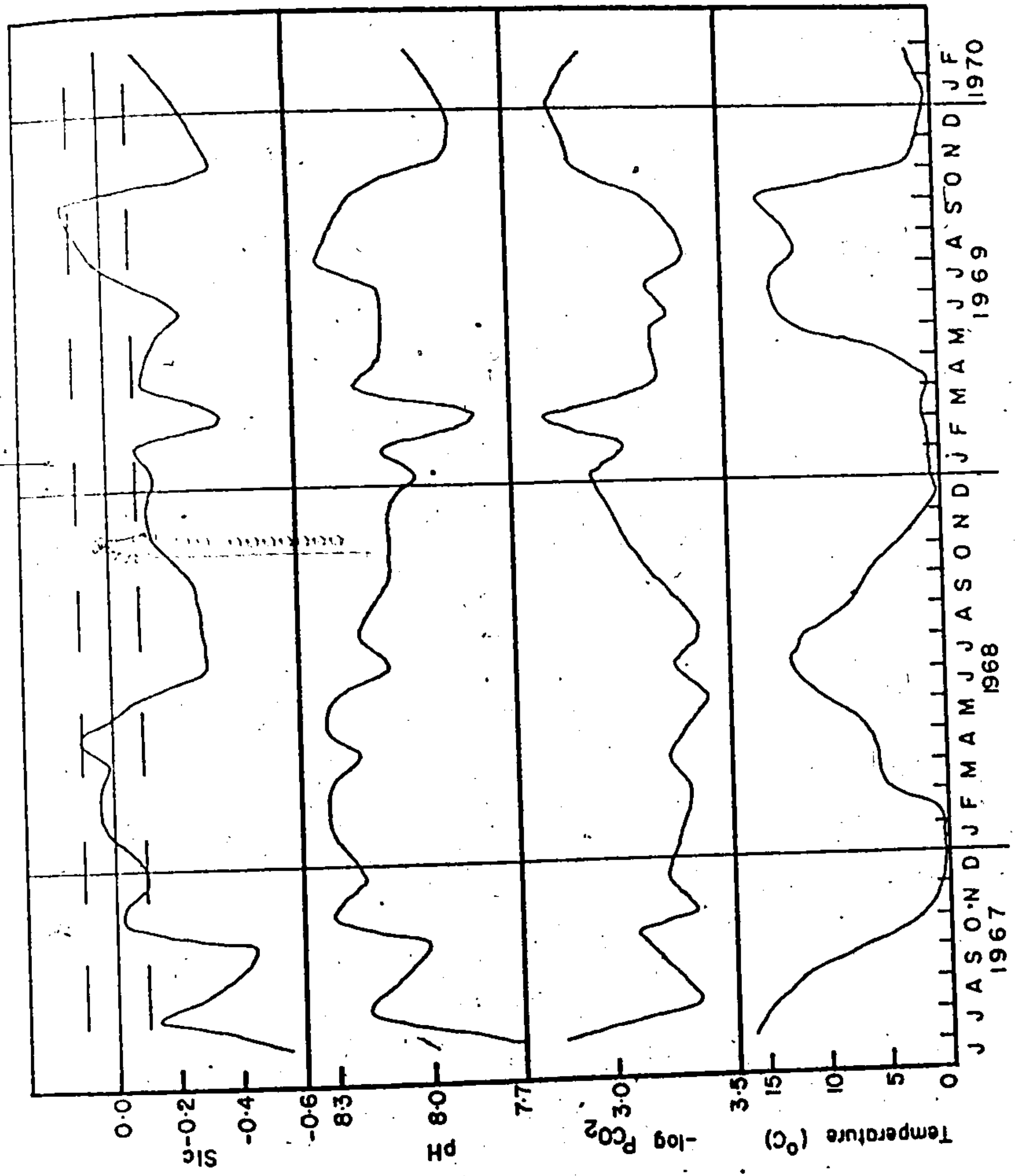


Figure 6.2b - Temperature, pH, SIc and P_{CO_2} of the Athabasca River at Hinton, 1967-70.

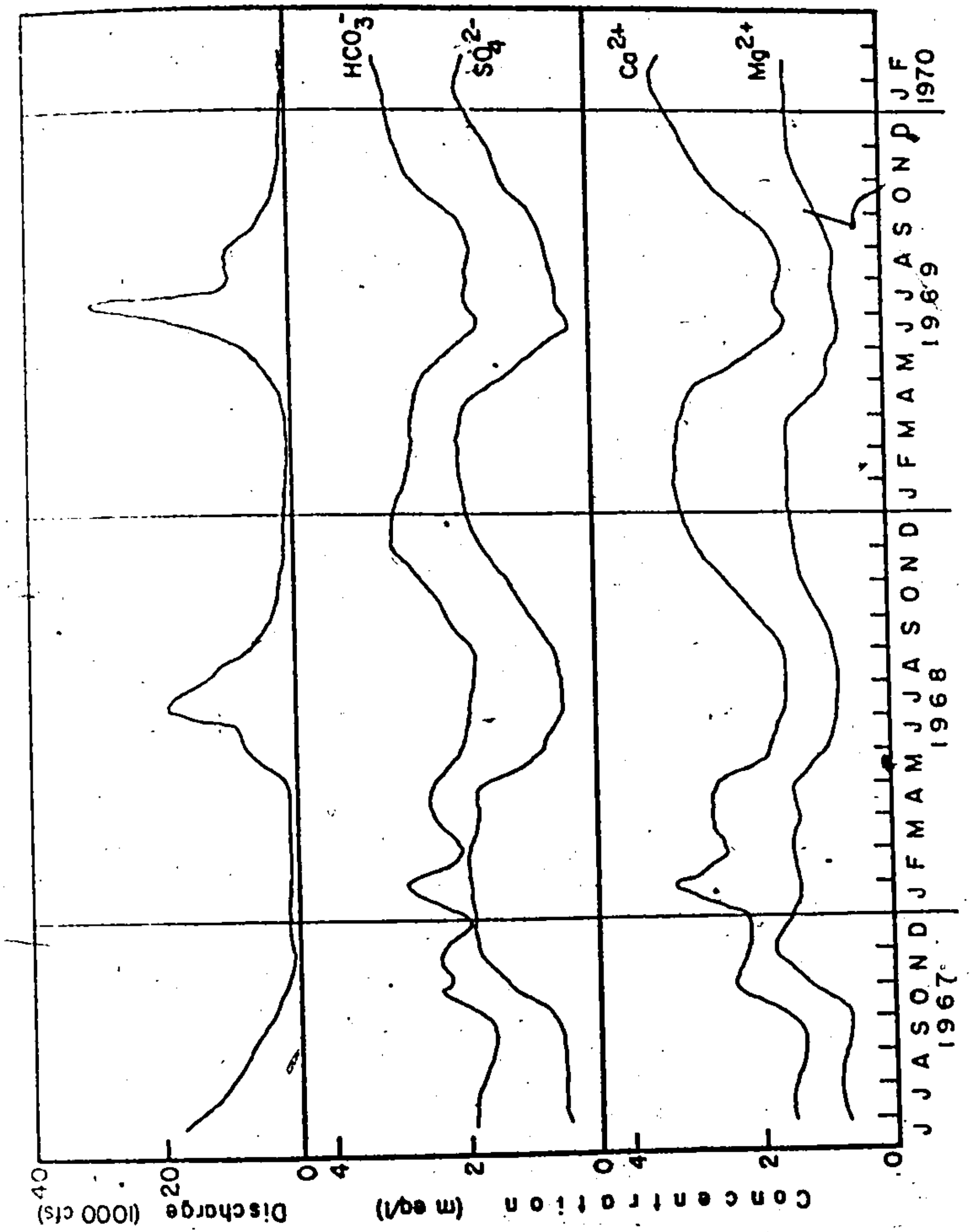


Figure 6.3a – Discharge and major ion concentrations of the North Saskatchewan River at Rocky Mountain House, 1967-70.

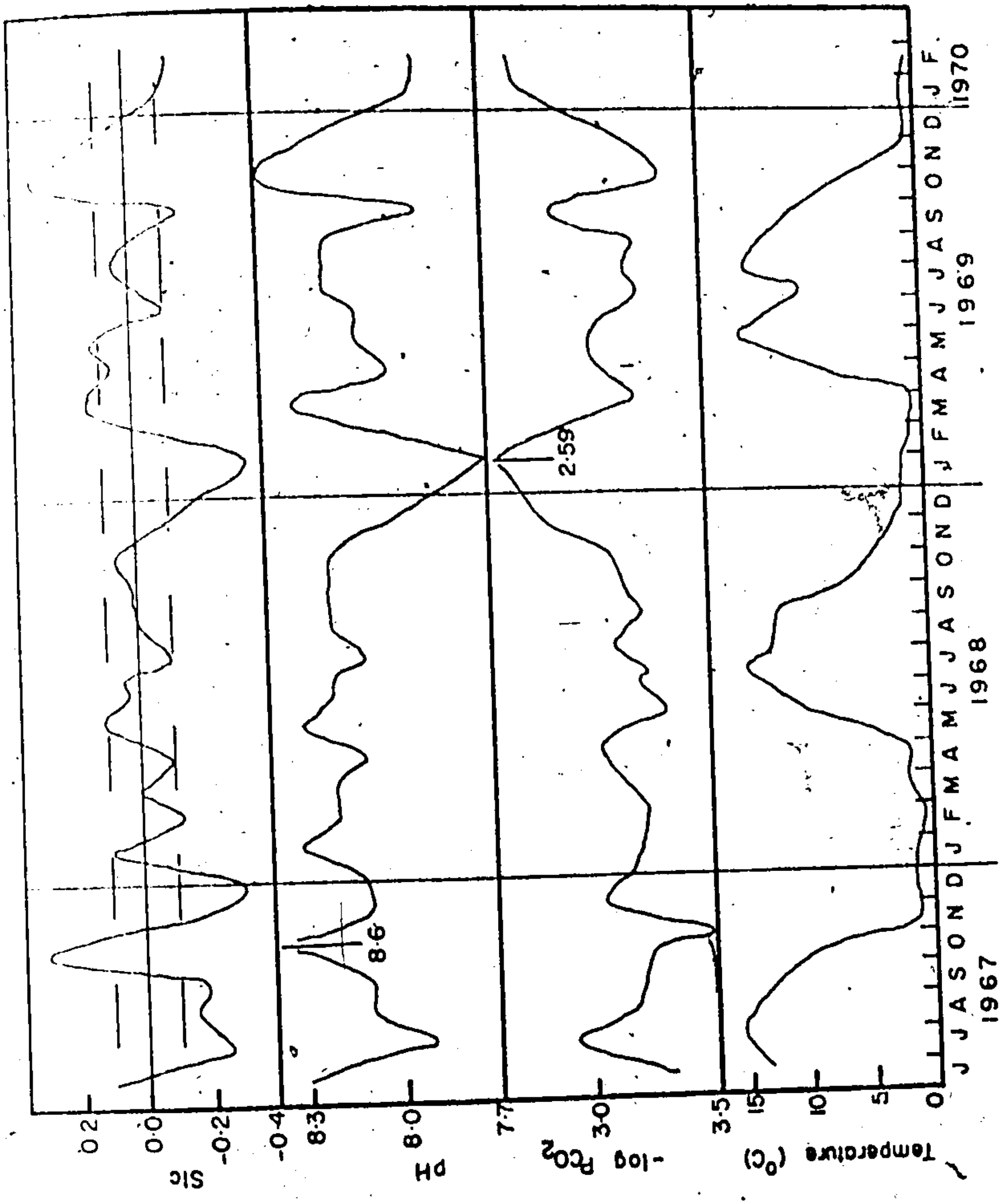


Figure 6.3b - Temperature, pH, SIc and P_{CO_2} of the North Saskatchewan River at Rocky Mountain House, 1967-70.

Figures 6.2b and 6.3b, also shows a strong annual cycle but in this case it is in phase with the discharge cycle. The pH of the two rivers throughout the period of record remains relatively constant at approximately 8.1 to 8.2. The strong functional relationship between pH and SIc and P_{CO_2} is evident in the general form of their curves. Both rivers exhibit P_{CO_2} values higher than the global mean atmospheric value ($10^{-3.5}$ atm) throughout the period, indicating that some admixture of water equilibrated with an atmospheric reservoir of elevated P_{CO_2} must occur at all times of the year. The saturation index with respect to calcite (SIc) shows that the North Saskatchewan River is generally saturated but that the Athabasca River is undersaturated with respect to this mineral for an appreciable part of the total period. Most of the extreme values of both SIc and P_{CO_2} arise from extreme values of pH. The pH values of 7.7 for the Athabasca and North Saskatchewan Rivers and 8.6 for the North Saskatchewan River may represent errors of determination and neither they nor the associated values of SIc and P_{CO_2} are considered reliable.

6.2 Controls of the Hydrochemistry

The simple correlation matrix of the various ionic concentrations and physical properties for the two rivers is shown in Table 6.2. There

Table 6.2

Correlation Matrices of Dissolved Ions

	T	CO_2	pH	SpC	C^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	SO_4^{2-}	Cl^-	F^-	NO_3^-	SiO_2
T				-.73	-.77	-.79	-.76							
CO_2			-.8											
pH		-.69												
SpC	-.95	.57			.99	.97	.95	.68	.92	.98	.75	.68		.75
Ca^{2+}	-.88	.55		.86		.96	.97	.69	.96	.97	.72	.73		.74
Mg^{2+}	-.94	.53		.98	.83		.92	.60	.92	.96	.77	.63		.77
Na^+	-.94	.55		.96	.86	.96		.72	.96	.91	.70	.77		.63
K^+	-.67	.44		.75	.57	.80	.79		.65	.66	.60	.80		
HCO_3^-	-.76	.69		.78	.92	.76	.80	.61		.87	.63	.66		.77
SO_4^{2-}	-.97	.48		.97	.88	.96	.94	.69	.74		.80	.69		.69
Cl^-	-.66	.45	.45	.73	.58	.70	.70	.62	.48	.74				
F^-	-.52			.53		.54	.46	.43		.55				
NO_3^-								.43						
SiO_2	-.74	.63		.80	.61	.82	.83	.72	.63	.74	.51	.45		

Upper: Athabasca River
Lower: North Saskatchewan River

Only those significant at the 5% level or 1% level (underlined) are shown are two main features evident in the interrelationships of the fourteen variables. Firstly, the major ion concentrations in both rivers are inversely correlated with temperature (as are the minor ion concentrations of the North Saskatchewan River) and secondly, almost all ion concentrations are positively intercorrelated. The pH in both cases shows a correlation only with dissolved CO_2. This is because pH remains relatively constant throughout the period under consideration and therefore reflects little of the variation observed in the other variables. Dissolved CO_2 is a function chiefly of the pH of the solution and a cause and effect relationship is to be expected. The lack of any such relationship between pH and the variables of the pH-dependent carbonate equilibrium (Ca^{2+}, Mg^{2+} and HCO_3^-) suggests that it is not this equilibrium that is the sole controlling factor in the chemistry of the water flowing in the two rivers. The fact that all ionic concentrations show an inverse correlation with the water temperature implies that in general the controlling factor is not the temperature-dependent mineral solubilities. If this were the case then the variables reflecting the carbonate equilibrium would show an inverse correlation with temperature but variables reflecting other mineral equilibria (such as sulphates) would be positively correlated with temperature. The low correlations observed with NO_3^- and with F^- for the North Saskatchewan River reflect the fact that many of the analyses found only trace amounts of these ions which were consequently reported to be present in the minimum detectable concentration.

Although the intercorrelation of the variables shown in Table 6.2 suggests that it is not in general the mineral equilibria that determine the ion concentrations in the two rivers, Figure 6.3b shows that the North Saskatchewan River is saturated with respect to calcite (within the limits of probable error) for much of the period of record. In this case it is the mineral solubility that is the controlling factor in the behaviour of the concentrations of Ca^{2+} and HCO_3^-. The waters of the two rivers are not saturated with respect to gypsum or dolomite. Table 6.3 shows the maximum values for SI_g and SI_d. The maximum values of SI_d are observed at the times of extreme pH, and are liable to the same potential error from this cause as is SI_c. The values of SI_d are otherwise less than -0.50. The solubility of carbonate minerals is a function of both temperature and P_{CO_2}, and the theoretical curves of the temperature-Ca^{2+} relationship for various values of P_{CO_2} are shown in Figure 6.4 together with the curves obtained by the regression of these two variables for the Athabasca and North Saskatchewan Rivers. The 95% confidence limits

Table 6.3

Maximum Values of SI_g and SI_d

	SI_g	SI_d
Athabasca River	-1.58	-0.05
North Saskatchewan River	-1.53	-0.04

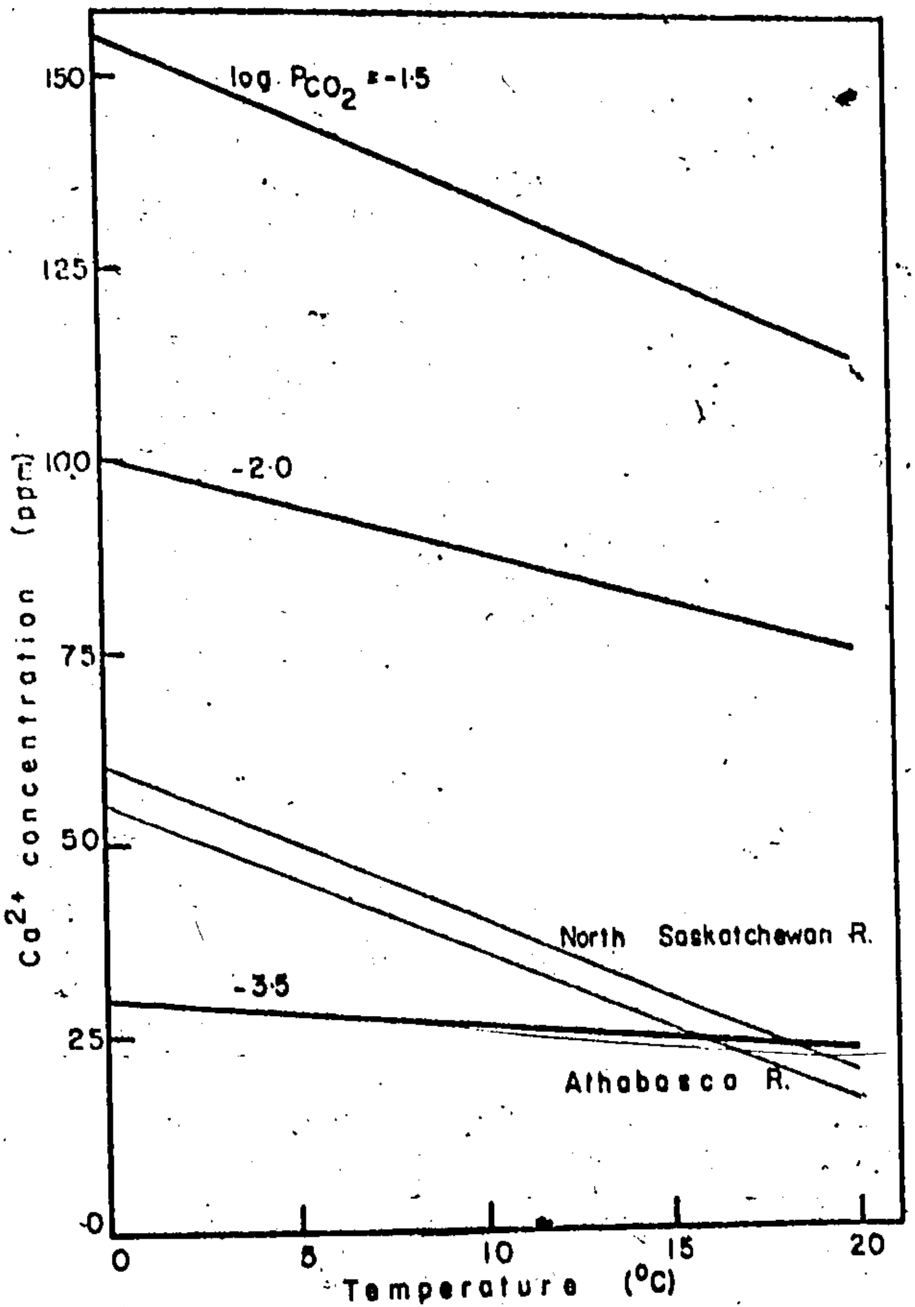


Figure 6.4 - Theoretical and observed temperature - Ca^{2+} concentration relationships of the Athabasca and North Saskatchewan Rivers.

of the regression coefficients are $-2.46 < b < -1.48$ ppm/°C for the Athabasca River and $-2.51 < b < -1.57$ ppm/°C for the North Saskatchewan River. The gradients of the theoretical curves for P_{CO_2} values of $10^{-3.5}$ atm, $10^{-2.0}$ atm and $10^{-1.5}$ atm are -0.35, -1.20 and -2.05 ppm/°C respectively. The temperature-Ca^{2+} concentration relationship in both of the rivers thus follows the trend that would be expected if the water were in equilibrium with an atmospheric reservoir of $P_{CO_2} \approx 10^{-1.5}$ atm. The measured concentrations are, however, only some 40% of the theoretical values for this P_{CO_2} and the river waters show an equilibrium P_{CO_2} of between $10^{-3.25}$ atm and $10^{-3.00}$ atm.

The observed behaviour of the variables of the calcite solution system of the two rivers suggest that the calcite equilibrium is one of the determining factors in the concentration of some of the dissolved ions. This particular factor is in turn a function of the temperature and P_{CO_2} of the system. The observed relationship between temperature and Ca^{2+} concentration together with the relatively constant P_{CO_2} exhibited by the river waters suggest that the water is not derived from a single environment. There is considerable evidence (Shuster and White, 1971; Pitty, 1968) that water from a single environment that interacts with carbonate minerals aquires either a stable character (the diffuse flow case) or exhibits a P_{CO_2} that varies with season (the conduit flow case). This latter pattern is attributed to the annual variation in the concentration of CO_2 in soil air consequent upon the annual variation in biological activity. The two rivers in this study thus show the temperature and Ca^{++} concentration behaviour that would be expected of a conduit flow system but the P_{CO_2} behaviour is more that of a large flow system in extensive contact with the atmosphere.

The observed characteristics of the carbonate equilibrium system could arise from the mixing of two bodies of water - one with a P_{CO_2} of $10^{-1.5}$ atm in which the equilibrium is a function of the temperature and the other in equilibrium with the atmospheric reservoir of CO_2 and in which the temperature and the state of carbonate solution is constant throughout the year. The analysis of the hydrology of the streams in the Rocky Mountain area presented in Chapter V suggested that their discharge could be regarded as the sum of two components. One of these is the relatively constant base flow component and the other in the main consists of water derived from the melting of accumulated snow. These two components are analogous to the two bodies of water introduced above.

If this mixing of water bodies is the explanation of the variation in the carbonate hydrochemistry of the Athabasca and North Saskatchewan Rivers then the analysis of other chemical components should reveal the same mechanism. Reeder et al. (1972) have shown that factor analysis of the hydrochemical variables of the streams of the Mackenzie River system can collapse the set of variables into a smaller number of factors that can be interpreted in hydro-geologic terms. Such an analysis of the data for the two rivers in this study yields the information summarised in Table 6.4. The first factor, which accounts for the approximately 60% of the total variance essentially represents the influence of a sedimentary rock province. Reeder et al. also obtained a single factor representing the influence of "carbonate materials and gypsum". The second factor shown in Table 6.4 represents the influence of the atmosphere which controls the pH and dissolved gas concentration of the water and the third and fourth represents the sources of the ions that are present in trace amounts. Because many analyses report the concentration of these ions as the lower limit of the analytical technique the variance of the concentrations is largely a function of the method of reporting rather than of actual variations of the concentration in the rivers. All of the major ions show similar behaviour and are grouped into the same factor. The technique is of very limited use in hydrochemical environments in which there are no radically different provenances or in which the major constituents of the dissolved load of the streams are derived from closely related geologic units.

If only the major ions are considered the composition of the dissolved load carried by the Athabasca and North Saskatchewan Rivers varies considerably through the year. Figure 6.5 shows the concentrations of Ca^{2+} and Mg^{2+} as proportions of the total cations in solution and the

Table 6.4

Factor Analysis of Hydrochemical Variables

Athabasca River

Factor	Main Components	Cumulative Explained Variance (%)
1	Temp., SpC, Ca^{2+}, Mg^{2+}, Na^{+}, HCO_3^{-}, SO_4^{2-}, SiO_2	59.7
2	Dissolved CO_2, pH	71.6
3	K^{+}, Cl^{-}, NO_3^{-}	77.0
4	F^{-}	80.7

North Saskatchewan River

Factor		
1	Temp., SpC, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, SO_4^{2-}, Cl^{-}, SiO_2	62.8
2	Dissolved CO_2, pH	76.4
3	NO_3^{-}	80.3
4	F^{-}	84.2

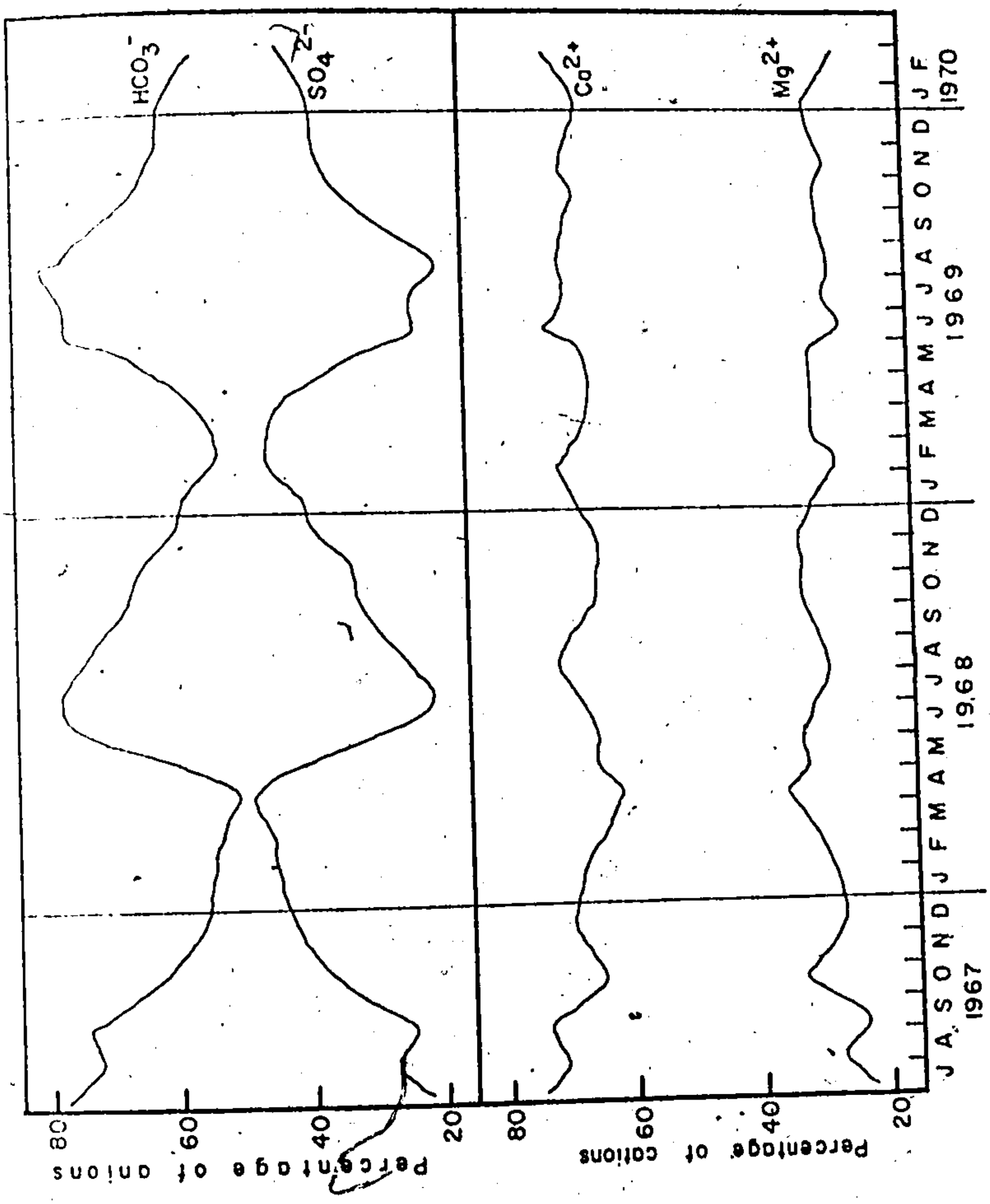


Figure 6.5a - Proportions of each of the major ions in the Athabasca River at Hinton, 1967-70.

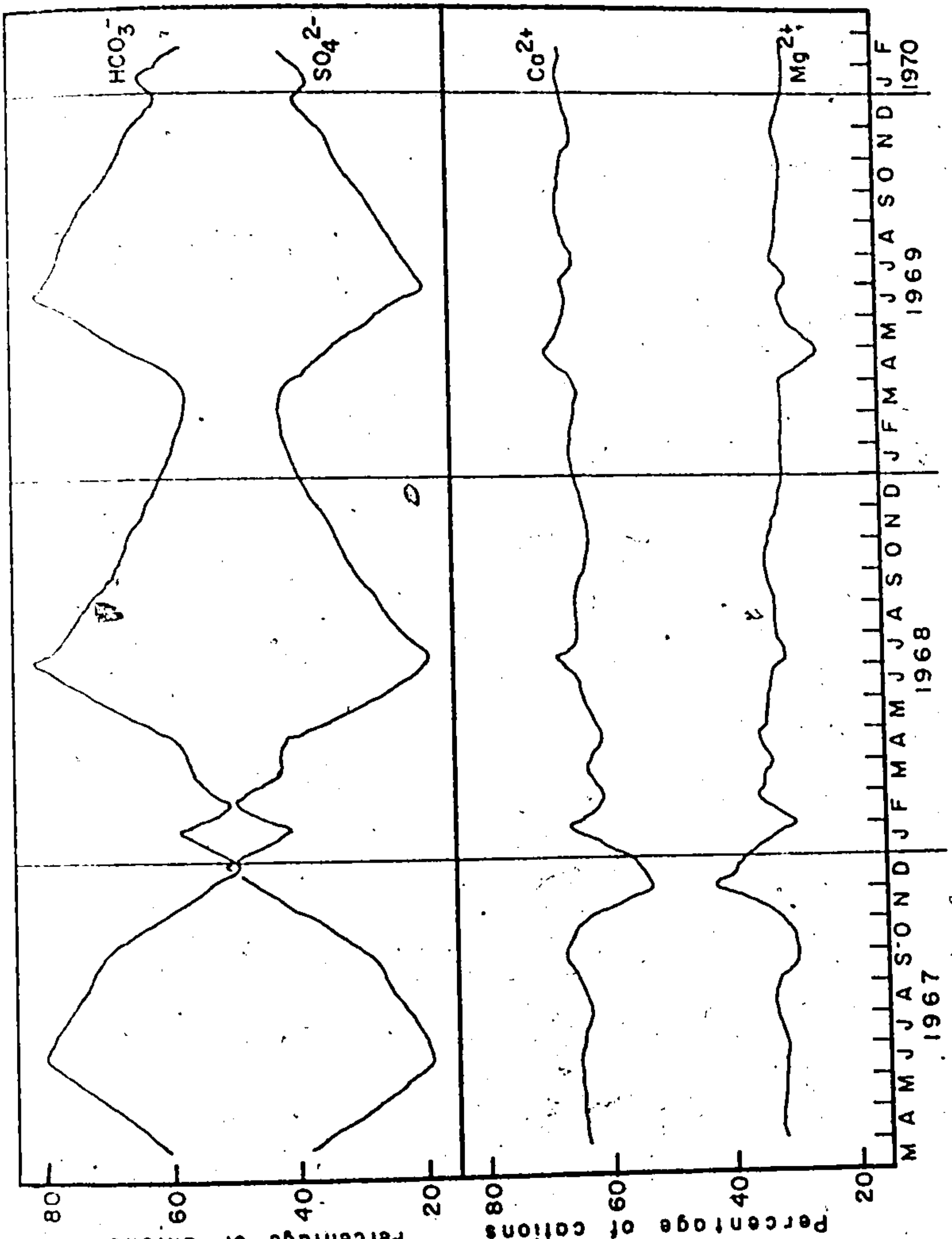


Figure 6.5b - Proportions of each of the major ions in the North Saskatchewan River at Rocky Mountain House, 1967-70.

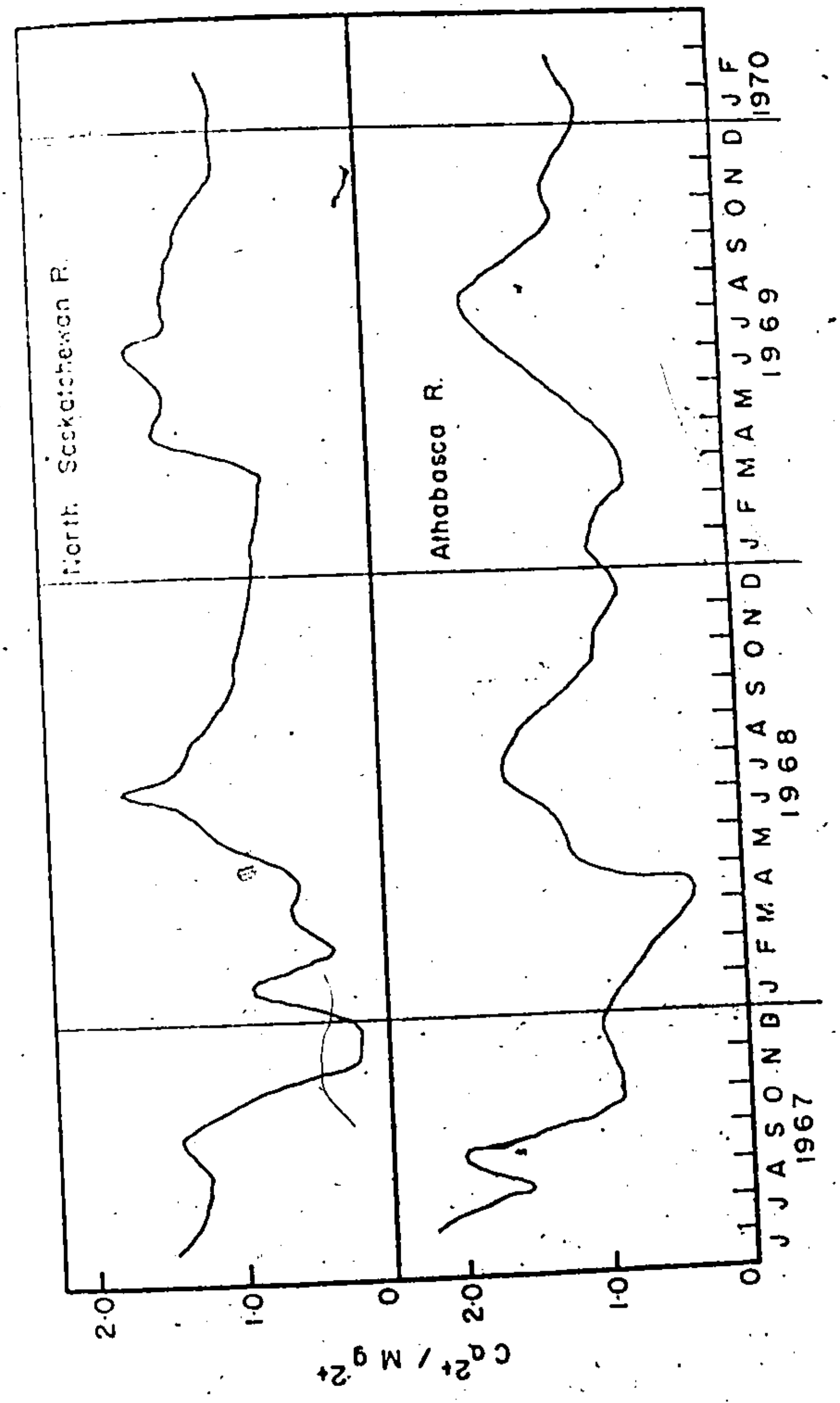
concentrations of HCO_3^- and SO_4^{2-} as proportions of the total anions in solution for the period of record. It is evident that the ratio Ca^{2+}/Mg^{2+} remains relatively constant whilst the ratio HCO_3^-/SO_4^{2-} varies seasonally. The proportion of SO_4^{2-} rises during the winter, base-flow period and reaches a maximum of over 45% of the total anions in solution. During the summer high discharge period the SO_4^{2-} proportion declines to a minimum of approximately 20% of the total. This variation can only arise from the intermixing of two or more water bodies which contribute varying proportions of the total discharge of the rivers through the year. The solution kinetics of gypsum and calcite or dolomite are such that a relative increase in the SO_4^{2-} concentration with respect to that of HCO_3^- (and hence a decrease of the value of HCO_3^-/SO_4^{2-}) would be expected if water were to flow at an increased rate through an environment containing these minerals. This is the opposite of the observed pattern - the value of HCO_3^-/SO_4^{2-} increases during periods of high discharge and consequently greater flow velocities. As already noted the temperature dependence of the mineral equilibria is such that it, acting alone, would decrease the value of HCO_3^-/SO_4^{2-} during the periods of increased discharge.

The sources of the SO_4^{2-} ion are the Triassic Spray River Formation and the Mississippian Mt. Head unit that are described in Chapter IV. These units both contain gypsum and anhydrite. The Mt. Head is a member of the Rundle Group which is widespread in the eastern parts of the study area. The conclusion that the hydrochemistry of the Athabasca and North Saskatchewan Rivers can be explained by the mixing of two water bodies implies that one is a groundwater body that has had extensive contact with rocks of either or both of the units detailed above and that the other is water from snowmelt that has had only limited contact with carbonate rocks. There are no magnesium sulphates reported in the area. The sulphate occurs in association with calcium in the form of gypsum or anhydrite. Of the total Ca^{2+} concentration observed in the samples of the two river waters an amount equal to the SO_4^{2-} concentration must therefore be derived from the solution of sulphate rocks. Figure 6.6 shows the Ca^{2+}/Mg^{2+} values for the Athabasca and North Saskatchewan Rivers computed after allowing for the Ca^{2+} associated with SO_4^{2-}. The mean values for the ratio calculated with no such allowance are 2.30 for the Athabasca River and 2.02 for the North Saskatchewan River. The values shown in Figure 6.6 may be divided into two groups (one for high discharges and one for low discharges) for each river. The mean values and standard deviations of these groups are shown in Table 6.5. It is apparent that there is a considerable difference between the two seasons for each river,

Table 6.5

Ca^{2+}/Mg^{2+} Ratios with Allowance for SO_4^{2-}

	Winter	Summer
Athabasca River	0.90 (0.22)	1.66 (0.37)
North Saskatchewan River	0.77 (0.23)	1.36 (0.17)



<u>Figure 6.6</u> - **Calcium - magnesium ratios with allowance for sulphate of the Athabasca and North Saskatchewan Rivers, 1967-70.**

but that the two rivers are quite similar. Langmuir (1971) derives values for Ca^{2+}/Mg^{2+} of water in equilibrium with both calcite and dolomite of 0.76 at 0°C and 0.99 at 10°C (Table 3, p. 1036). Ford (1971a) gives a value of 2.5 as a mean for many measurements taken in the summer months throughout the southern Rocky Mountains. Ford's work has been mainly in calcite areas in which the development of karst landforms has been most pronounced. The ratios observed in the Athabasca and North Saskatchewan Rivers is at all times less than the mean value for waters in these calcite areas. The ratios corrected for the SO_4^{2-} concentrations during the winter period are very similar to those of Langmuir quoted above.

6.3 Mixing Models

Because the discharge of the Athabasca and North Saskatchewan Rivers appears as the result of the mixing of two components each with different hydrochemical characteristics the simple two-component mixing model described in Section 3.2 should provide a good description of the behaviour of the ions in solution. The basic model may be represented as

$$\left.\begin{aligned} C\ Q &= \sum_i C_i Q_i \\ Q &= \sum_i Q_i \end{aligned}\right) \qquad (6.1)$$

where C and C_i represent the concentration of a particular ion in the mixed flow and in the i^{th} component respectively and Q and Q_i are defined similarly for discharge. The two-component system is thus

$$\left.\begin{aligned} C\,Q &= C_1 Q_1 + C_2 Q_2 \\ Q &= Q_1 + Q_2 \end{aligned}\right\} \qquad (6.2)$$

which may be combined in the form

$$C = \frac{(C_1 - C_2)\,Q_1}{Q} + C_2 \qquad (6.3)$$

Edwards (1973) describes the behaviour of the dissolved ions in several rivers in eastern England with a similar model and observes that if $C_2 = 0$ then equation 6.3 may be linearised as

$$\ln C = \ln(C_1 Q_1) - \ln Q \qquad (6.4)$$

but states incorrectly that the general linear form for $C_2 \neq 0$ is

$$\ln C = \ln(C_1 Q_1) - b \ln Q \qquad (6.5)$$

If C_2 and $(C_1 - C_2)Q$ are assumed constant in equation 6.3 then the equation has the form of a linear regression of C on $1/Q$. The assumption that C_2 is constant is equivalent to the assumption that the surface runoff component has a constant ionic concentration. The assumption that $(C_1 - C_2)Q$ is constant is equivalent to the assumption that either both C_1 and Q are constant or that

$$C_1 = \frac{k}{Q_1} + C_2 \qquad (6.6)$$

Table 6.6 shows the regression equations and correlation coefficients for the model expressed by equation 6.3 for the four major ions in both

Table 6.6

Mixing Model for the Major Ions

	Athabasca River				North Saskatchewan River			
	Ca^{2+}	Mg^{2+}	HCO_3^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	HCO_3^-	SO_4^{2-}
$(C_1 - C_2)Q_1$ (ppm-cfs)	34600	10300	64300	78700	24000	10200	45800	69400
C_2 (ppm)	28.4	7.1	91.4	22.0	34.0	9.2	116.0	24.1
r	.94	.92	.90	.95	.79	.96	.69	.96
Standard Error of Estimate (ppm)	4.5	1.5	11.1	8.8	7.4	1.2	19.0	8.3
	$n = 26, r_{.001} = .496$				$n = 34, r_{.001} = .461$			

the Athabasca and North Saskatchewan Rivers. It is apparent from this table that the simple two-component mixing model in general explains about 80% of the variance of the ionic concentrations of the two rivers. The lower correlation coefficients for the Ca^{2+} and HCO_3^- concentrations in the North Saskatchewan River are due to the fact that this river is saturated with respect to calcite for much of the time and there is thus direct geochemical control exerted by the mineral solubility. Hall ([illegible], v.s., section 3.2) has shown that a number of other mixing models may be approximated by a linear regression of simple transforms of the concentrations and the discharges of the various components. Table 6.7 shows the correlation coefficients for six such models for the major ion concentrations of the Athabasca River. No model gives significantly better results than the two-component model, and none are the result of such simple and reasonable assumptions as is the model described above.

6.4 Summary

The theoretical equilibrium Ca^{2+} concentrations of the solution of calcite shows in Figure 2.1 for $P_{CO_2} = 10^{-3.5}$ atm compare well with the values for C_2 of 28.4 ppm and 34.0 ppm derived above. The value of Ca^{2+}/Mg^{2+} for the C_2 component, when corrected for the presence of SO_4^{2-} is very close to that of the summer flow given in Table 6.5. The Ca^{2+},

Table 6.7

Correlation Coefficients of Regression Models for the Major Ions

Dependent Variable	Independent Variable*	Athabasca R.				North Saskatchewan R.			
		Ca^{2+}	Mg^{2+}	HCO_3^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	HCO_3^-	SO_4^{2-}
C	Q	-.79	-.83	-.78	-.84	-.74	-.79	-.63	-.85
C	lnQ	-.93	-.94	-.90	-.96	-.84	-.94	-.71	-.97
C	1/Q	+.94	+.92	+.90	+.95	+.79	+.96	+.69	+.96
lnC	Q	-.82	-.84	-.80	-.91	-.77	-.81	-.65	-.91
lnC	lnQ	-.94	-.94	-.91	-.98	-.87	-.94	-.73	-.98
lnC	1/Q	+.93	+.88	+.88	+.92	+.76	+.84	+.67	+.90

Ca^{2+} and HCO_3^- concentrations of the presumed snowmelt component are similar to values reported by Ford (1971a,b), Ford et al. (1972) and Brown (1973) for surface runoff in the Rocky Mountains in the summer months. The values for the concentrations of SO_4^{2-} of this flow component are shown to be approximately 22 ppm to 24 ppm whereas the analyses reported in the works listed above find no sulphate. The sampling points on the rivers in this study are downstream from surface outcrops of the sulphate bearing units. Analyses of the water flowing from Crowsnest Pass in Crowsnest River also show that SO_4^{2-} is present in a minimum concentration of 13.0 ppm. It is suggested that only in small local areas consisting almost entirely of single formations of carbonate rocks is the concentration of SO_4^{2-} negligible. Figure 4.4 shows the geologic column of the general area and the units that are associated with extensive karst development. It is evident that each local karst area is associated only with a limited part of the column and that in the Main Ranges none of these areas is developed on the sulphate bearing units.

The characteristics of the groundwater component of the total discharge of the Athabasca and North Saskatchewan Rivers are summarised in Table 6.8. These figures are derived from the values of $(C_1 - C_2)Q_1$ given in Table 6.6 by assuming that Q_1 for each river is 1000 cfs. This can only be an approximation to the true value, but is representative of the period under consideration. The Ca^{2+} concentrations shown in

Table 6.8

Chemical Concentrations in Groundwater Discharge
(ppm)

	Ca^{2+}	Mg^{2+}	HCO_3^-	SO_4^{2-}
Athabasca R.	63.0	17.4	155.7	100.7
North Saskatchewan R.	58.0	19.4	161.8	93.5

Table 6.8 are similar to the closed system equilibrium value for P_{CO_2} = $10^{-1.5}$ atm of approximately 60 ppm at 10°C. Harmon (1973) has shown that groundwaters in the Appalachian region of Pennsylvania follow the closed system solution process. The temperature dependence of the closed and open systems are similar and it has been shown in section 6.2 that the temperature dependence of the Ca^{2+} concentrations in the winter, base-flow months is similar to that of a system in equilibrium with a P_{CO_2} = $10^{-1.5}$ atm. The SO_4^{2-} concentration of the groundwater component of the total discharge is much less than the equilibrium saturation concentrations of gypsum or anhydrite (which are of the order of 1000 ppm). It is therefore concluded that either only a small proportion of the groundwater discharged to the rivers flows through sulphate rocks or the sulphate rocks are distributed in such a way that water does not reside in them for a long enough time to reach equilibrium.

The Ca^{2+}/Mg^{2+} values corrected for the presence of SO_4^{2-} derived in section 6.2 for the winter period are very similar to those given by Langmuir (1971) for waters in equilibrium with calcite and dolomite. The sulphate bearing units shown in Figure 4.4 are both associated with dolomites, and the groundwater concentrations given in Table 6.8 are thus in keeping with the geology of the contributing areas. Langmuir (1971) and Wigley (1973) both observe that the solutional reaction of calcium-rich dolomites is an incongruent process and involves the simultaneous precipitation of calcite. Wigley (1973) predicts the same depositional phenomenon in the solution of ideal dolomite at temperatures below 10°C and also in situations where water flows sequentially through calcite and gypsum beds. The groundwater component of the total discharge thus has a potential to precipitate calcite in the materials through which it flows. The river valleys are for the most part floored by glacial deposits through which the groundwater flows into the rivers. These deposits may therefore be the site of calcite deposition rather than of carbonate erosion. Ford (Dept. of Geography, McMaster Univ., pers. comm.) has observed glacial tills to be strongly cemented by secondary calcite in a tributary valley near Medicine Lake, Jasper National Park.

The downstream changes in the pH, the HCO_3^- and SO_4^{2-} concentrations and the total hardness are illustrated in Figure 6.7. The analyses of the North Saskatchewan River at 105 Street bridge are available from the Water Pollution Branch, (Alberta) Department of the Environment. Samples have been taken intermittently since 1950 but only the data for the period that coincides with the period of record for the river at Rocky Mountain House is shown. The unusually low pH and high HCO_3^- reported for the Edmonton sample of July 9, 1969, are anomalous. In

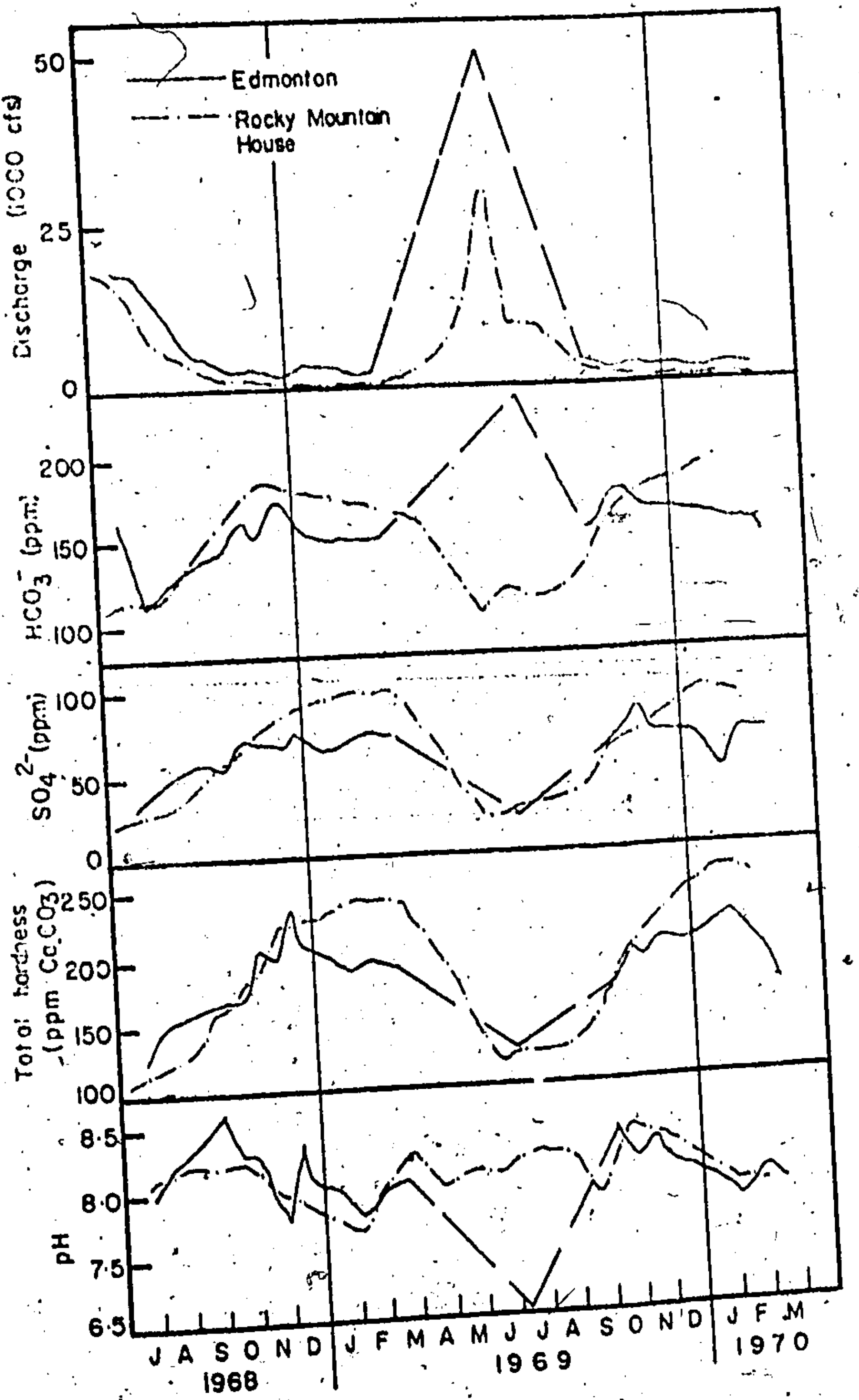


Figure 6.7 - Hydrochemistry of the North Saskatchewan River at Rocky Mountain House and Edmonton, 1968-70.

general, however, the trends at the two sites during the period from July 1968 to March 1970 are very similar. The concentrations at Edmonton in the winter months are generally lower than those at Rocky Mountain House while the discharges are higher. This shows that the increment of discharge has a low concentration of dissolved ions, and that some flow is derived from the Alberta Plains even during periods of below-freezing temperatures. The additional runoff is most probably snowmelt running overland or over snow into the stream channel.

CHAPTER VII

DISCUSSION AND CONCLUSIONS

7.1 Summary

The hydrochemistry of the North Saskatchewan and Athabasca Rivers has been shown to be well represented by a two-component mixing model. The hydrologic characteristics of the rivers also indicate that most of the annual variance of the mean daily discharge record is accounted for by the annual snowmelt event. Both the hydrology and the hydrochemistry of these two rivers, each of which drains some 4000 sq mi of the southern Rocky Mountains, are a response to the behaviour of two flow components - a groundwater body and snowmelt water. In the winter months almost all of the discharge of the Athabasca and North Saskatchewan Rivers is derived from groundwater bodies and the hydrochemistry of the rivers approaches that predicted for one flow component of the mixing model. At the time of maximum annual discharge the groundwater component is but a minor part of the total discharge and the hydrochemistry of the rivers approaches that predicted for the other flow component of the mixing model. A comparison of the predicted hydrochemistry of the two components and that of typical summer and winter flows for both rivers is shown in Figure 7.1.

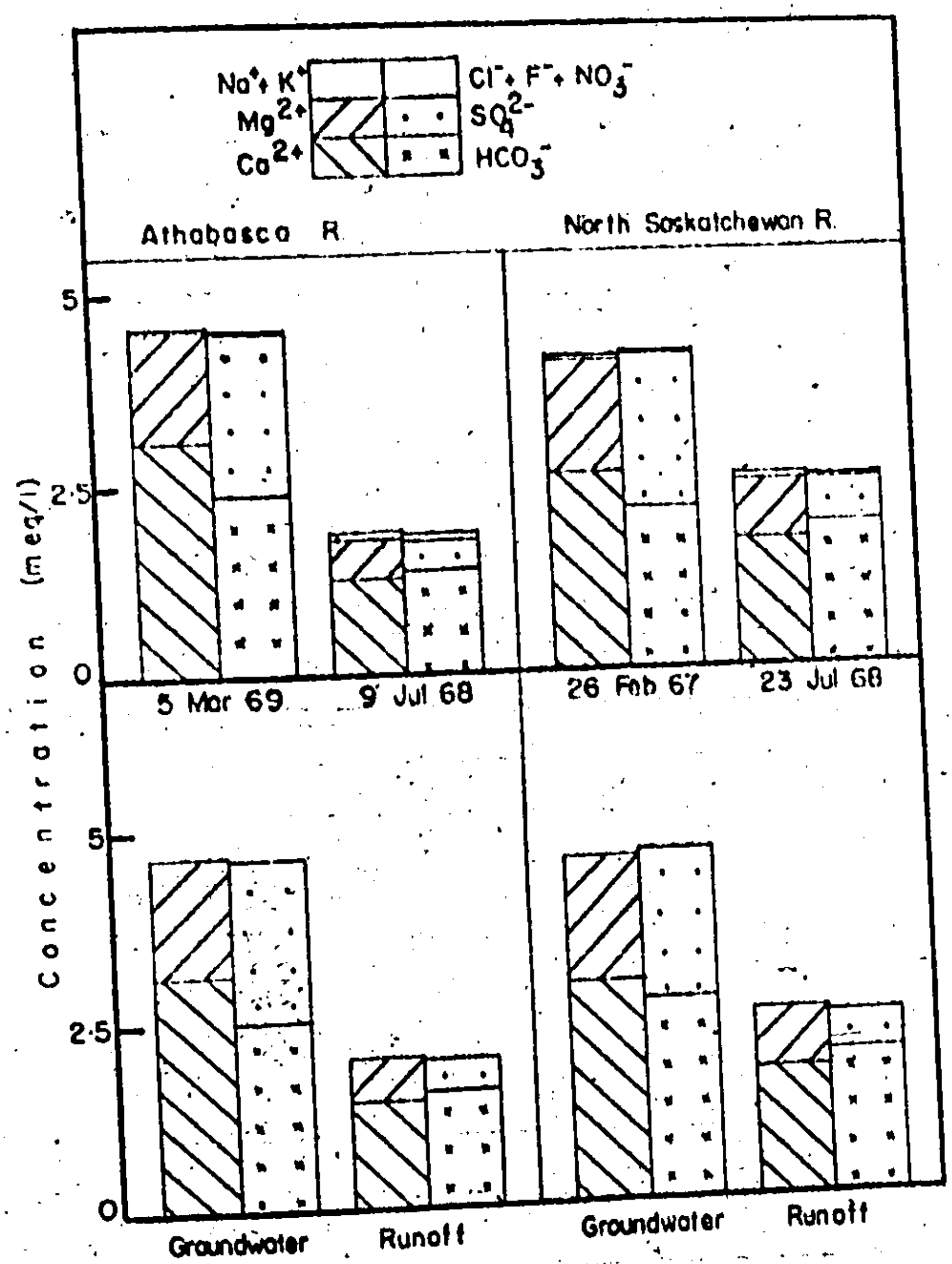


Figure 7.1 - Ion concentrations in typical winter and summer conditions (top) and in the derived groundwater and runoff components (bottom) for the Athabasca and North Saskatchewan Rivers.

It has been shown (v.s., Chapter IV) that the snowmelt discharge peak in the Athabasca River basin was a response to the annual trend of mean daily temperatures. It is evident that models at this level of generality are of little use for the prediction of discharge. The lack of predictive power stems in large part from the facts that the discharge of the Athabasca River at Hinton is the sum of the discharges of many sub-basins and that the trends of temperature at Hinton reflect the trends in these individual sub-basins only in the broadest terms. In a similar manner each of the two components of the total discharge of the Athabasca and North Saskatchewan Rivers is the sum of many sub-components. The hydrochemistry of the runoff component of the Athabasca River may, for example, be regarded as the sum of the runoff components of the Maligne, Snake, Indian, Miette, ... Rivers. Each of these sub-components is in turn the sum of a number of yet smaller individual components. Ford (1971a) has illustrated in qualitative terms that the hydrochemistry of the Maligne River may be regarded as being produced by the mixing of runoff from limestone and from sandstone areas. That the simple representation of the hydrochemistry of the Athabasca and North Saskatchewan Rivers is so effective is an expression of the fact that there are a number of common factors underlying the behaviour of each of the smallest elements. The statistical justification for the use of the linear regression form of the two-component mixing model is precisely this presence of innumerable sub-basins each of which may deviate from the overall model, but which together yield a normal distribution of ion concentrations at a given discharge.

The areas that have been described in previous studies of the hydrochemistry of streams in the Rocky Mountains, of karst landform development or of karst hydrology (Corbel, 1956, 1958; Ford, 1971a,b; Ford et al., 1972; Brown, 1973; McPherson, Dept. of Geography, Univ. of Alberta, pers. comm.) are all small in comparison to the Athabasca and North Saskatchewan River basins. They are examples of the small units which contribute to the two large rivers and therefore may show different hydrologic and hydrochemical responses. The basic responses at the large rivers should, however, be similar in kind if not in extent to those found at the small scale. Basins in which karst conduits carry an appreciable proportion of the total discharge are not the usual type in which the limestone aquifer acts in a manner similar to a granular aquifer. Most basins in which the effects of large karst conduits are pronounced (e.g. in the Crowsnest Pass and Mount Castleguard areas) lie above the altitude to which massive glacial valley-fills extend. In this case the groundwater component (as defined in Chapter V) of discharge is virtually absent and the hydrodynamics of the carbonate solution processes are of greater importance.

7.2 Limestone Solution in Small Basins

Ford (1971a) has given a comprehensive review of the nature of limestone solution in a number of small areas in the southern Canadian Rockies in which he concludes that in general it is the availability of carbon dioxide which governs the solution process. Figure 7.2 shows the Ca^{2+} concentration measured in waters in the southern Rockies and the Selkirk Mountains by Ford and co-workers (including the present author) as a function of altitude. This figure distinguishes between four classes of water - surface waters, cave streams, springs and cave seeps (which are drips within caves with a flow of only a few ml/min). There is evidently a strong agreement between the general trend of this diagram and that shown by Figure 2.3 which shows the P_{CO_2} of atmospheric and soil air samples in the same areas. Because of this agreement and because Figure 2.3 shows a good correlation between the P_{CO_2} of the ambient gas phase and the equilibrium P_{CO_2} of the water at various altitudes, Ford's conclusion is strongly supported. The apparent correlation between Ca^{2+} concentration and altitude is not a direct functional relationship but is the result of an altitudinal control on the P_{CO_2} of the ambient gas phase which in turn controls the equilibrium Ca^{2+} concentration.

The effects of different environments at the same altitude is illustrated by Figure 7.3. The two-component mixing model described in

Figure 7.2 (over) - Altitudinal variation of the Ca^{2+} concentration of karst waters in the southern Canadian Rockies.

Surface water

1. Snowmelt
2. Clear glacial melt stream
3. Meadow Ck.
4. Turbid glacial melt stream

Mt. Castleguard area

5. Creeks in Maligne valley
6. Ptolemy Ck.
7. Athabasca and North Saskatchewan Rivers

Crowsnest Pass

● Cave streams

1 Nakimu Cave

△ Springs

1 Cave Spring
2 Big Spring

Mt. Castleguard area

3 Ptolemy Spring
4 Old Man River Rising

Crowsnest Pass

▲ Cave seeps

1 Castleguard Cave
2 Nakimu Cave
3 Old Man River Rising Cave

Crowsnest Pass

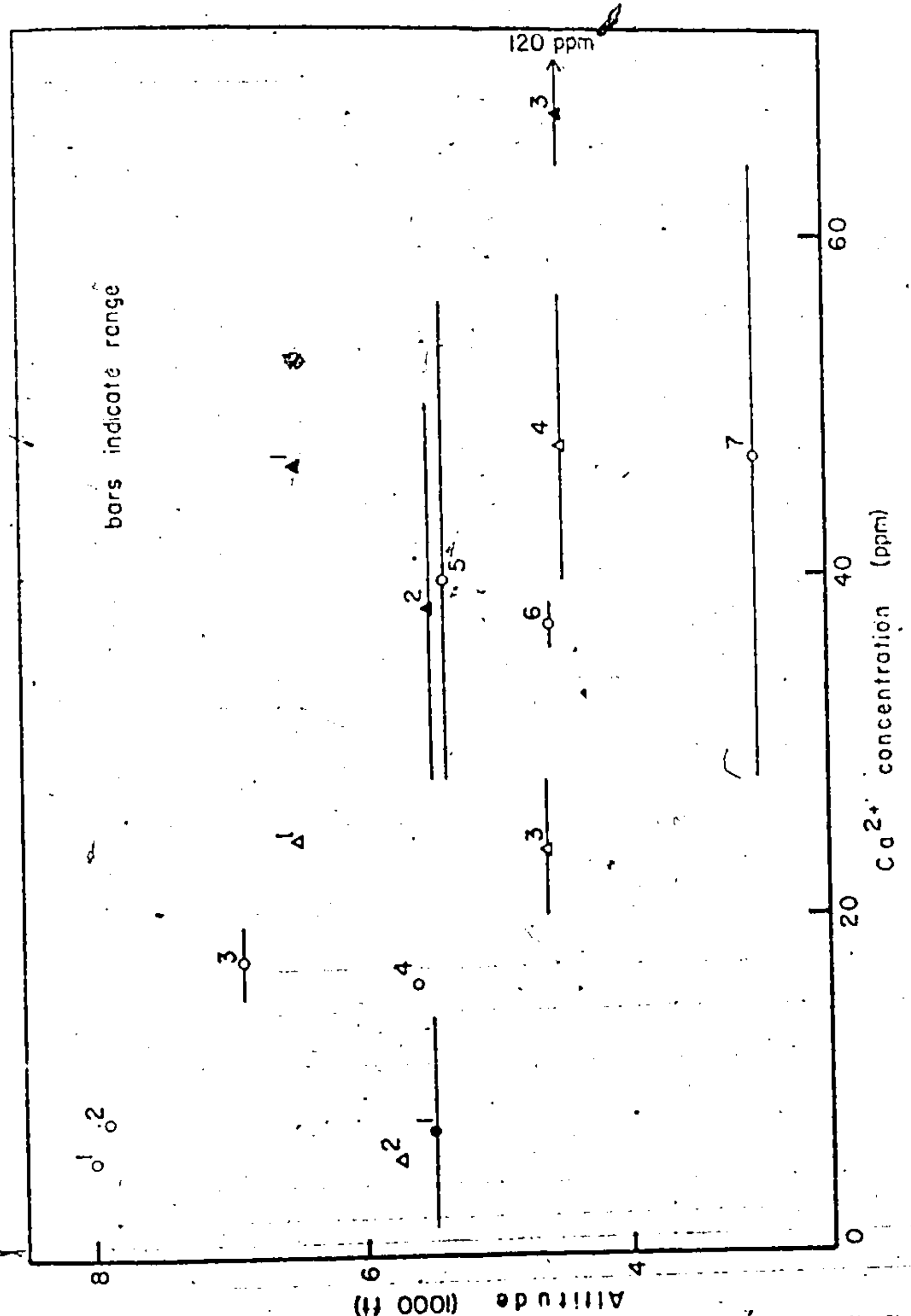
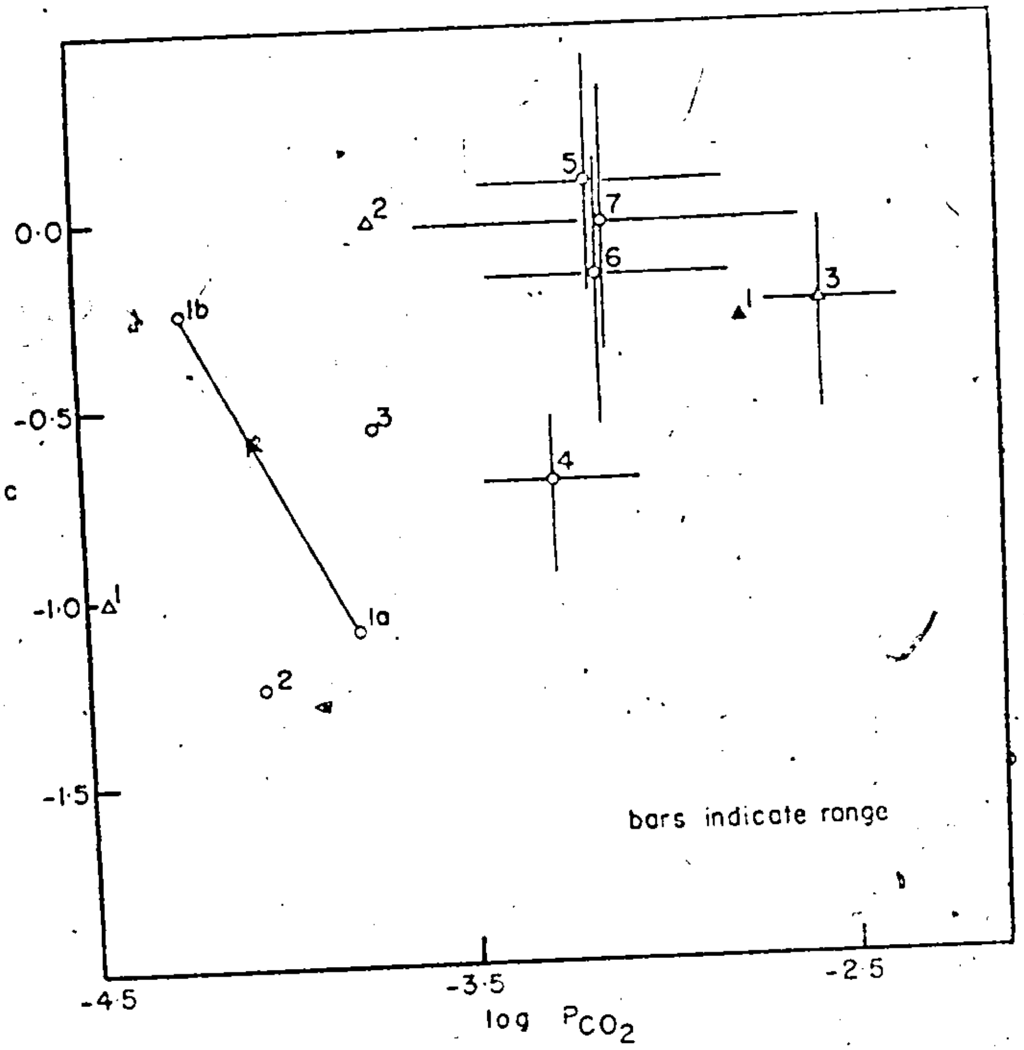

bars indicate range
120 ppm
Altitude (1000 ft)
8
6
4
Ca2+ concentration (ppm)
0
20
40
60
1
2
3
4
5
6
7

Figure 7.3 (over) - SIc and P_{CO_2} of karst waters in the southern Canadian Rockies.

○	Surface water	
1a	Snowmelt, at snow patch	Mt. Castleguard area
1b	Snowmelt, 100' from snow patch	
2	Clear glacial melt stream	
3	Turbid glacial melt stream	
4	Meadow Creek	
5	Ptolemy Creek	Crowsnest Pass
6	Athabasca River	
7	North Saskatchewan River	
△	Springs	
1	Big Spring	Mt. Castleguard area
2	Cave Spring	
3	Old Man River Rising	Crowsnest Pass
▲	Cave seeps	
1	Castleguard Cave	


0·0
-0·5
-1·0
-1·5
SIc
-4·5
-3·5
-2·5
log P_{CO_2}
bars indicate range
5
7
6
3
1
4
2
3
1b
1a
1
2

CHAPTER VII

DISCUSSION AND CONCLUSIONS

7.1 Summary

The hydrochemistry of the North Saskatchewan and Athabasca Rivers has been shown to be well represented by a two-component mixing model. The hydrologic characteristics of the rivers also indicate that most of the annual variance of the mean daily discharge record is accounted for by the annual snowmelt event. Both the hydrology and the hydrochemistry of these two rivers, each of which drains some 4000 sq mi of the southern Rocky Mountains, are a response to the behaviour of two flow components - a groundwater body and snowmelt water. In the winter months almost all of the discharge of the Athabasca and North Saskatchewan Rivers is derived from groundwater bodies and the hydrochemistry of the rivers approaches that predicted for one flow component of the mixing model. At the time of maximum annual discharge the groundwater component is but a minor part of the total discharge and the hydrochemistry of the rivers approaches that predicted for the other flow component of the mixing model. A comparison of the predicted hydrochemistry of the two components and that of typical summer and winter flows for both rivers is shown in Figure 7.1.

Chapter VI for the Athabasca and North Saskatchewan Rivers is applicable to waters in small karst basins if the two components are defined slightly differently. One component may be regarded as soil water that has equilibrated with the enhanced P_{CO_2} of the soil air (analogous to the groundwater component of the large rivers) and the other may be regarded as surface runoff in equilibrium with the atmospheric P_{CO_2} (as is the case for the surface runoff component of the large rivers). Such a model implies that in general the Ca^{2+} concentration of spring waters at equilibrium should be greater than that of surface waters and less than that of soil waters (or seeps) because the water emerging from the springs is a mixture of the two. The series of observations in the Crowsnest Pass area (Ptolemy Creek, Old Man River Rising and the seep) supports this hypothesis, as does the series in the Mount Castleguard area (Meadow Creek, Cave Spring and the seep). In each of these areas there is also one sample or site that is anomalous - Ptolemy Spring in the Crowsnest area and Big Spring in the Castleguard area. Each of these springs is a conduit spring and is fed by a conduit which transports water rapidly from a higher, non-vegetated area to the spring point. The source areas for both of these springs are at an altitude of more than 7000 ft and the water issuing from the springs has a Ca^{2+} concentration similar to that of surface water at this altitude. The turbid glacial meltwater shown in Figure 7.2 is a surface stream sampled approximately 1.5 mi from the glacier and which has little inflow from ground- or soil-waters. The

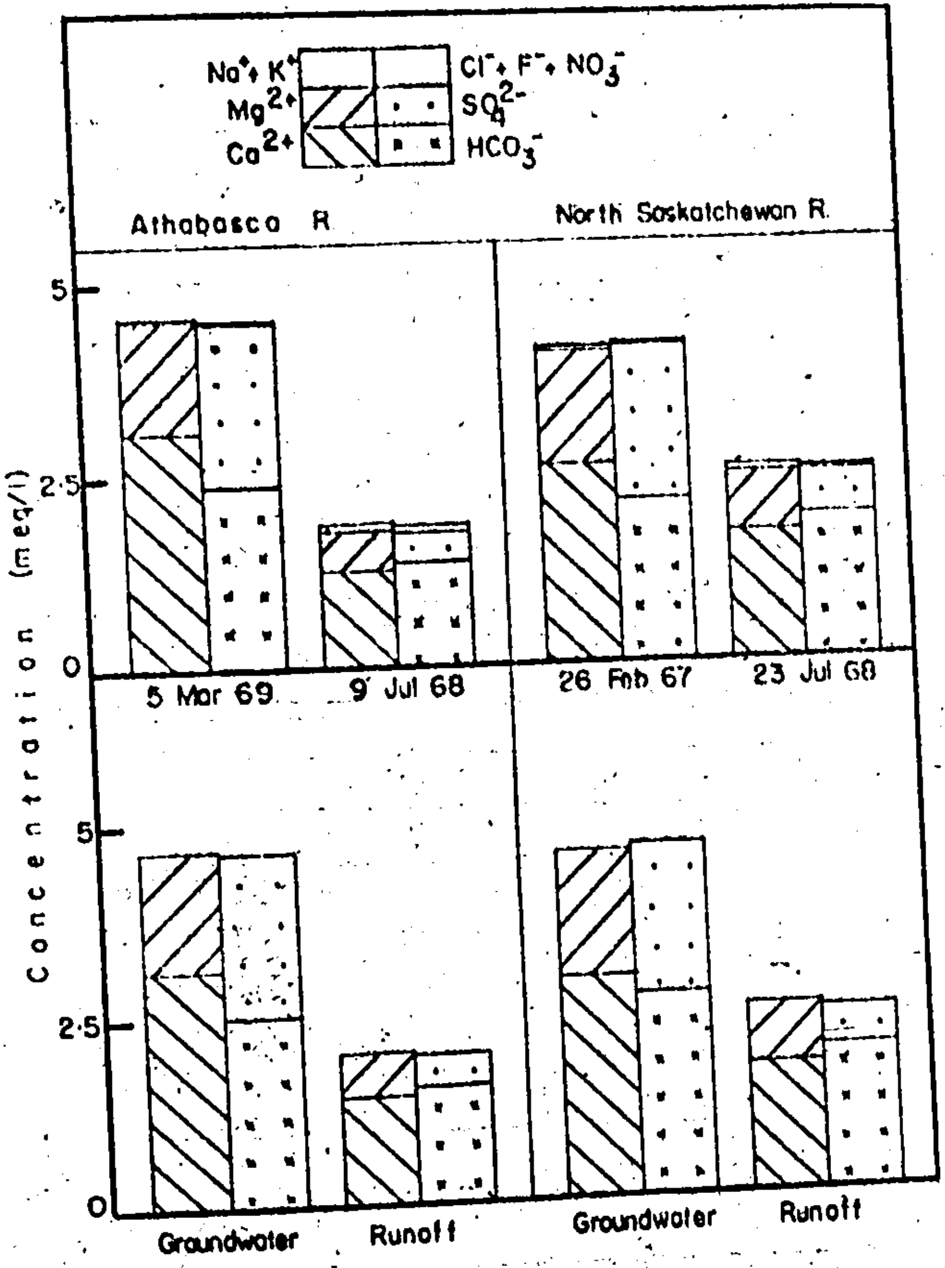


Figure 7.1 - Ion concentrations in typical winter and summer conditions (top) and in the derived groundwater and runoff components (bottom) for the Athabasca and North Saskatchewan Rivers.

Samples from the Nakimu Cave area near Rogers Pass, B.C., show again the contrast between seeps which originate from soil-water and streams flowing through the aquifer in conduits (or caves).

Figure 7.3 shows those samples in Figure 7.2 for which complete analyses are available in the SIc-P_{CO_2} diagram used by Drake and Harmon (1973) to differentiate between hydrochemical environments in a karst terrain. Only samples from the Crowsnest and Castleguard areas, and from the Athabasca and North Saskatchewan Rivers are shown. Of the eleven sites shown only three surface streams, Ptolemy Creek, Athabasca River and North Saskatchewan River, and Cave Spring are saturated for all or part of the periods during which they were sampled. The characteristics of the surface streams that drain limestone areas in the Rockies are that they are saturated (or nearly so) and that they are in equilibrium with a P_{CO_2} similar to that of the atmosphere. Old Man River Rising approaches saturation as the summer progresses (see Ford, 1971a, Fig. 7) but is in equilibrium with a P_{CO_2} ten times that of the atmosphere, which indicates that it is fed largely by soil-water. This is supported by Ford (1971a) who shows that the discharge of this spring declines only slowly during the summer.

The set of samples from the Castleguard area shows considerable variation. The seep is in equilibrium with the highest P_{CO_2} as would be expected of water originating from a forest soil. It is undersaturated because the water traverses only a thin limestone band before emerging

It has been shown (v.s., Chapter IV) that the snowmelt discharge peak in the Athabasca River basin was a response to the annual trend of mean daily temperatures. It is evident that models at this level of generality are of little use for the prediction of discharge. The lack of predictive power stems in large part from the facts that the discharge of the Athabasca River at Hinton is the sum of the discharges of many sub-basins and that the trends of temperature at Hinton reflect the trends in these individual sub-basins only in the broadest terms. In a similar manner each of the two components of the total discharge of the Athabasca and North Saskatchewan Rivers is the sum of many sub-components. The hydrochemistry of the runoff component of the Athabasca River may, for example, be regarded as the sum of the runoff components of the Maligne, Snake, Indian, Miette, ... Rivers. Each of these sub-components is in turn the sum of a number of yet smaller individual components. Ford (1971a) has illustrated in qualitative terms that the hydrochemistry of the Maligne River may be regarded as being produced by the mixing of runoff from limestone and from sandstone areas. That the simple representation of the hydrochemistry of the Athabasca and North Saskatchewan Rivers is so effective is an expression of the fact that there are a number of common factors underlying the behaviour of each of the smallest elements. The statistical justification for the use of the linear regression form of the two-component mixing model is precisely this presence of innumerable sub-basins each of which may deviate from the overall model, but which into the cave and does not have time to reach equilibrium with the rock. The samples from Meadow Creek have P_{CO_2} values higher than the atmosphere and are also undersaturated. This creek flows across peaty soils and is fed in part by water from the soil. The undersaturation results from the fact that much of the inflow to the creek from the soil has had little interaction with carbonate materials. The two ~~glacial~~ meltwaters and the two springs also demonstrate the effects of the availability of carbon dioxide and of the hydrodynamics of the limestone solution processes. The Cave Spring water and the turbid glacial meltwater are in equilibrium with a P_{CO_2} slightly below that of the atmosphere and the clear glacial meltwater and the water rising from Big Spring are in equilibrium with progressively lower values of P_{CO_2}. The sources of the two springs are not known, but that of the Big Spring is presumed by Ford (1971a,b) to be the sole of the Columbia Icefields. The compaction of snow has been observed by Cogley (1972) to result in the lowering of the P_{CO_2} of the contained air. The lessening of P_{CO_2} from the Cave Spring and the turbid glacial meltwater to the clear meltwater at a higher elevation to the Big Spring may therefore arise from the progressively increasing compaction of the frozen water bodies that are feeding these sampling sites.

The values of SIc for these four sites are largely controlled by the hydrodynamics of their environments. The clear glacial meltwater flows from a high altitude glacier onto a bare limestone surface and was sampled a short distance from the snout of the glacier. There is little together yield a normal distribution of ion concentrations at a given discharge.

The areas that have been described in previous studies of the hydrochemistry of streams in the Rocky Mountains, of karst landform development or of karst hydrology (Corbel, 1956, 1958; Ford, 1971a,b; Ford et al., 1972; Brown, 1973; McPherson, Dept. of Geography, Univ. of Alberta, pers. comm.) are all small in comparison to the Athabasca and North Saskatchewan River basins. They are examples of the small units which contribute to the two large rivers and therefore may show different hydrologic and hydrochemical responses. The basic responses at the large rivers should, however, be similar in kind if not in extent to those found at the small scale. Basins in which karst conduits carry an appreciable proportion of the total discharge are not the usual type in which the limestone aquifer acts in a manner similar to a granular aquifer. Most basins in which the effects of large karst conduits are pronounced (e.g. in the Crowsnest Pass and Mount Castleguard areas) lie above the altitude to which massive glacial valley fills extend. In this case the groundwater component (as defined in Chapter V) of discharge is virtually absent and the hydrodynamics of the carbonate solution processes are of greater importance.

opportunity for this water to reach equilibrium. The Big Spring is the outlet of a high discharge conduit system in which the velocities are high enough that water leaves the system before it can reach equilibrium with the conduit walls. The turbid glacial meltwater stream is a fast flowing stream which carries a heavy load of glacial flour. This added load of fine particles of limestone evidently does not increase the opportunities for solution sufficiently to allow saturation to be attained upstream of the sampling point. In addition the P_{CO_2} of the water may be increasing downstream as the water equilibrates with the higher P_{CO_2} of the atmosphere. The Cave Spring is a low discharge spring and consists of many water-conducting joints and bedding planes in a small vertical cliff. The interaction between rock and water in this more diffuse flow situation is sufficient to allow chemical equilibration in the system.

The hydrodynamic controls on the equilibrium state of the water flowing from the Big Spring and the Cave Spring can be estimated from Figure 2.7. The Big Spring has been observed to discharge over 400 cfs (Ford, 1971b). This implies that the conduit through which the water flows is at least 1 m in radius, because the flow velocity through a smaller conduit would have to exceed 3.5 m/sec. In a tube of this size the relaxation length of the calcite solution process under conditions of turbulent flow exceeds 10^6 cm (6.2 mi). The total length of the system is unlikely to be more than 10 mi (Ford, 1971b), and saturation of the water flowing from the Big Spring is therefore not to be expected during the high discharge period. The Cave Spring, in contrast, discharges

7.2 Limestone Solution in Small Basins

Ford (1971a) has given a comprehensive review of the nature of limestone solution in a number of small areas in the southern Canadian Rockies in which he concludes that in general it is the availability of carbon dioxide which governs the solution process. Figure 7.2 shows the Ca^{2+} concentration measured in waters in the southern Rockies and the Selkirk Mountains by Ford and co-workers (including the present author) as a function of altitude. This figure distinguishes between four classes of water - surface waters, cave streams, springs and cave seeps (which are drips within caves with a flow of only a few ml/min). There is evidently a strong agreement between the general trend of this diagram and that shown by Figure 2.3 which shows the P_{CO_2} of atmospheric and soil air samples in the same areas. Because of this agreement and because Figure 2.3 shows a good correlation between the P_{CO_2} of the ambient gas phase and the equilibrium P_{CO_2} of the water at various altitudes, Ford's conclusion is strongly supported. The apparent correlation between Ca^{2+} concentration and altitude is not a direct functional relationship but is the result of an altitudinal control on the P_{CO_2} of the ambient gas phase which in turn controls the equilibrium Ca^{2+} concentration.

The effects of different environments at the same altitude is illustrated by Figure 7.3. The two-component mixing model described in water through a series of planar openings of the order of 1 cm in width. The velocity of the resurgent water is of the order of 1 cm/sec. Although Figure 2.7 is not strictly applicable to flow between plane surfaces it does suggest that the relaxation length of the process is of the order of 10^3 to 10^4 cm. Water originating from the Columbia Icefield that is discharged by the Cave Spring can therefore be expected to be saturated.

The behaviour of the P_{CO_2} of the water flowing from the snowpatch is unexpected. The Ca^{2+} concentration increases by 2 ppm and the water evolves towards saturation as it flows from the snowpatch over 100 ft of a bare limestone surface. The P_{CO_2} decreases considerably from $10^{-3.78}$ atm to $10^{-4.22}$ atm. The P_{CO_2} of the atmosphere at this altitude is more than $10^{-4.0}$ atm (see Figure 2.3) and the decrease shown by the snowpatch meltwater cannot be a response to the atmospheric value. Harmon (1972) has noted that water emerging from springs in Pennsylvania with a P_{CO_2} greater than that of the atmosphere equilibrates only slowly with the atmosphere. A decrease in P_{CO_2} is expected if the reaction between water and limestone occurs under closed system conditions. If the exchange of carbon dioxide between the water from the snowpatch is slower than the solution of the limestone over which it flows the overall effect would be a decrease in the P_{CO_2} and an increase in the Ca^{2+} concentration and SIc. This explanation is satisfactory in this extremely small system.

The general behaviour of the limestone solution process in these small karst basins is thus in agreement with theoretical considerations,

Figure 7.2 (over) - Altitudinal variation of the Ca^{2+} concentration of karst waters in the southern Canadian Rockies.

Surface water

1. Snowmelt — Mt. Castleguard area
2. Clear glacial melt stream
3. Meadow Ck.
4. Turbid glacial melt stream
5. Creeks in Maligne valley

Crowsnest Pass

6. Ptolemy Ck.
7. Athabasca and North Saskatchewan Rivers

● Cave streams

1 Nakimu Cave

△ Springs

1 Cave Spring — Mt. Castleguard area
2 Big Spring
3 Ptolemy Spring — Crowsnest Pass
4 Old Man River Rising

▲ Cave seeps

1 Castleguard Cave
2 Nakimu Cave

Crowsnest Pass

3 Old Man River Rising Cave

with the detailed model established by Drake and Harmon (1973) and with the general behaviour of the large river basins of the present study.

7.3 Transport Rates of Dissolved Minerals

The instantaneous rate of transport of a dissolved mineral out of a river basin is given by

$$\frac{dM}{dt} = CQ \tag{7.1}$$

where C is the concentration of the mineral and Q is the instantaneous discharge. If the SO_4^{2-} ion in the stream originates entirely from gypsum or anhydrite and the HCO_3^- ion entirely from the solution of limestones (or other carbonates of similar composition) then the rate of transport of these minerals is

$$\frac{d}{dt}(CaSO_4) = C_s Q \times 4.01 \times 10^{-5} \text{ kg/s} \tag{7.2a}$$

and

$$\frac{d}{dt}(CaCO_3) = C_h Q \times 2.32 \times 10^{-5} \text{ kg/s} \tag{7.2b}$$

where C_s and C_h represent the concentrations of SO_4^{2-} and HCO_3^- in ppm and Q is expressed in cfs. These scaled equations may be combined with the mixing models which describe the interrelationships of the ion concentrations and the discharge (shown in Table 6.6) to give expressions for the rate of transport of limestone and sulphate as functions of discharge. The discharge figures used in this study are daily means and the resulting rates of transport of dissolved minerals are therefore also daily mean values. Table 7.1 shows these functions for the Athabasca and North Saskatchewan Rivers, and Figure 7.4 illustrates them for discharges of up to 30,000 cfs. The effect of the surface runoff component is to greatly increase the rate of transport of carbonate minerals. The rate of transport of sulphate minerals becomes much less in proportion to the total dissolved load at higher discharges because most of these minerals are transported by the groundwater component which has been assumed to have a constant discharge throughout the year. Because the mixing models in the regression equation form are estimated from concentration and discharge data at discharges of between approximately 1000 cfs and 30,000 cfs the rates of transport shown in Table 7.1 and Figure 7.4 cannot be extrapolated reliably beyond these limits. The winter base-flow of both the Athabasca and North Saskatchewan Rivers in of the order of 1000 cfs and if this figure is taken to represent the groundwater component of the total flow it is possible to estimate the proportion of the total daily mean dissolved load contributed by this source at various values of the total river

Table 7.1

Daily Mean Dissolved Mineral Transport Rates (kg/s)

	Limestone	Gypsum
Athabasca River	$1.59 + 2.12 \times 10^{-3} \times Q$	$3.16 + 0.88 \times 10^{-3} \times Q$
North Saskatchewan River	$1.06 + 2.69 \times 10^{-3} \times Q$	$2.78 + 0.97 \times 10^{-3} \times Q$

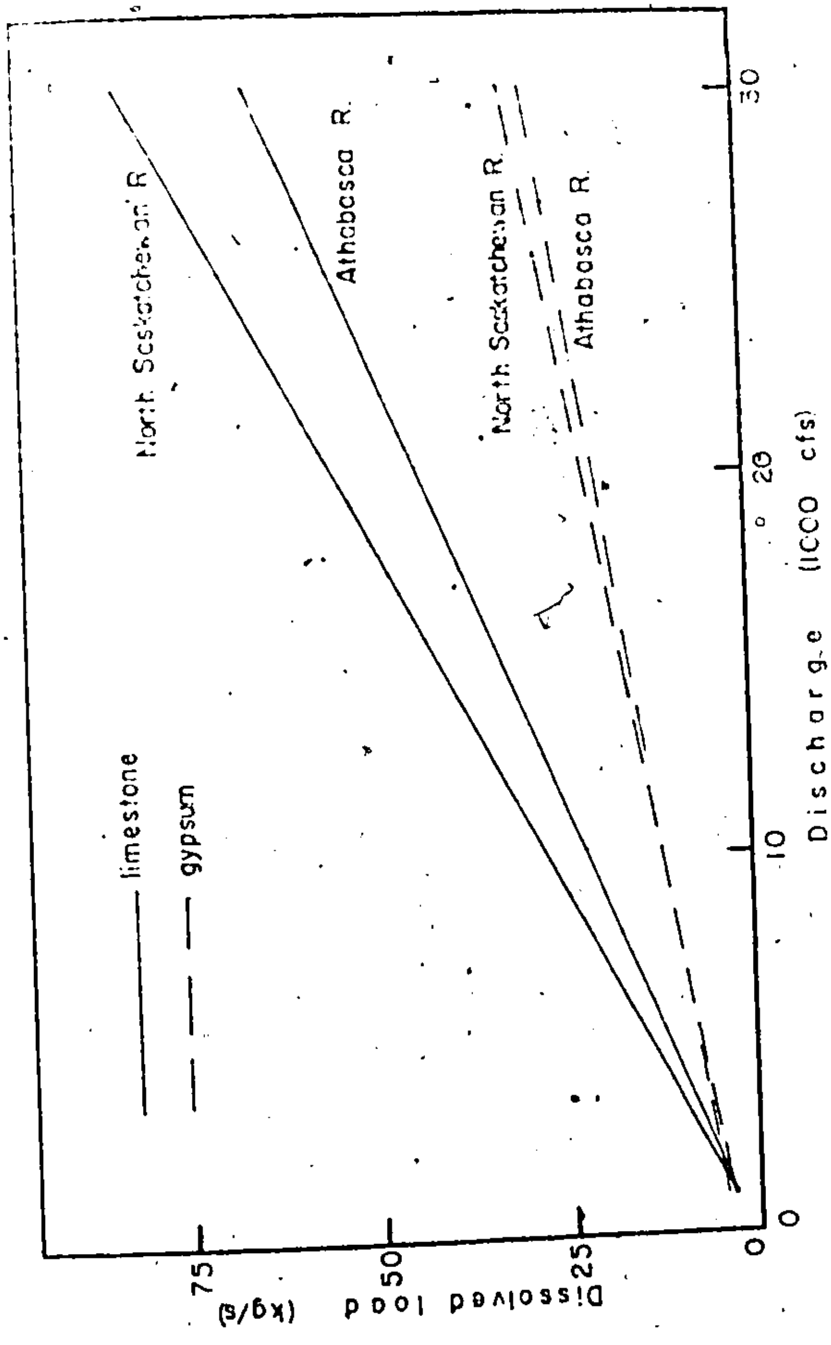


Figure 7.4 - Daily dissolved mineral transport of the Athabasca and North Saskatchewan Rivers as a function of discharge.

discharge. Figure 7.5 shows the percentages of the total transported gypsum and limestone contributed by the groundwater discharge. In both river basins the groundwater component accounts for some 10% of the gypsum and 5% of the limestone being transported in solution by the rivers at the highest observed discharges. Over 50% of the dissolved limestone leaving the basins is contributed by groundwater flow at total discharges of less than 2500 cfs and over 50% of the gypsum comes from this source at discharges of less than 5000 cfs.

Figure 7.6 shows the percentage of the total dissolved loads of the Athabasca and North Saskatchewan Rivers that are sulphate minerals. Slightly less of the total load consists of sulphate minerals in the North Saskatchewan River, but for both the proportion varies from between 50% and 55% during base-flow conditions to approximately 30% at a discharge of 30,000 cfs. It is evident that the solution of sulphate minerals is an important part of the overall geomorphic evolution of these river basins; a part that has previously been overlooked by other workers.

7.4 Erosion Rates

The figures given above for the daily mean transport rate of dissolved minerals out of a drainage basin can be summed to provide an

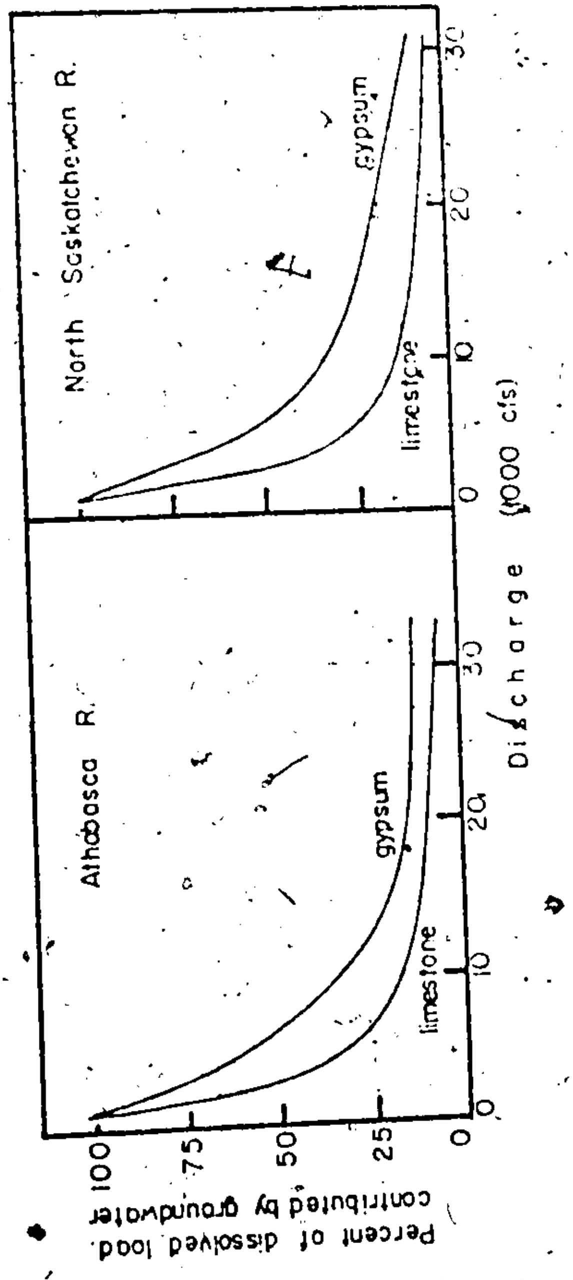


Figure 7.5 - Proportion of dissolved load contributed to the Athabasca and North Saskatchewan Rivers by groundwater inflow at various discharges.

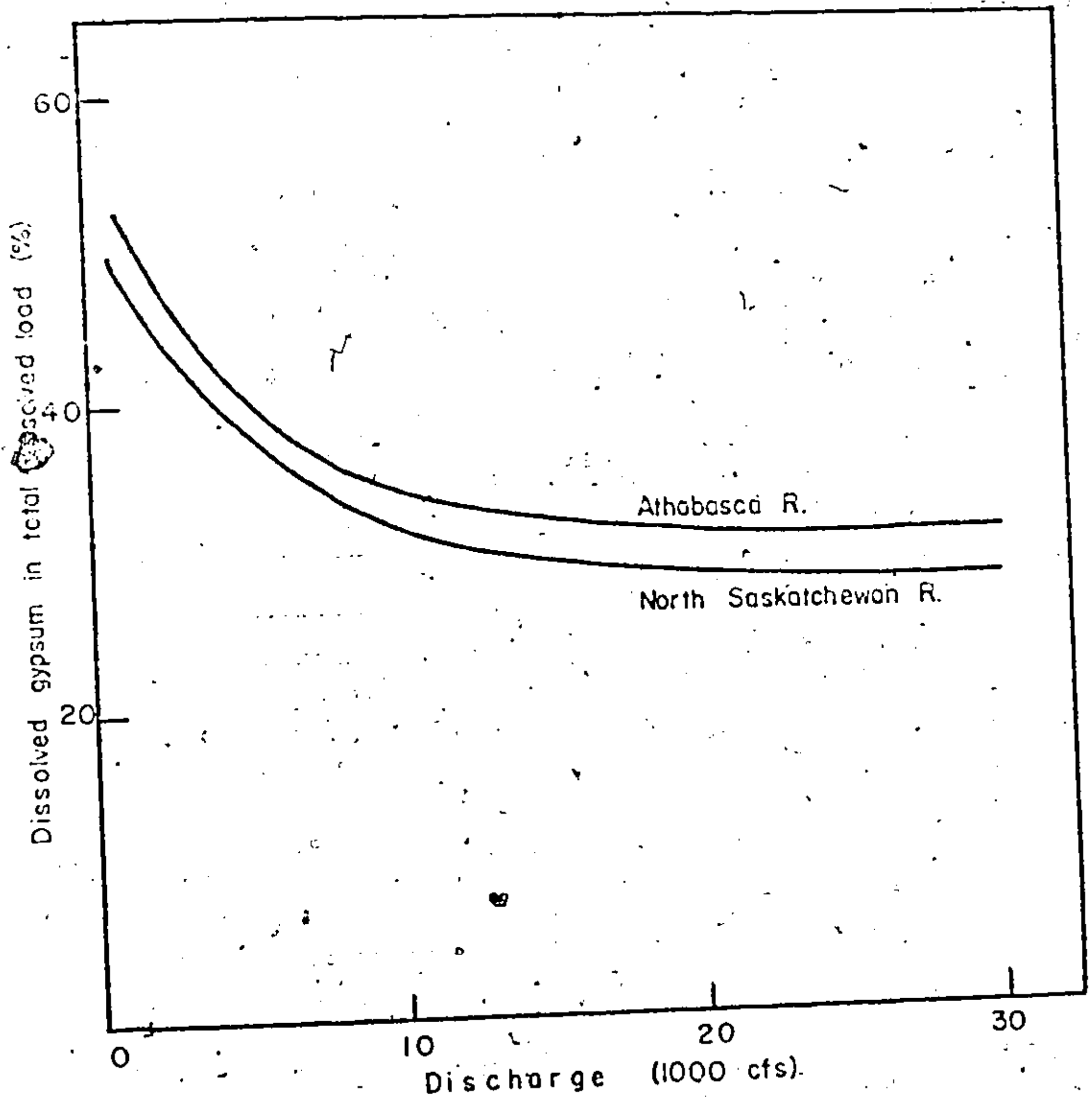


Figure 7.6 – Proportion of dissolved load contributed from gypsum to the Athabasca and North Saskatchewan Rivers at various discharges.

estimate of the annual rate. If the contributing area of each of the minerals is known the annual rate can be converted to a mean annual specific erosion rate expressed in terms of a mass loss per unit area per year. An assumption of the mean bulk density of the minerals then allows this specific erosion rate to be converted to the erosion rate as it was defined by Corbel (1956), i.e. as an average rate of lowering of the surface of the basin usually expressed in terms of mm/1000 yr. Drake and Ford (1973) have shown that the formula given by Corbel

$$X = \frac{4ET}{100} \qquad (7.3)$$

where X is the erosion rate (mm/1000 yr), E is the annual runoff (dm) and T is the mean total hardness of the stream leaving the basin (ppm $CaCO_3$) overestimates the erosion rate for basins in which the stream shows an inverse relationship between the discharge and the ion concentrations. In the case of the Athabasca and North Saskatchewan River basins the overestimate is of the order of 30% when compared to the better estimate derived using the sum of 12 monthly values computed according to equation 7.3.

The ion concentrations can be estimated accurately for the two rivers in this study by the use of the mixing models, and the daily mean transport rate of dissolved minerals is given by equation 7.2. The erosion rate is then

$$E = \frac{n(a + b\overline{Q})}{A} \times F \qquad (7.4)$$

where E is the erosion rate, n is the number of days in the year under consideration, Q is the mean daily discharge of that year, A is the area of the basin, a and b are the regression constants for the relevant mineral from Table 7.1 and F is a scaling factor to rationalise the various units used. Table 7.2 shows the erosion rates calculated for the carbonate and gypsum minerals in the Athabasca and North Saskatchewan River basins for 1968 and 1969. These figures have been calculated with the assumptions

Table 7.2

Erosion Rates in the Athabasca and North Saskatchewan River Basins (mm/1000 yr)

	Athabasca Basin			North Saskatchewan Basin		
	Limestone	Gypsum	Total	Limestone	Gypsum	Total
1968	18.17	11.08	29.25	15.11	8.22	23.33
1969	17.99	10.51	28.50	16.87	8.85	24.92
Mean	18.08	10.80	28.88	15.99	8.54	24.53

that the bulk density of both minerals is 2.5 and that the outcrop area of each mineral is the entire basin. The latter assumption is particularly questionable for the case of gypsum which occurs in only two of the lithologic units within the basins. The erosion rates given in Table 7.2 are for comparative purposes only and are not meant to represent the rate of erosion of the exposed gypsum or of the unexposed gypsum within the basins.

More accurate estimates of the erosion rates of the carbonate minerals in the two basins can be made. Approximate figures for the percentage of the Athabasca and North Saskatchewan River basins underlain by carbonate rocks are 31.4% and 33.4% respectively (v.s., Section 4.3). The mean carbonate erosion rates shown in Table 7.2 can be corrected for this to give figures of 58 mm/1000 yr and 48 mm/1000 yr. These figures are greater than the 37-50 mm/1000 yr that Corbel (1958) gives for the general area. They are the mean figures for two years of average discharges but are approximately twice the likely maximum figure of 24.1 mm/1000 yr derived in Section 4.1.4 for the erosion by processes that result in the transport of material from the basin in suspension.

Quinlan (U.S. Parks Service, pers. comm.) has estimated that each of the Athabasca and North Saskatchewan River basins contains approximately 660 mi^3 of carbonate minerals. This estimate is based upon the areal outcrop of carbonate-containing lithologies and upon the approximate proportion of carbonate minerals in each of these units estimated from the descriptions in Douglas (1969). The annual rate of erosion of the carbonate minerals in the basins shown in Table 7.2 implies that all such minerals could be removed from the basins by solution in a period of time of the order of 10 million years. Because the areal outcrop of sulphate minerals is much smaller than that of carbonate minerals their erosion rate is correspondingly much greater. This rapid erosion rate in part explains the absence of sulphates in much of the lithologic units in which they are reported and also the presence of extensive collapse breccias in these units and in particular those reported by Gibson (1968) in the Triassic Whitehorse Formation.

7.5 Temporal Variation of Erosion by Solution

The percentages of the total amounts of limestone carbonate and sulphate minerals transported in solution by the Athabasca and North Saskatchewan Rivers when flowing at various discharges is shown in Figure 7.7. This figure covers the period 1968-1969. Low discharges (less than 4000 cfs) transport some 32% of the sulphate and some 23% of the carbonate minerals. 60% of the daily mean discharges fall within this range, and account for 16% of the total runoff from the basin. High discharges (of more than 20,000 cfs) occur on only 7% of the days in 1968 and 1969, but carry approximately 26% of the total runoff, 21% of the total carbonates and 19% of the total sulphates discharged from the basin. The remainder of the total runoff (58%), of the total carbonates (56%) and of the total sulphates (49%) is transported by discharges of between 4000 cfs and 20,000 cfs. Low discharge periods are therefore important in the overall pattern of the transport of dissolved minerals as are the very short high discharge periods. The importance of the low discharge period in the transport of dissolved minerals is in contrast to its minor role in the transport of suspended material and bed load.

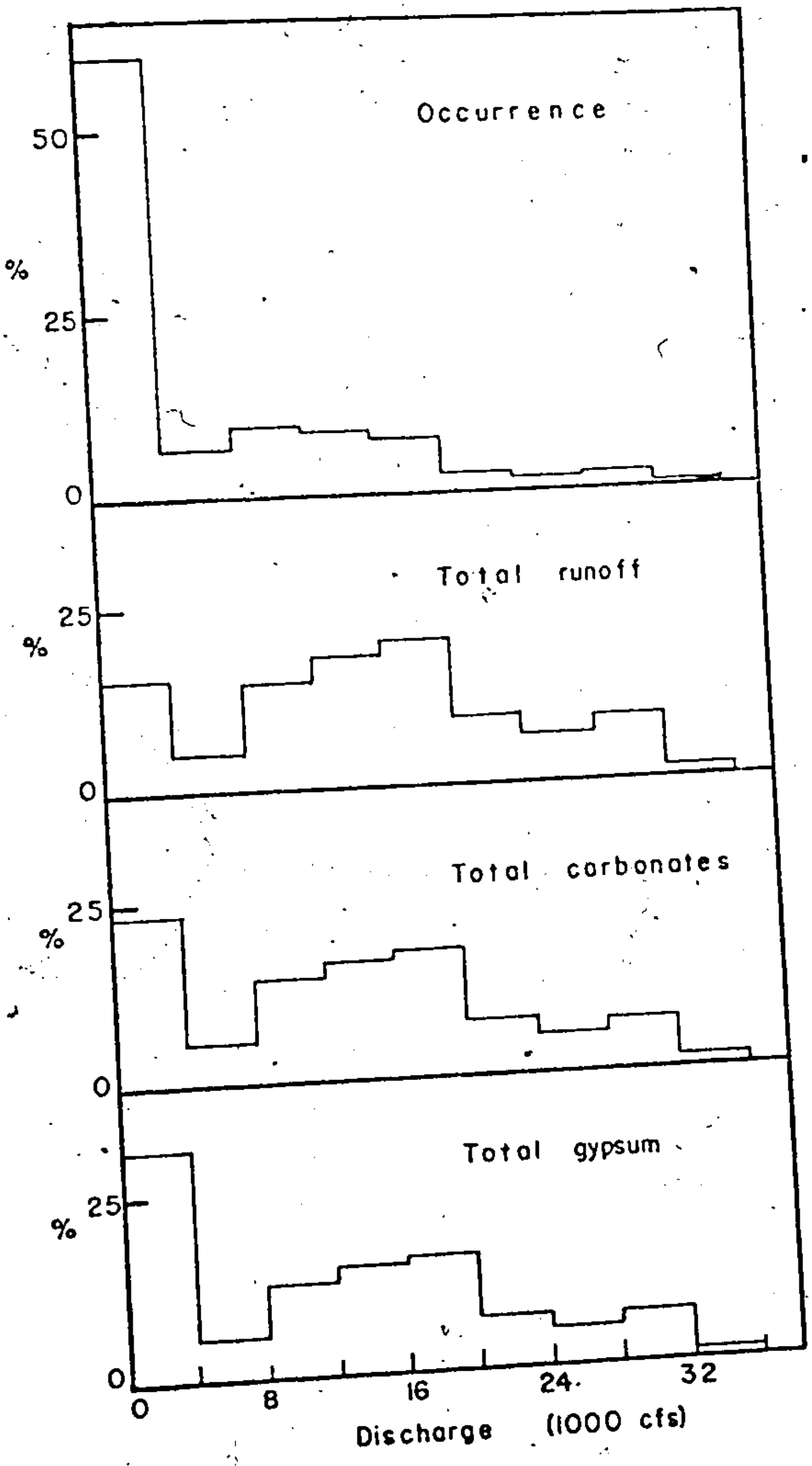


Figure 7.7 - Proportion of the total runoff and dissolved load of the Athabasca and North Saskatchewan Rivers carried by various discharges.

Figure 7.8 shows the mean percentages of the total runoff, of the total dissolved carbonates and of the total dissolved sulphates transported during each month by the Athabasca River during 1968-1969. The histogram of the percentages of the total runoff is a representation of the mean annual hydrograph, and the histograms for the dissolved carbonates and sulphates show the same general shape. Previous studies of the nature of limestone solution in the southern Rocky Mountains have for the most part been undertaken in the summer months (June, July and August). During these months some 58% of the total dissolved carbonates and 51% of the total dissolved sulphates are transported out of the Athabasca River basin. Almost 50% of the dissolved materials carried from the basin flow from it during the nine month period that has received little attention from karst geomorphologists. Previous work has, as has been discussed above, been limited to the study of small karst basins in the headwater zones of the Rockies in which the most (or only) significant component of the discharge is derived locally from snow or ice melt. In such circumstances it is likely that most of the solutional erosion does occur during the summer melt season. A great amount of the geomorphic evolution of the lower parts of the larger basins in the Rockies must occur during the winter period of snow cover. This is true of the geomorphic evolution of the sulphate rocks in particular because the amount of dissolved sulphate transported from the Athabasca River basin does not fall below 4% of the total annual amount in any month.

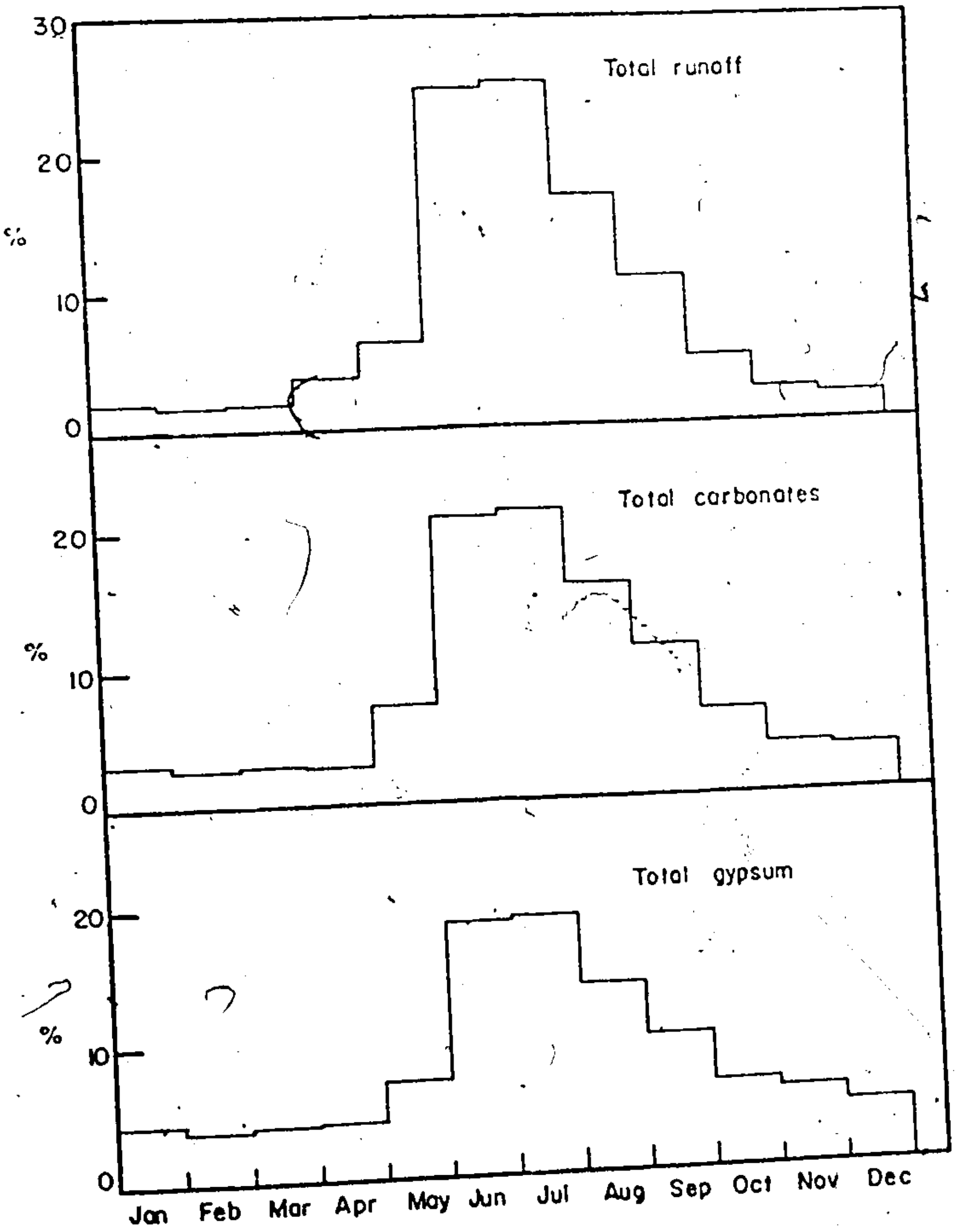


Figure 7.8 - Proportion of the total runoff and dissolved load of the Athabasca and North Saskatchewan Rivers transported in each month.

7.6 Conclusions

The main conclusions of this study with respect to the geomorphology and hydrology of the southern Canadian Rocky Mountains are summarised below.

1) The single most important factor in determining the mean annual runoff of drainage basins in this area is the altitude of the fiftieth percentile of the basin area. The effect of altitude acts both through orographic and topographic influences on the distribution of precipitation and through an influence on the vegetation in the basin which is in turn a primary factor in the rate of evapotranspiration.

2) The hydrologic regime of the Athabasca and North Saskatchewan Rivers is well described by a model incorporating two components. One component is groundwater which has a relatively constant discharge and the other is surface runoff primarily derived from the melting of the annual snow accumulation.

3) The nature of the snowmelt component of the discharge of the Athabasca and North Saskatchewan Rivers is similar to that of a storm hydrograph in a small basin. Snowmelt progresses upward through the basins. A considerable

proportion of the total runoff of these two rivers in late summer and fall is derived from the melting of high altitude permanent snow and ice masses.

4) The pattern of snowmelt in the Athabasca and North Saskatchewan River basins is largely governed by the annual trend of daily mean air temperatures as estimated from data recorded at the mouths of the basins. Short term fluctuations in the discharge flowing from these basins are responses to local climatic disturbances: Such fluctuations account on the average for only 11% of the total annual variance of discharge.

5) The hydrochemistry of the Athabasca River and that of the North Saskatchewan River are very similar. Because all the major chemical components of the dissolved load are derived from the sedimentary rocks which occur throughout the basins, multivariate statistical methods are of no practical use in defining source areas or common features amongst any subsets of these components.

6) The hydrochemistry of both rivers is well described by a two-component mixing model. One component consists of more mineralised water (which in particular contains more sulphate)

and is of relatively constant discharge and the other component consists of less mineralised water and has a highly variable discharge.

7) The two components of the hydrochemical mixing model are equivalent to the two components of discharge which describe the hydrologic regime of the Athabasca and North Saskatchewan Rivers.

8) The erosion rates within the Athabasca and North Saskatchewan River basins are similar to one another. The erosion rate of the sulphate minerals is much greater than that of the carbonates. The rapid erosion of the sulphates accounts for the formation of collapse breccias in the sulphate-bearing lithologic units.

9) The average rate of erosion by solution of the carbonate minerals is comparable to the expected maximum erosion rate by other processes that result in the transport of suspended materials out of the basins.

10) All seasons of the year are important in the solutional erosion of the southern Canadian Rockies. Both the winter period and the presence of sulphate minerals must be considered in any geomorphic study of the area.

11) The glacial gravels infilling a large part of the major river valley systems are more likely to be a site of carbonate deposition than one of carbonate solution.

In addition to those conclusions which concern the large river basins in the area, a number of conclusions concerning the nature of limestone erosion in the small holokarstic basins that comprise much of the headwater zones of the Rockies may be drawn.

12) In most instances the availability of carbon dioxide governs the extent of limestone solution in small basins. The hydrodynamics of the solution process in very local areas can influence the location of the greatest erosion.

13) The water flowing in these small basins may be divided into two components that are similar in concept, though not in scale, to those in the major river basins. One of these components is soil water equilibrated with the partial pressure of carbon dioxide in the soil air and the other is water that flows directly over or through carbonate rocks and that is in equilibrium with the partial pressure of carbon dioxide in the atmosphere.

14) The chemical characteristics of water flowing within a small karst basin depends on the extent of the intermixing of the two components described above. The nature of the aquifer feeding a spring in these areas may be inferred from the hydrochemistry of the emerging water.

15) The most useful measures of the chemical state of waters in a small karst basin are the saturation with respect to calcite and the equilibrium partial pressure of carbon dioxide.

7.7 Unresolved Problems

This study has revealed the nature of the hydrology and hydrochemistry of the large river basins in the Rocky Mountains. Conclusions have been drawn concerning the significance and nature of the solution process in the overall geomorphic development of the area. Some problems arise from the findings listed above. They are stated simply below but are in fact sufficiently complex to warrant detailed investigation.

1) The exact source of the groundwater component of the discharge of the Athabasca and North Saskatchewan Rivers is unknown. A detailed program of water level measurements throughout the year in the glacial fills in the major valleys

could reveal the role of these materials in the hydrologic regime of the basins.

2) The exact source of the sulphate present in the water draining from the two basins is unknown. A comprehensive water sampling program along the length of these rivers and their tributaries throughout the year could locate the most important source areas more precisely. Stable isotope studies might indicate the most important source materials.

3) The erosion rates calculated in this study are only very generalised approximations. There is no precise information on the nature of solutional activity in small basins except during the summer months. Such information is necessary in order to estimate more accurately the nature of karst evolution in the Rockies.

APPENDIX 1

THE CALCULATION OF SATURATION INDICES AND P_{CO_2}

The program used in this study was originally written by the present author, and later expanded and improved by Wigley (1972), who gives a listing and a description of the FORTRAN IV source. The basic steps are:

1) Compute the ionic strength of the water sample from the analytical report, assuming in the first instance that all activity coefficients are unity.

2) Estimate the activity coefficients for all species from the Debye-Huckel equation.

3) Re-evaluate the ionic strength and iterate steps 2 and 3 until a pre-set error criterion is satisfied.

4) Compute the values of the various equilibrium constants at the temperature of the water sample from the temperature dependent forms described by Wigley (1972).

5) Compute SIc, SId, SIg, and P_{CO_2}.

APPENDIX II

ERRORS IN THE CALCULATION OF SIc AND P_{co_2}

SIc is calculated as

$$SIc = \log [Ca^{2+}] + \log [HCO_3^-] + pH - pK_2 + pK_s$$

and thus

$$\Delta SIc = \left|\frac{\partial SIc}{\partial [Ca]} . \Delta[Ca]\right| + \left|\frac{\partial SIc}{\partial [HCO_3]} . \Delta[HCO_3]\right| + \left|\frac{\partial SIc}{\partial pH} . \Delta pH\right| + \left|\frac{\partial SIc}{\partial pK_2} . \Delta pK_2\right| + \left|\frac{\partial SIc}{\partial pK_s} . \Delta pK_s\right|$$

or

$$\Delta SIc = \frac{0.4343}{[Ca]} . \Delta Ca + \frac{0.4343}{[HCO_3]} . \Delta[HCO_3] + \Delta pH + \Delta pK_2 + \Delta pK_s$$

In most natural situations in a calcite system the pH of a karst water is such that

$$2[Ca] = [HCO_3]$$

Traversy (1971) provides estimates of the accuracy of the analyses made by the Water Quality Division and suggests that $\Delta[Ca] = 0.02$ mM/l, $\Delta[HCO_3] =$ 0.02 mM/l and $\Delta pH = 0.05$. Wigley (1971a) suggests that $\Delta pK_2 = 0.01$ and $\Delta pK_s = 0.02$.

Thus

$$\Delta SIc = \frac{0.013}{[Ca]} + 0.08$$

and the assumption that $\Delta SIc = 0.1$ is thus reasonable for waters in which $[Ca] > 24$ ppm.

Pco_2 is calculated as

$$Pco_2 = pH - \log [HCO_3^-] + pK_o + pK_1$$

and thus

$$\Delta Pco_2 = \left|\frac{\partial Pco_2}{\partial pH}.\Delta pH\right| + \left|\frac{\partial Pco_2}{\partial [HCO_3]}.\Delta [HCO_3]\right| + \left|\frac{\partial Pco_2}{\partial pK_o}.\Delta pK_o\right| + \left|\frac{\partial Pco_2}{\partial pK_1}.\Delta pK_1\right|$$

or

$$\Delta Pco_2 = \Delta pH + \frac{0.4343}{[HCO_3]}.\Delta [HCO_3] + \Delta pK_o + \Delta pK_1$$

A reasonable value for ΔpK_o and ΔpK_1 is 0.02 (Wigley, 1971a) and thus

$$\Delta Pco_2 = 0.09 + \frac{.0086}{[HCO_3]}$$

The assumption that $\Delta Pco_2 \simeq 0.1$ is thus valid for waters in which $[HCO_3] > 52$ ppm.

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