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STREAMWATER SOLUTE VARIATIONS IN A PARTIALLY URBANIZED WATERSHED AT NORTH BAY, ONTARIO

by

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requirements for the degree of
Doctor of Philosophy

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ABSTRACT

Solute response is examined in the partially urbanized watershed of Chippewa Creek in the city of North Bay, Ontario. Solute concentrations were monitored for eight sub-basins within the watershed and are statistically related to a series of explanatory hydro-temporal and geo-urban variables. Comparisons are made between the relationships derived for the three flow regimes, springflow, stormflow, and lowflow at the rural and urban sites. As well storm-period response is analyzed by study of an individual storm event and solute yields for the three flow regimes are calculated and compared.

Results show that both temporal and spatial variations of solutes exist in Chippewa Creek solute loads. Moreover this variability is controlled principally by hydrologic conditions and solute supply which are both functions of the physical and human character of the sub-basin studied. Within-site urban and rural solute responses are generally quite different on the basis of magnitudes, controls and intensities of controlling processes over the three flow regimes studied. Solutes derived from principally surficial sources (i.e. Cl^-) exhibit flushing responses; whereas, those derived from principally subsurface sources (i.e. Ca^{++}) exhibit dilution responses. Intensities of these responses are found to vary over the three flow regimes and between the rural and urban settings. Between-site or downstream variation in solute concentrations is found to be a function of degree of ruralness or conversely the degree of urbanization present in the sub-basins as defined by a series of geo-urban variables. Solute export is shown to be greater from the city environment.

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CHAPTER I

Introduction

1.1 Subject of Research

The subject of research for this thesis is streamwater quality where quality refers to the condition of the water in terms of dissolved constituents. Hem (1970) in a landmark paper has discussed the various aspects of the chemical characteristics of natural waters in great detail. He defines and develops the nature of water quality from the perspective of the nature of the dissolved constituents, their detection, their sources and their variabilities. More specifically this thesis research addresses the topic of variability of these dissolved constituents or solutes. Solute variability is studied within the environs of a partially urbanized watershed and the research is directed to detect differences in solute response within differing urban environments.

The relevance of water quality studies to geographers and geomorphologists has been emphasized by many authors (Douglas, 1972; Gregory and Walling, 1973; Walling, 1974, 1975 and 1978, for example). Streamwater quality reflects both the physical and human aspects of river basin development and management and can, therefore, be an excellent environmental indicator. Concentrations and species of dissolved constituents can reflect the chemical character of incident precipitation into the basin, the geochemical processes operating within the basin, the physical character of the basin and the degree and type of human activity

in the basin. As well, water is a vital resource and its chemical quality often restricts its use in both the home and industry. In order to better plan for water use and conservation, it is necessary to realize and to understand the many sources and controls which operate within a watershed to generate a specific and variable water quality. Likewise it is important to understand these sources and controls in the study of the denudation rates on land surfaces through chemical weathering and erosion, often the concern of the geomorphologist. Such rates are often calculated from the total dissolved constituents exported from watersheds in streamwaters.

Much work has been done on the quantity of water in streams, the nature of flooding and flood predictions (see Chow, 1964; Chorley, 1969; and Dunne and Leopold, 1978, for example). A great deal of research has also been conducted on the supended loads of rivers. Authors such as Guy and Ferguson (1962), Keller (1962), Guy (1970), Guy and Jones (1972) and others have pioneered and developed the study of the role of sediment in the urban environment. Less work has been done on the chemical quality of water in streams. However in recent years more attention has been paid to this aspect (see Chapter II). Spatial diversity of streamwater quality has been addressed by Miller (1961) and more recently by Walling and Webb (1975) as well as others. Studies of the temporal aspects of solute variation have been investigated by many authors such as Korven and Wilcox (1964), Pionke and Nicks (1970), Edwards (1973), Walling (1974 and 1978), for example. The temporal variation in solute concentrations has more recently come under intensive scrutiny

with the introduction of automated equipment so that storm-period variance as well as long-term variance can be measured reliably.

The study of streamwater quality is not restricted to geography and geomorphology. Many studies have been conducted by ecologists concerned with nutrient budgets (Likens et al., 1977), by public health and housing agencies interested in pollution aspects (Waller, 1971) and by geologists undertaking geochemical studies (Krauskopf, 1967; or Garrels and MacKenzie, 1967). However geographers and geomorphologists appear to be the most interested in the spatial and temporal variability of solutes in streamwaters.

Although a great number of studies have been done on urban watersheds they have for the most part concentrated on streamflow or sediment aspects (Gregory, 1974; Hollis, 1974; Guy, 1970; and others). By comparison much less research has been done on chemical water quality and its spatial and temporal variability within the urban setting. Most research on the chemical quality of streams draining urban watersheds has dealt specifically with the problems of deicing salts (Boecker et al., 1971; Huling and Hollacher, 1972; Wulkowicz and Saleem, 1974; and others). Discussion and research of a more general nature on urban solute yield has been presented by Leopold (1968), Koch (1970), Waller (1971), Dunne and Leopold (1978) and others. Generally speaking most of these studies report the increases in concentration of solutes in the urban setting as compared to rural background values. Few have attempted to quantify the relationships between solute variability and urbanization or to determine if the temporal relationships of solute variation established in the rural, undeveloped watersheds apply in the urbanized watersheds.

Thus the rationale for the research contained in this thesis becomes evident. It is essentially undertaken to try to bridge the gap from rural to urban in solute studies, to try to examine in an urban setting the validity of temporal and spatial concepts established for the most part in undeveloped rural watersheds. Moreover the subject of research is also valuable in terms of the future planning of urban activity such as sewage disposal, landfill operations, building activity and in general urbanization itself as it relates to the chemical quality of water draining from such environments.

1.2 Objectives of the Research Programme

1.2.1 The Problem

The thesis addresses several aspects of chemical water quality in the Chippewa Creek watershed. Generally it researches selected solute responses in an urban watershed in an attempt to quantify the relationship between degree and type of urbanization and the dissolved load of Chippewa Creek. More specifically it is concerned with the variability of individual chemical constituents making up the dissolved load within the urban setting. Such variability may be introduced by either the human influence in the watershed or by the natural physical controls introduced by hydrologic, biologic, geologic and climatic processes or by both. Thus variability is analyzed both from the human and the physical points of view.

The thesis problem or purpose then is to investigate and to explain the variability and nature of selected solute outputs from differing

human and physical environments within an established urban setting. Both spatial and temporal solute variability are examined and statistical relationships developed to provide explanation for the presence and the degree of variation in solute loads in Chippewa Creek.

1.2.2 The Approach

A small partially urbanized watershed within the city of North Bay, Ontario was selected for investigation of solute variance. The investigation was carried out through an extensive multi-year sampling programme on the small urban watershed of Chippewa Creek lying within the city of North Bay, Ontario. Eight different sampling sites were selected on the creek effectively dividing the major watershed into eight sub-basins for gauging, sampling and comparison. The design is essentially modelled on the multiple-watershed approach often used in hydrologic and water-quality studies where the catchments studied are in a small area of uniform climatic condition (Gregory and Walling, 1973). In the multiple-watershed approach the sub-basins or catchments are subjected to different treatments and comparisons made. However it is not often possible due to time constraints to cause or allow the respective treatments to occur. Thus in the approach used in this thesis, the treatments are "imposed" on the sub-basins by virtue of the selection of the gauging and sampling sites within the urban setting. In fact the choices were made arbitrarily to ensure different types and degrees of urbanization or human activity per site.

Analyses on samples were conducted in the laboratory in accordance with accepted procedures (see Appendix A) yielding values for selected

solute and chemical parameters at the eight sampling sites. Variance in these values is investigated by statistical regression techniques to determine the influence of temporal factors (hydrological, seasonal and diurnal effects) and of spatial factors (geological, pedological and human effects) on solute variability. In order to deal effectively with the hydrological influence, the data is partitioned into groups corresponding to springflow, stormflow and lowflow hydrologic regimes.

The investigation of spatial variance of solutes leads to the quantification of the urban influence on solute variability. Initially the watershed is considered in two sections, urban and rural, and temporal variance is studied to examine the possible differences due to these distinctly different settings. Then all eight sites are examined for spatial or downstream variability to determine the influence of differing degrees of development. Conclusions are made based on the results of the statistical studies supported by observed watershed data and the accepted theories explaining watershed process and streamwater solute variation.

1.3 The Scope

The scope of the thesis is somewhat limited by the constraints of time, labour and equipment. The water quality sampling programme was limited to approximately two years. Samples were collected in ice-free periods only to eliminate sampling and gauging problems of the winter months. Watershed characteristics were determined as accurately as possible from existing data or from abbreviated field survey. Full watershed inventories, for example, a complete soil survey and analysis,

were not possible due to time and labour limitations. Continuous stream gauging was carried out only at two critical sites, one marking the transition from urban to rural and the other at the stream mouth, due to the availability of gauging equipment. Likewise laboratory analyses were restricted to inorganic elements and were also conditioned by available time, labour, and equipment.

The thesis research is also restricted in space. Study is confined to a single small watershed in Northern Ontario. No comparison watersheds in alternate climatic or geologic environments have been monitored to test or to compare to the Chippewa setting. However comparisons are made to existing studies found in the literature. Thus the universality of the thesis results may be rather restrictive. This problem is discussed later in the conclusions.

The thesis is organized into six chapters. Chapter I is an introduction to the subject of research and a statement of the problem. Chapter II is a discussion of the principles of solute dynamics; that is, the processes and interactions which occur in the watershed that ultimately control the concentrations of solute in streamwaters. Following this discussion, the watershed is described and discussed in Chapter III. Watershed characteristics are considered in the context of the hydrological, geological, biological, chemical and human controls on solute variability. Only data relevant to these controls is presented and discussed. Chapter IV outlines the data collection and analysis procedures. Selections of chemical constituents, sites and sampling frequencies are rationalized as well as a general presentation of the results. Chapter V describes the methods of analysis of the results presented in Chapter IV.

The total data base from two years of sampling is partitioned by flow, time and spatial characteristics and the variability of chemical constituents analyzed. Finally Chapter VI draws the thesis together in conclusions about the findings of the research. Suggestions are also made with respect to possible further investigation of the thesis subject. References and appendices round out the thesis with supporting information and technical description.

CHAPTER II

Solute Dynamics: Sources and Controls

2.1 Introduction

Many authors have reported studies dealing with the investigation of stream water chemistry. Many are inventories; others report specific investigations of solute response or variation in streams to watershed characteristics such as geology and soil types. Recently stream water quality studies have become quite sophisticated with the seeking of interrelationships amongst the dynamic aspects of solute production and transport to and within stream waters (for example, Walling, 1978; Chyrulia, 1976).

Solutes find their way into streams from many sources both natural and man-induced. A principal source of supply in humid areas is the chemical weathering of rocks and soils within the watershed or basin supplying the stream. Additional amounts may be added from the precipitation (rain and snow) falling onto the watershed and channel. Biological cycling of nutrients at and near the soil surface also complicates the controls on the solute loads of waters feeding streams. As watersheds become more developed the human-induced solute loads augment and in some cases dominate the natural loads, through the discharge of effluents into channels and indirectly through the use of fertilizers, waste disposal practices, deicing salts and atmospheric pollution.

Although fresh waters vary greatly in solute composition, Gorham (1961, p. 797) notes that few ions account for the total solute load in most natural waters. He lists calcium, magnesium, sodium and potassium as the principal cations and bicarbonate, sulphate and chloride as the principal anions. Both lists are in descending order of abundance. He also argues that ionic proportions in natural waters may not reflect the proportions of constituents in the underlying rock. As an example he notes that the proportion of calcium in some Finnish river waters is nearly fifty per cent more than in the local bedrock from which they drain. This fact suggests sources and controls other than the rock substrata are operating on the chemical quality of stream and river waters.

Apart from the differential effects of the spatially diffuse sources mentioned above, certain geomorphic, hydrologic and chemical processes can also control the levels of solute concentrations in stream waters. For example, degree of slope can affect residence times of water and weak acids in soil and at the bedrock interface (Pitty, 1971). A short residence time may reduce ion concentrations or produce selective solution of rock constituents. However, a longer residence time may provide an equilibrium of dissolved constituents, or an "average fresh water" toward which all fresh waters would trend if given sufficient time for the ion-exchange between water, soil and rock to run to completion (Gorham, 1961).

Hydrologic processes can control delivery of solutes from soil and rock horizons to stream waters as well as the concentration of those

solutes within the channel water. Increased stream discharge dilutes concentrations of certain ions and concentrates others (Likens et al., 1967). However, recent studies have uncovered more complex relationships between hydrologic factors and stream water solute concentrations. Concentrations exhibit a "looped" relationship (called hysterisis) with stream discharge when monitored over both the rising and falling stages of stormflow (Gregory and Walling, 1973). Response of solutes to stormflow may also be complicated by flushing effects within the basin (Walling and Foster, 1975). Seasonal effects likewise add variance to the pattern of solute concentrations in stream waters. Johnson et al. (1969) and Edwards and Thornes (1973) have identified distinct seasonal trends in solute data from rivers in the United States and England respectively. Variation in vegetation and precipitation patterns with season appear to enhance or reduce the concentrations of specific ions in stream waters. Concentrations of certain ions in stream water may likewise be controlled by the thermodynamics and chemical kinetics of chemical reactions taking place both in the stream itself and the soil/rock substrate of the watershed. Chemical weathering of the rock and soil, ion exchange in the soils and the various chemical reactions in stream waters, both abiotic and biotic, will produce variability of ionic concentrations through time (Lee and Hoadley, 1967).

A final source of variance may well be due to the geographically distinct man-induced sources of solutes such as road salting, landfill sites and sewer outfalls. Spatial diversity of or variable delivery from such sources in a watershed will certainly produce spatial variability

of solute concentrations in stream waters (e.g. Wulkowicz and Saleem, 1974). Thus the sources and controls of solute supply to streams may be summarized under the following topics: atmospheric supply, weathering of rocks and soils, biota, hydrology, time and human systems. These topics are discussed in the following pages in some detail.

2.2 Atmospheric Supply

Although the major sources of ions in natural waters are the soil and rock in the watershed, it has been shown by many studies that the atmosphere can be a source as well. Gorham (1961) examines in great detail the contribution of precipitation chemistry in the determining of stream and lake water solute concentrations. He identifies certain lakes in Britain where rain contributes nearly all of the chloride, sulphate, sodium and potassium to these natural waters. Many of the geochemical studies done on small watersheds in the eastern United States have determined the importance of precipitation inputs to solute concentrations in stream waters. For example, Cleaves et al. (1970) found that 38 per cent of dissolved solids entering the watershed of Pond Branch in Maryland were from precipitation sources. River water quality studies in New South Wales, Australia by Douglas (1972), have also revealed that precipitation supplies between 25 and 70 per cent of the total solute loads. Conversely many studies have shown atmospheric supply of solute to be minimal (Kramer, 1976; Miller, 1961; Feth, Roberson and Polzer, 1964; Scheider et al., 1979).

Solutes are supplied by the atmosphere in various ways. Basically most are "washed" from the air during precipitation events while the

remainder are supplied through dry fallout (Gorham, 1961). Dry fallout is apparently a large factor in supplying ions to streamwaters in industrial areas but diminishes to minor importance in rural, forested areas (Likens et al., 1967). Snowfalls appear to be less efficient at clearing the air than is rain although snowmelt in the spring can cause acute depression of pH in streamwaters (Jeffries et al., 1979). In many cases the dissolved constituents in rain constitute the dissolution of the nucleii of rain drop formation and some researchers suggest that the invariable presence of chloride in rain (from sea salt) is due to this phenomenon (Hutchinson, 1957). Gorham (1961) further suggests that all major anions in natural waters may be cycled through the atmosphere in a gaseous state. He notes carbon dioxide, sulphur dioxide, and hydrogen chloride as probable sources of bicarbonate, sulphur and chloride respectively in precipitation. Gorham also discusses the sources of these atmospheric solutes.

Sea spray may supply chloride, sulphate, sodium and magnesium ions to the air and precipitation in maritime areas tends to display chloride/sodium, chloride/magnesium ratios similar to sea water. However, inland sites show less influence from the sea and more influence from soil dust or industrial activity. Soil dust appears to be a major contributor of calcium, potassium and silica to rain water. Pollution both industrial and domestic, contributes both cations and anions to the atmosphere. Smelting operations contribute principally metals and sulphur compounds to the atmosphere. Smoke solids (soot) collected from London chimneys by Gorham (1958a) were found to be especially rich in calcium, sulphate and chloride. Thus solution of the dust

particles and chemical combination of atmospheric gases with rain and snow both work to alter the chemical composition of precipitation.

Of note are the reactions between atmospheric gases and precipitation. These reactions generate various acids such as carbonic, sulphuric, and nitric acids. Hence, rainfall is most often acidic with a pH value usually less than 5.6 which represents the equilibrium between $CO_{2(g)}$ and water in the atmosphere. Values lower than 5.6 indicate the presence of other acid radicals such as Cl^-, NO_3^-, and SO_4^{--}; whereas, values higher than 5.6 indicate buffering by airborne carbonates where free H^+ ions in atmospheric moisture would combine with CO_3^{--} and a metal to produce a more stable bicarbonate compound. The acid radicals may be produced by volcanic activity, industrial pollution and in the case of NO_3^- even by photo chemical processes in the atmosphere (Hutchinson, 1957). In the absence of pollution, bicarbonates may predominate as in the snow analyses reported by Miller (1961). Acidic rain produced by combinations of acid radicals and free H^+ in the rain, upon reaching the mineral surface of the earth promotes the chemical weathering of rocks and soils; however, solution of soil $CO_{2(g)}$ by the precipitation on percolation likely plays a more important role in this respect (Garrels and Christ, 1965).

The influence of precipitation on the variability of stream water quality is obvious. Air masses derived from different source areas may generate different chemical qualities of rain and snow. Thus, for each precipitation event the chemical character of the precipitation may be different, thus introducing variability to streamwater chemistry over time (Jeffries et al., 1978, 1979). In addition the elevation

at which precipitation occurs may also influence its chemical quality (Gorham, 1961; and Likens et. al., 1977), particularly that quality controlled by anthropogenic sources of solutes. All of these possibilities have the potential to produce variance in the chemical quality of streamwaters if the chemical load of the precipitation is of major dimension.

2.3 Geochemical Weathering

Fresh rock at the earth's surface is altered through a complex of interacting physical, chemical and biological processes which are collectively called weathering (Ritter, 1978). The result of weathering is the destruction and recombination of rock and its mineral components into an unconsolidated blanket of debris called regolith or into a granular rock called saprolite. Further weathering of the regolith produces the finely divided and nutrient rich surface cover which forms the mineral component of soils. Certainly the characters of weathering products and resultant soil and rock solutions will be a function of rock and soil type within the watershed. Several studies (for example, Miller, 1961; Feth et al., 1964; Garrels, 1967; and Walling and Webb, 1975) have shown that rock and soil lithology has a strong effect on the chemical quality of streamwaters. However, this relationship is true for areas of more or less homogenous climate. When the scale of studies increase (i.e. global), climate plays a more dominant role in controlling water quality. Nevertheless for small experimental catchment studies lithological homogeneity or heterogeneity will necessarily influence streamwater quality.

Weathering occurs both as physical and chemical processes; however, the two are not necessarily mutually exclusive. For example, the disintegration of rocks into fine particles greatly increases the surface areas for ion exchange and chemical bonding (Ritter, 1978). Because this thesis concerns itself with solute dynamics, further discussion of weathering is confined to chemical aspects. Chemical weathering occurs both as geochemical weathering (the decomposition of rocks to saprolites) and as pedochemical weathering (the formation of soils). These two processes are discussed in greater detail in the following paragraphs as relevant sources of ions for stream waters.

Rock type is a significant factor in determining the quantity and quality of solutes available for stream transport in the drainage basin. The chemical composition of the rocks and the presence, quality and movement of water in the substratum will condition the chemical composition of groundwater and ultimately streamflow. The presence of water is critical to the decomposition of rock. It is supplied to the rocks initially by the vertical percolation of precipitation into exposed rock materials or as surplus soil moisture from overburden. Horizontal movement of this water in rock will also expose additional mineral assemblages to the weathering process. Ultimately these ground waters enter the stream channel as baseflow or as seepage flow depending on the saturation levels of the soil and rocks as dictated by the water table levels (Dunne and Leopold, 1978).

When water penetrates into the mineral components of rocks by seeping into small fractures or along cleavage planes, chemical reactions

occur at the atomic level. Undisturbed, exposed mineral surfaces are not electrically neutral and many have negative charges due to domination of oxygen molecules at these surfaces (Hem, 1972). The negative sites will attract the dipolar water molecules thereby splitting them into H^+ and OH^- ions (Ritter, 1978). These H^+ ions are free to replace mineral cations through ion exchange thus releasing metallic ions to combine with the OH^- ions producing hydroxyls. As hydroxyls collect, the pH of the fluid surrounding the mineral changes and eventually reaches an equilibrium or abrasion pH value which is alkaline or acidic depending on the mineral being decomposed (Ritter, 1978). Thus chemical weathering can also be defined using equilibrium concepts as Krauskopf (1967) has by stating that "weathering [is] the approach to equilibrium of a system involving rocks, air and water".

The chemical weathering system thus involves the reactions between gases (CO_2) and water (H_2O) and between the resulting gas-water system and the minerals within the rocks. These various reactions have already been discussed in earlier pages. Whether and how the reactions will occur and at what rate they will occur are of importance in the generation of solutes for streamwaters. The reactions occur because certain elements are unstable in the presence of others and therefore recombine to form more stable configurations. In natural waters these reactions are often ionic in nature. The extent of these reactions is reflected in their equilibria relationships and reaction rates.

Chemical equilibria of weathering and natural water systems have been investigated and discussed by many authors, especially in the study

of the weathering of carbonate rocks (i.e. Garrels et al., 1960; Garrels and Christ, 1965; Krauskopf, 1967; Langmuir, 1968; Stumm and Morgan, 1970; Freeze and Cherry, 1979; and others). Basically equilibrium is a dynamic balance between the reactants and the products in a chemical reaction. This statement translates into the law of mass action which states that the driving force of a chemical reaction is related to the concentrations of the reactants and products (Freeze and Cherry, 1979). In chemical notation it can be written as below:

$$bB + cC \rightleftharpoons dD + eE \qquad 2.1$$

where b, c, d and e are the number of moles of chemical constituents B, C, D and E respectively.

Equation 2.1 for equilibrium situations can be written as:

$$K = \frac{[D]^d \cdot [E]^e}{[B]^b \cdot [C]^c} \qquad 2.2$$

where K is the equilibrium constant and the brackets indicate concentrations. An example is given below for the solution of carbon dioxide in water and is taken from Krauskopf (1967).

$$CO_{2(g)} + H_2O \rightleftharpoons H_2CO_3 \qquad 2.3$$

This reversible reaction represents a heterogeneous equilibrium situation (i.e. combining two different phases--gas and liquid). At some point in the reaction the formation of H_2CO_3 occurs at the same rate as it reverts back to CO_2 and H_2O. The reaction is in balance

or at equilibrium and an equilibrium constant can be derived.

$$K = \frac{[H_2CO_3]}{[CO_2] \cdot [H_2O]} = \frac{[\text{Conc. of Product}]}{[\text{Product of conc. of reactants}]} \qquad 2.4$$

Chemical equilibrium can also be studied within the context of chemical thermodynamics (e.g. Krauskopf, 1967; Morgan, 1967; Camp and Meserve, 1974; and Statham, 1977). All chemical reactions either consume or give off energy and a chemical reaction can be written as...

$$H \text{ products} - H \text{ reactants} = \pm \Delta H \qquad 2.5$$

Where H is the enthalpy or heat content or total free energy

ΔH is the change in enthalpy.

If the total free energies of the products and reactants are not equal the reaction will proceed in the direction of lower free energy (Statham, 1977, p. 27). So if ΔH is negative, the example reaction of 2.5 above will proceed towards the products of the reaction. In an equilibrium the energy change on both sides of the reaction must be equal and opposite (i.e. $\Delta H = 0$). If one is exothermic then the other must be endothermic with the same amount of energy involved. Thus when the temperature of the environment housing the chemical reaction changes, the equilibrium must shift to reduce the effect of temperature change. If environmental temperatures rise, then the endothermic reaction is encouraged and the exothermic reaction depressed.

The importance to this thesis of the equilibrium concept is the effect of changing equilibria on the fluctuation of streamwater chemistry.

Many geochemical reactions are very slow and may take long periods to reach an equilibrium state under natural conditions, for example, the hydrolysis of potassium feldspar (Krauskopf, 1967). More soluble compounds such as NaCl may readily reach an equilbrium in aequeous solutions. The interesting aspect of equilibria is that changing environments and concentrations of reactants and products can change the direction and rate of the reactions. For example, in the reaction of equation 2.3 above, if more CO_2 is added then more H_2CO_3 is produced. If CO_2 is reduced then the equilibrium shifts left ~~and~~ H_2CO_3 concentrations are lowered. If a base (NaOH) is added then some H_2CO_3 will be used up and the reaction will go to the right thereby using up more CO_2. With added heat the solubility of CO_2 is lowered and the reaction goes to the left. In addition equilibria can be upset by the presence of other ions in solution. The solubility of a salt decreases when one of its own ions is already in the solution from another source and conversely the solubility is enhanced when ions different from the salt are present.

All of these adjustments to equilibria have led to the formulation of Le Chatelier's Rule (Krauskopf, 1967, p. 18) which states

> "A chemical equilibrium responds to any disturbance by trying to undo the effects of the disturbance."

Thus if temperature is raised in the system the equilibrium change will favour the concentration of the side of the reaction requiring the greater amount of heat (endothermic) to proceed. For most salts the solubility increases as temperature rises and therefore the concentrations of dissolved ions increase. When pressure is increased the reaction

that gives a smaller total volume will be favoured; however, pressure changes do not affect solid and liquid equilibria appreciably and only exert a marked influence on equilibria involving gas (Morris, 1976).

In the end, products of weathering will be conditioned by the process of destruction, the weathering environment and the abrasion pH. Some silicates may recombine to form clay minerals if the proper cations are available and other decomposed mineral components may be dissolved and transported away by percolating soil or rock fluids. This translocation of water and ions from the weathering environment is important in that it prevents chemical equilibrium from being achieved. It removes weathering products, changes pH and brings in new reactants which may combine with those escaping the mineral surface. The rate of chemical reaction is proportional to the flow rate of these waters; however, there is an upper limit to the effect which is governed by the maximum possible weathering rate of the mineral surfaces (Statham, 1977).

The processes of chemical decomposition are outlined in many texts: Marshall, 1964; Krauskopf, 1967; Statham, 1977; and Ritter, 1978; and others. The common chemical processes involved in chemical decomposition of rocks are oxidation and reduction, solution, hydrolysis and ion exchange. Each process plays a particular role but all may operate together simultaneously. Oxidation occurs when an element gives up electrons to oxygen and it takes place in presence of air in rock or soil. Reduction occurs below the water table in the absence of air. Ferrous iron is one of the easily oxidized elements and when combined with oxygen becomes ferric iron. Virtually all common minerals and elements are soluble to some extent in normal ground waters and

when atoms are dissolved from a mineral, it collapses. Soluble salts such as the chlorides of sodium, potassium, magnesium and calcium and the sulphates of magnesium and calcium are readily dissociated in water to form true ionic solutions (Gregory and Walling, 1973). However, aluminum oxides and ferric iron are not easily dissolved by normal groundwaters and usually remain behind as residues in soils and decomposed rocks.

Hydrolysis is especially important in the decay of silicate minerals. If free acids are lacking in the weathering environment, then water can dissociate into H^+ and OH^- to provide the necessary H^+ ions for ion exchange as outlined earlier in this section. A typical reaction between olivine and water is cited from Bloom (1978) below:-

$$Mg_2SiO_4 + 4H^+ + 4OH^- \longrightarrow 2Mg^{++} + 4OH^- + H_4SiO_4 \qquad 2.6$$

Thus a magnesium silicate combined with four ionized water molecules produces two magnesium ions, four hydroxyl ions and a molecule of silicic acid. This reaction in Equation 2.6 is overly simplified because pure water is not a good donor of H^+ ions. It is not easily dissociated as evidenced by its low conductivities. However when acids are added to water the reactivity of water and silicate increases dramatically.

Carbonic acid, produced by the solution of CO_2 from the atmosphere by rain and from the upper soil horizons by percolating soil moisture is undoubtedly the major source of hydrogen ions for the weathering of rocks and soil. The importance of carbonic acid in weathering is evident from the high concentrations of bicarbonate ions

in most natural waters, even in waters draining only igneous rocks (Gorham, 1961; Miller, 1961; and others). The atmosphere contains only 0.03 per cent CO_2 by volume but enough CO_2 is dissolved to lower the pH of rain to 5.6 or less. Solubility of CO_2 is temperature and pressure sensitive being more soluble in colder conditions and under pressures greater than one atmosphere. The reversible reactions between CO_2 and water are as follows:

$$\underset{\text{gas}}{CO_{2(g)}} + H_2O_{(aq)} \rightleftharpoons \underset{\substack{\text{carbonic}\\\text{acid}}}{H_2CO_{3(aq)}} \rightleftharpoons \underset{\substack{\text{hydrogen}\\\text{ion}}}{H^+_{(aq)}} + \underset{\substack{\text{bicarbonate}\\\text{ion}}}{HCO_3^-{}_{(aq)}} \qquad 2.7$$

For every temperature and pressure there is an equilibrium (Bloom, 1978) and changes in the system will drive the reaction to the left or right. If air pollution acidifies the rain with HCl or H_2SO_4 molecules then the equation is driven left and fewer bicarbonate ions may be formed in the resultant drainage waters. The reactions are also sensitive to temperature and pressure and react according to Le Chatelier's Principle mentioned earlier. Thus, if temperature rises, the reaction will go left because $CO_{2(g)}$ becomes less soluble in water and therefore is in short supply. Similarly rises in pressure tend to drive gases into liquids and increase solubilities so that an increase in pressure would drive the reaction to the right. Thus higher temperatures and pressures produce environments where CO_2 is more or less soluble in water and therefore greater or fewer H^+ ions to displace metallic ions from minerals and greater or fewer HCO_3^{--} ions to react with these displaced ions.

When carbonic acid is added to water, it dissociates readily to provide even greater concentrations of H^+ to render hydrolysis even more effective in the decomposition of silicate minerals. For example equation 2.6 above now becomes:

$$Mg_2SiO_{4(s)} + 4CO_{2(g)} + 4H_2O_{(aq)} \longrightarrow 2Mg^{++}_{(aq)} + 4HCO_3^-{}_{(aq)} + H_4SiO_{4(aq)} \quad 2.8$$

olivine — carbon dioxide — water — magnesium and bicarbonate ions in solution — silicic acid in solution

The results of the reaction are soluble products of weathering and these are transported eventually to stream channel waters by groundwater percolation. Also as the carbonic acid is consumed the solution becomes more alkaline due to the dissolved bicarbonates produced.

Another very common weathering reaction occurs between feldspar and carbonated water, in this case potassium feldspar (orthoclase) and an example is presented below from Bloom (1978):

$$2KAlSi_3O_{8(s)} + 2H_2CO_{3(aq)} + 9H_2O_{(aq)} \longrightarrow Al_2Si_2O_5(OH)_{4(aq)} + 4H_4SiO_{4(aq)} + 2K^+_{(aq)} + 2HCO_3^{--}{}_{(aq)} \quad 2.9$$

orthoclase — carbonic acid — water — kaolinite clay — silicic acid in solution — potassium and bicarbonate in solution

Calcium and sodium feldspars hydrolysize readily in carbonated water to produce a clay mineral, silica in solution and a bicarbonate in solution. Clay minerals are stable except under most humid, tropical conditions and remain as residues of weathering to form major constituents of soils. A summary of the weathering products of the minerals constituting

granitic and similar rocks is given in Table 2.1 (p. 26).

Dissolution of feldspars is not a simple, uniform process. Lerman (1979) discusses in detail the steps in the chemical decomposition of feldspars of all types and has identified four distinct phases through which reaction mechanisms pass as dissolution progresses. They are as follows:

(1) Surface solution, H^+ cation exchange (duration $<$ 3 minutes)

(2) Concentration of solution rises as a low power function of time (duration of up to 50 hours)

(3) Increase in concentration obeying the parabolic rate law (duration up to 20 days after stage two)

(4) Concentration increases linearly with time (duration up to 30 days following stage three)

During the first two stages more cations are released than silica but as time progresses the dissolved constituents in the ground fluids eventually take on the same proportions as in the original rock. Thus it could be argued that the "average fresh water" of Gorham, discussed earlier, should contain the same proportion of the various soluble constituents of the regional rock and soil given a sufficient residence time. That the ionic concentration of this water remains proportional in its travels to the stream channel and the sampling site is doubtful. Many controls act to cause variation in the original ionic concentrations. These controls are discussed on later pages.

Another factor in the removal of ions from rock surfaces is the relative chemical mobilities of the various cations. Certain cations are more readily exchanged than others. These mobilities are a function of ionic radius and certain external factors such as the action and

TABLE 2.1

WEATHERING PRODUCTS OF COMMON SILICATE MINERALS *

MINERAL	CHEMICAL COMPOSITION	WEATHERING PRODUCTS	
		SOLUBLE	INSOLUBLE
ORTHOCLASE	K, Al, SiO_n	K^+ (minor) soluble silica	Clay with K^+ adsorbed on it
PLAGIOCLASE	Na, Ca, Al, SiO_n	Na^+, Ca^{++} soluble silica	Clay with K^+
HORNBLENDE	Ca, Fe, Mg, Al, SiO_n	Ca^{++}, Mg^{++} soluble silica	Clay, hematite and/or limonite
BIOTITE	K, Fe, Mg, Al, SiO_n	K^+ (minor) Mg^{++}, soluble silica	Clay, hematite and/or limonite
QUARTZ	SiO_2	none	quartz grains

* modified from Cargo and Mallory (1977)

residence time of leaching solutions (Lerman, 1979), the pH of the groundwater, the Eh of the weathering environment and the processes of fixation, retardation and chelation (Ritter, 1978). The relative mobilities of major ions and compounds are given in Table 2.2 (p. 28).

The pH will condition the concentrations of ions in groundwater in that pH is a measure of the available H^+ present. In areas of sufficient rainfall the H^+ is in good supply and is easily replenished to produce continual exchange with mineral cations. For this reason soils in humid regions are often low in highly mobile elements such as calcium, sodium, magnesium and potassium (Pitty, 1979). Not only does pH affect the actual chemical weathering process but it can also affect the relative concentrations of the weathering products in soil and rock solutions and ultimately streamwaters. Introduction of acid waters via rainwater percolation, organic sources or other mineral breakdown (sulphides) will increase the concentrations of H^+ ions and expedite weathering to produce more weathering products including HCO_3^-. Thus, the groundwaters will become a more basic solution. If waters containing excessive OH^- ions are introduced, weathering is slowed because the H^+ ions are used up neutralizing this strong base and are not free to displace cations from mineral surfaces. Thus changing the pH of the weathering environment will produce variable concentrations of weathering products.

The effect of the Eh (redox potential) on ion mobility is to control the release of less mobile elements such as iron and titanium (Ritter, 1978). The Eh of the weathering environment is often controlled

TABLE 2.2

MOBILITY OF CERTAIN ELEMENTS *

ACTIVITY	ELEMENTS
actively removed	Cl (Br, I) S
easily removed	Ca, Mg, Na, K, F, SiO_2 (silica)
mobile	P, Mn, Co, Ni, Cu
inert (weakly mobile)	Fe, Al, Ti
practically immobile	SiO_2 (quartz)
easily dissolved (ionic solution)	NaCl, KCl, $MgSO_4$, $MgCl_2$, $CaSO_4$, $CaCl_2$
lesser solubility	$CaCO_3$, $MgCO_3$, Na_2CO_3, silica
very low solubility (from colloidal solutions)	Fn, Mn, P, etc.
essentially unsoluble	quartz, various silicate and aluminum silicate minerals

* modified after Gregory and Walling (1973, pp. 279-80)

by the presence of water. When soils become waterlogged, for example, oxygen is lacking and reducing conditions become prevalent.

Some ions, especially K^+, may become fixed in the weathering environment and display mobilities less than expected. In the case of K^+, the ion often is adsorbed to clay mineral surfaces or absorbed in clays with expandable lattices such as chlorite, illite, micas, vermiculite and montmorillonite. Retardation of mobility occurs due to the thin coating of the weathering surface with such compounds as $Al(OH)_3$, prohibiting the efficient transfer of other ions into the surrounding fluid. This is especially significant in the initial phase of orthoclase hydrolysis but becomes less of an effect in lower pH where $Al(OH)_3$ is soluble.

Another control on ion mobility to be discussed here is chelation. Complexing agents are produced by the alteration of humus into humic or fulvic acid. These agents can then incorporate into their ring structure various metallic ions including those which may be extremely immobile under normal conditions (Ritter, 1978). Often the complexing agents become soluble on oxidizing and carry the metals with them in the vadose and groundwater solutions.

In summary, then, the character of solutions emanating from rock and soil to feed streamflow will be to some degree a legacy of the chemical makeup of the rock, the nature of the weathering environment, the rates and equilibria of chemical decay and the rates of removal of weathering products. If any of these factors change over time or space, they will potentially introduce variability in the chemical

character of streamwaters draining such materials. Even so, there are additional controls operating to introduce further variance and these possibilities are discussed in the following sections.

2.4 Pedochemical Weathering and Ion Exchange

The processes of pedochemical weathering are similar to those for rocks. The various chemical reactions described earlier operate to further change the minerals in soils. Precipitation, with its inherent supply of H^+ ions, percolates into the upper layers of soil and dissolves more CO_2 (generated by organic decay) to become even more acidic. Thus with a generous supply of H^+ ions, this water begins to decay the soil minerals through solution and exchange processes mentioned earlier. The products of the chemical reactions are often clay minerals, soluble compounds and free cations in solution. However, the freedom of the cations to move away with soil moisture is often restricted in that they are adsorbed onto negatively charged clay and soil particle surfaces (Marshall, 1964). The ability of a clay or soil to adsorb cations is called its cation exchange capacity (CEC). Both H^+ and metallic cations are held and the relative amounts of each will govern the pH of the soil water complex. The ratio of metallic cations to the total CEC multiplied by 100 is called percentage of base saturation (% BS) and the higher its value the higher the soil pH because most of the surface sites will be occupied by metallic ions rather than H^+ ions.

If a wealth of H^+ ions exist in the surrounding solutions then, they will exchange with the metallic cations freeing them from soil

and clay particle surfaces into these solutions. These cations are then transported away by movement of soil moisture and ground waters (Hunt, 1972). The above processes are not restricted to clays alone. Kennedy (1965) has measured sizeable CEC values in sand-sized particles from river bottoms. The CEC of soils is commonly expressed in total milli-equivalents of ions per 100 gms. of solids. The values obtained for soils will indicate the behaviour of soils to solutions percolating through them. Low % BS values would indicate few cations are available to displace adsorbed H^+ to form bicarbonates and raise the pH of the soil; therefore, a poor supply of such cations would be available to stream waters. On the other hand high % BS values would indicate good cation retention by the soil and subsequent supply to stream waters would occur when pH values drop low enough from percolating precipitation to free them from exchange sites into the soil solution or ground water. Lai and Jurinak (1971) confirm this fact and state that the concentration of cations supplied to the soil solution is directly proportional to their volume held by adsorption to soil particles. As base saturation and soil pH increase, more metallic cations are available to the soil solution through release by cation exchange.

Movement of dissolved constituents progresses vertically in the soil through eluviation in the upper layers and illuviation in lower layers. These processes produce the soil horizons common to more mature soils. The rates and amounts of ions removed from the soil depends again on ion mobility, the cation exchange capacity of the soil particles, presence and movement of water and the soil pH.

2.5 Biological Nutrient Cycling

As discussed earlier, pedochemical weathering is an important geologic source of natural water solutes. The products of weathering in soils are not entirely free to migrate downgradient with soil waters. Not only do the chemical controls discussed earlier provide constraint but also plants, through their roots, selectively remove ions from the soil. Rootlets hold a negative charge and water films surrounding them are high in H^+ ions which are exchanged for needed cations (Hunt, 1972). Nutrients required and taken in are classed as macronutrients and micronutrients. They have been identified by Miller et al. (1966) as:

Macronutrients	Micronutrients
Carbon	Manganese
Hydrogen	Copper
Oxygen	Zinc
Nitrogen	Molybdenum
Phosphorous	Boron
Potassium	Chloride
Calcium	Iron
Magnesium	
Sulphur	

These nutrients are taken into the biomass in various quantities at different times and by different species. Thus, annual as well as seasonal and even diurnal cycles can be present. Duvigneaud and Denaeyer-DeSmet (1970) identify two major pathways of cycling of nutrients within the forest ecosystem: the biological "closed" cycle and geochemical "open" cycle. The biological cycle involves (1) uptake by root systems (absorption from the soil); (2) retention (increment of nutrients in the woody biomass); (3) restitution or losses (release of nutrients back to soil via leaf litter, organic debris, or washing by throughfall and

stemflow). Thus the interaction among these three processes will control on an annual, seasonal or diurnal basis the availability of chemical constituents to surface and subsurface waters.

The geochemical system (which also includes the hydrological system) involves the input and output of fresh mineral elements from the cycle. Principal inputs occur from precipitation, from rock and soil weathering and from the atmosphere through nitrogen-fixation by plants. Losses from the cycle occur in drainage waters (both surface and subsurface) and through biomass harvesting.

Of interest to this particular thesis is the return of the nutrients to the soil by throughfall and stemflow and decomposing litter because precipitation, in "washing" the forest of leaf excretions and dry aerosols, carries with it these dissolved nutrients into storm runoff and groundwater recharge. Throughfall and stemflow water qualities in a Northern hardwood forest have been studied by Eaton et al. (1973). Their results show that throughfall beneath maple was enriched in Na^{+}, SO_4^{--}, and Cl^{-}, more so than for yellow birch or beech. Yellow birch produced higher Mg^{++} concentration; whereas, beech produced higher values of NO_3^{-} than either of the other two species. Stemflow added little to the total loss from trees.

Variations of note in the quality of throughfall occurred principally due to seasonal, aging and precipitation quality effects. Concentrations of Ca^{++} and Mg^{++} remain constant during June, July and August but reach their maxima in September just prior to leaf fall, after which they decline . Values for N, SO_4^{--} and Na^{+} were variable

for the summer and reached maxima in September like Ca^{++} and Mg^{++}. However, K^{+} and Cl^{-} were low during summer and increased to maxima following leaf fall. Leaf aging by physical damage or through physiological changes also increases the concentration of K^{+} in throughfall during the growing season.

Eaton, et al. (1973) also report that the amount of nutrients leached per unit quantity of rain is greater during low intensity rain and also in the first few hours of leaf wetting. Thus as the storm progresses throughfall concentrations decrease, apparently due to a shortened residence time and diminishing nutrient supply on leaf surfaces. Generally the leachability of elements from trees during the summer occurs in order of importance as:

$$Na > S > K > Mg > Ca > N > P \qquad 2.10$$

Thus the solute content of precipitation can be significantly increased during percolation through a forest canopy and Gregory and Walling (1973) report 18-fold, 4-fold and 3-fold increases in potassium, calcium and sodium respectively. Stemflow solute loads tend to be higher than that of throughfalls but parallel the throughfall in seasonal variation (Eaton et al., 1973). Generally stemflow effects are considered minor in that only five per cent of the precipitation percolating through the forest cover occurs as stemflow.

Of significance also in the biological controls on solute variability in stream waters is the decomposition of forest floor litter. Accumulation of nutrients occurs in the rooting zone of the soil slowing

down the cycling of elements and causing uptake from lower soil horizons and the weathering of parent rock (Duvigneaud and Denaeyer-De Smet, 1970). As well nutrients are leached from the forest litter to be carried downwards into soil horizons or laterally on surface towards drainage courses during overland flow. Rates and volumes of nutrients released have been reported by several authors (Attiwill, 1968; Gosz et al., 1973; Likens et al., 1977; and Holker, 1979, for example). Attiwill, from studies in Australia, reports a loss of 5 to 15 per cent per year for Ca^{++}, P and Mg^{++} from leaf litter and loss of 60 to 80 per cent for K^{+} and Na^{+} which are easily leached but the others, being bound in plant structure, are released more slowly during decomposition.

Gosz et al. (1973) report statistics on the Hubbard Brook confirming these figures. Total release of Ca^{++}, K^{+} and Mg^{++} per year from leaf litter was about 42 per cent, 70 per cent and 54 per cent respectively. Release of these nutrients from the litter showed a strongly seasonal pattern. Peak release rates occurred for all three elements in the month immediately following leaf fall in the autumn as a result of leaching and a slower release occurred through winter and summer due to decomposition. Conversely, outputs from the watershed via streamflow were high in spring runoff. Overall it was concluded that the release of nutrients in the litter contributed very little to the streamflow export of nutrients from the watershed. Release of Ca^{++} occurred evenly throughout the year with a small peak in autumn. Potassium, on the other hand, was primarily leached in the autumn and

little was released through the rest of the year during decomposition. Magnesium was intermediate between Ca^{++} and K^{+} in release pattern.

Movement of released nutrients is bound intrinsically to the hydrologic processes occurring at the soil/litter interface. Precipitation and snowmelt can be stored in the litter, penetrate the soil or run laterally over the ground surface while transporting the released nutrients. Water storage in the litter can be significant in low intensity, low volume rainfall. Hocker (1979, p. 252) reports that from 93.7 to 11.1 per cent of rainfall of magnitude 6.4 mm. (0.25 in.) to 27.9 mm. (1.10 in.) respectively can be stored in hardwood leaf litter. Thus under low volume storm conditions released nutrients likely remain in the litter; whereas, during larger volume storms less water is stored and more runoff occurs. Maximum transport of litter nutrients would occur during larger storms especially in the autumn subsequent to leaf fall.

When soil infiltration occurs, nutrients are transported downward and are not immediately available to streamwater. McColl (1969) reports a fifteen hour time lapse between the onset of a typical storm and the arrival of the wetting front at the 120 cm. depth in the soil. Thus transport of litter nutrients is slow. In addition the nutrients react with the humus soil layers and plant roots to be absorbed from or released to soil and rock solutions depending on chemical activity further slowing or inhibiting release to streamwaters.

Biological controls on solute movement in the watershed can also be present in the channel itself. Aquatic organisms by removing nutrients

from streamwaters change concentrations of dissolved constituents and cause chemical reaction when the system attempts to regain equilibrium (Lee and Hoadley, 1967). Thus abiotic equilibria are upset by biologic metabolisms which tend to produce changes in pH and in the precipitation, complexation, redox and sorption reactions of streamwaters on a diurnal and seasonal basis (Cleaves, et al., 1970). Although it is generally accepted that biologic cycling of nutrients (especially carbon, nitrogen and phosphate) does influence the chemical composition of natural waters, few studies have led to reliable estimates of the extent of this influence (Lee and Hoadley, 1967).

From the above discussion on biological controls on inorganic nutrients, it is apparent that (1) the overall contribution of inorganic solutes to streamwaters from throughfall and leaf litter is generally small; (2) the periods of maximum contribution of ions to streamflow occur during storms producing overland flow especially during the autumn and to a minor extent during the spring and summer; (3) biological recycling can produce conditions which could cause variability in stream water solute concentrations both temporally (seasonal and hydrological events) and spatially (special distributions and densities).

2.6 Hydrological Controls

The role of precipitation in solute generation and variability has been discussed earlier in Section 2.2 (p. 12) but its importance is reviewed again here in light of hydrological considerations. Precipitation not only contributes a good supply of H^+ ions and a minor supply of other cations and anions, but also provides water for the

transportation of weathering products from forest litter, soils and rocks. Precipitation (rainfall and snowfall) is chemically aggressive having a pH usually lower than 5.6 and can attack minerals to produce soil and rock solutions containing the solutes of weathering reactions. As soon as precipitation enters the biomass, it begins to change in chemical quality and by the time it filters downslope through the soil and rock to the stream channel, its aggressivity is substantially reduced (Chyurlia, 1976). If the watershed is rather heterogeneous with respect to vegetation, soil and rock, then these solutions will arrive at the stream with different chemical qualities. On the other hand, if precipitation finds its way to the channel over the ground surface, it will arrive rather dilute and relatively free of the solutes of weathering products. Thus the ultimate chemical composition of the stream waters will be a function of the mixing of the waters from the various sources, precipitation, groundwater, soil water and overland flows. The flow paths of streamflow source waters affect solute loads differently. Generally concentrations are most dilute in precipitation and increase progressively for overland flow, soil water and groundwater sources. At low discharges a constant maximum concentration of dissolved constituents is achieved in stream water; this maximum is then diluted by rainwater and runoff during storm events. At some point diluted concentrations level off to the actual concentration of the incoming storm waters (Gregory and Walling, 1973). As well, further variations and complexity are introduced to this simple relationship by the biological recycling processes discussed earlier.

The relationships between dissolved constituents and discharge, known as dilution models, have been investigated and reported by many authors (for example, Langbein and Dawdy, 1964; Korven and Wilcox, 1964; Johnson et al., 1969; Hem, 1970; Nelson, 1970; Edwards, 1973; Edwards and Thornes, 1973; Oxley, 1974; Walling, 1974; Walling and Foster, 1975; and Walling, 1978). The simplest model, a two-component mixing model, has been reviewed by Hem (1959), Langbein and Dawdy (1964) and Pinder and Jones (1969). It is an inverse hyperbolic function and has been verified by Gunnerson (1967), Korven and Wilcox (1964), Nelson (1970) and Pionke and Nicks (1970). The relationship is expressed as follows:

$$C = aQ^{-b} \qquad 2.11$$

where C is the concentration
a is the constant
b is the slope of the relationship

The slope can vary for different ions and Nelson (1970) notes seasonal changes in slopes indicating that the degree of dilution varies under differing watershed conditions. He suggests that when $b = 1$, C is directly proportional to Q; when $b > 1$, the accrual of stream load (C) is greater than water (Q); and when $b < 1$ or negative, stream load (C) is diluted by incoming water (Q). This model of dilution is very simplistic and does not account for other possible sources of variance in the hydrologic environment, especially during storm events. Therefore, the degree of explanation offered varies from 36 to 98.5 per cent (Pionke and Nicks, 1970) and therefore, the behaviour of individual ions is often not in total correspondence to the relationship expressed

by Equation 2.11. In fact it often becomes linear in form (for example, the results of Johnson et al., 1969; Cleaves et al., 1970; Oxley, 1974; Smith and Newson, 1974 and Chyurlia, 1976). On the other hand, many relationships become more complex when the normally expected dilution during a storm event is preceded by a rise in concentration (Walling and Foster, 1975). For example, a summary of ion response during storm events is given below in Table 2.3 (p. 41) for several studies.

The simplistic dilution model of Equation 2.11 assumes a constant source concentration and does not consider such sources of variance such as the heterogeneity of runoff production, hysteretic effects, seasonal effects, chemical buffering, flushing effects and biological effects, all of which are capable of producing scatter about the line defined by the above rating equation (Gregory and Walling, 1973). Thus Equation 2.11 is often not significant and often explains considerably less than 100 per cent of the variance in C.

In order to explain the relationships between concentration and discharge better, several authors (Johnson, 1969; Hall, 1970; and Walling, 1974) have designed and investigated more complex dilution or mixing models. Basically these models involve the consideration of concentrations at the sources of flow to streamwaters, some holding them constant (Walling, 1974) and others allowing for a variable concentration at source (Hall, 1970). Essentially both involve the relationship of Equation 2.12 below:

TABLE 2.3

EFFECT OF INCREASING DISCHARGE ON IONIC CONCENTRATIONS

AUTHOR(S)	IONS						
	Cl	HCO_3	Ca	Na	K	Mg	T.D.S.
Korven and Wilcox (1964)			-	-	-	-	
Johnson et al. (1969)	I		-	=	+	-	
Cleaves et al. (1970)	-	-	+	I	+	+	++
Edwards (1973)		-	+	-	+	-	
Walling and Foster (1975)			-	-	++	-	
Walling (1978)	-		-	-	+	-	=

Key

- \- dilution
- = strong dilution
- \+ concentrated
- ++ strongly concentrated
- I inconclusive

$$Q_t C_t = (Q_1 \times C_1) + (Q_2 \times C_2) + \ldots (Q_n \times C_n) \qquad 2.12$$

where Q_t and C_t are total flow and concentration at time of sampling.

and Q_1, Q_2 etc. and C_1, C_2 etc. are related to different sources for flow and concentration.

Different sources of flow have been used in various watersheds to obtain the best explanation of concentration variations. Walling (1974) has employed various combinations of quickflow and delayed flow discharges and concentrations of solutes to get as high as 53 per cent explanation of solute concentration variance by discharge. A further universal explanation by discharge is not likely possible due to the influence of other environmental factors and due to the difficulty of measuring the ever-changing chemical qualities of the various flow components (Edwards, 1973).

Another type of variation is introduced by hysteresis (Toler, 1965; Cleaves et al., 1970; Oxley, 1973; Walling, 1973; and Walling, 1978) where, for a similar discharge on the rising and falling stages of a storm event, the solute concentrations will be different. Concentrations may be lower on the rising stage to produce anticlockwise hysteresis (Toler, 1965) or higher on the rising stage to produce clockwise hysteresis (Walling, 1974). The latter seems to be the usual case and can be explained by the flushing of accumulated solutes from the watershed in the initial runoff thereby delaying the subsequent dilution. However, in the case of anticlockwise hysteresis, changing source areas for the flood waters cause a larger concentration on the falling stage where waters come from more distant parts of the watershed and have had longer contact

with soils and litter (Cleaves et al., 1970). Thus initial storm effects and changing source areas can introduce further variance to solute concentrations in streamwaters.

The result of the above events is that peak discharge of water seldom coincides with the peak concentration of a particular solute. Walling and Foster (1975) have investigated these response lags illustrated in the chemographs of ionic species. Some ions peak prior to hydrograph peak while others peak after the flow peak. Response lag times for ions are apparently related to the logarithms of the hydrograph rise (M^3/S), preceding flow level and a season index.

The complex relationship between discharge and solute concentration has been well documented (for example, Douglas, 1973; Edwards, 1973; and others) and in attempts to improve on the relationship, researchers have used several other hydrologic parameters as independent variables to explain variance in solute concentrations. Edwards (1973) has used the volume of rain, the mean discharge and the maximum discharge of the week prior to the collection of each sample to try to increase the explanation provided by just instantaneous discharge alone. No significant increases in explanation resulted for the catchments that he studied. Pionke and Nicks (1970) have used measures of precipitation and anteoedent conditions, as well as streamflow in a study on West Bitter Creek and Beaver Creek, two ephemeral streams in Oklahoma. The best individual predictor was the maximum daily precipitation ($R^2 = 0.51$) which explained nearly twice the variance than that of flow. Using a multivariate regression involving monthly precipitation, maximum daily

precipitation, antecedent precipitation, pan evaporation and distance to rain gauge, they were able to increase the total explanation to 65 per cent. This study was undertaken on ephemeral streams lacking sustained baseflow, conditions under which precipitation would provide greater influence. However the inclusion of antecedent conditions has some merit even in perennial stream studies in forested areas where nutrient levels build up in the soil, leaf litter and biomass to be flushed out in storm conditions.

Seasonal solute variance, although strongly tied to biological cycling, can also be induced by hydrological effects. Several studies allude to seasonal variance in ion concentrations. Many of these studies have been executed in geographic locations where the seasonal cycles are not so diverse and strong as in Canada (for example, Douglas, 1972; Edwards, 1973; Lewin et al., 1974; Oxley, 1974). More relevant to this thesis research are those studies done by Drake and Ford (1974) in the Alberta foothills and by Cleaves et al. (1970) and Likens et al. (1977) in the Hubbard Brook System of New Hampshire.

Basically the cations (Na^{+}, Ca^{++}, Mg^{++}, K^{+}) display two peaks, a major one in the spring (late March to early May) and a minor one in the autumn (October). The spring peak is likely due to the flushing action of the spring melt transporting accumulated nutrients from the biomass and soil layers. Similarly the autumn peak results from storm-waters flushing readily-dissolved constituents from decaying leaf litter and also due to the lessened demand of the biomass on the nutrients in soil and rock waters. During the summer months small variations

occur due to storm dilution effects and diurnal effects again related to biologic uptake (Cleaves et al., 1970). Bicarbonate displays low concentrations during the winter months and begins to gradually build up in the spring and summer to peak in the autumn. On the other hand Cl^- shows little variation because of the undeveloped nature of the watersheds in question.

A final control on streamwater quality is chemical buffering and it is discussed here using the definitions below taken from Camp and Meserve (1974). In natural waters any electrolyte (NaCl) which ionizes in water to yield or to react with neither H^+ or OH^- is considered to be a neutral salt. However if HCl ionizes to yield H^+ or to combine with OH^- then it is considered to be an acid. When NaOH ionizes to produce OH^-, or Na_2CO_3 ionizes to produce CO_3^{--} which combine with H^+ to reduce acidity, they are called bases or alkalis. When a substance such as HCO_3^- ionizes to yield either H^+ or OH^-, for example,

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{--} \qquad 2.13$$

$$HCO_3^- \rightleftharpoons OH^- + CO_2 \qquad 2.14$$

it is called an ampholyte or amphoteric substance. Thence HCO_3^- is a buffer supplying acidity when alkali is added and supplying alkali when an acid is added. Thus changing pH values in the stream environment will have an effect on the concentrations of bicarbonate and will introduce variability of this anion over time and space.

Other buffering actions occur within both the watershed and the stream channels as well. The CEC of the watershed soils often works to produce a constant supply of cations to streamwaters (Likens et al., 1967). Similarly the suspended and bed loads of streams can exert buffering action through CEC. Kennedy (1965) reports CEC values for sands from 0.3 to 13 meq. per 100 g. and notes that in streams less than 30 cm. deep, the bed sediment may have greater concentrations of cations held by adsorption than the actual streamwater itself. Presumably as the pH and chemical quality of the streamwater changes, the exchangeable cations in bed load and suspended sediments will be adsorbed or released to stabilize the ionic concentrations in the water itself. This is particularly true during flood conditions when the suspended load is at maximum concentrations.

In addition basic chemical equilibria will play a role in determining the relative concentrations of ions in streamwaters. The concepts of chemical kinetics and thermodynamics have been discussed earlier and they apply to in-channel waters as well as to groundwaters. Thus with changes in concentrations of chemical constituents, temperatures or pressures, chemical reactions will shift in order to maintain their equilibria. Certainly, of the factors controlling solute concentrations in natural stream waters, saturation indices of the various dissolved species are important (Freeze and Cherry, 1979). When saturation conditions are achieved, ions pair and may precipitate as solids. In natural streams, where pressure is relatively constant, temperature and concentration changes may work to bring about such phenomena. Temperature and concentration changes are often brought about by the influx

of waters from divergent sources to a reasonably uniform baseflow so that chemical changes are often associated with changing discharge conditions.

In summary, then, discharge volumes, source, antecedent condition and temporal behaviour all tend to influence or control the variability of solutes in streamwaters. The degree of control varies with season, geographic location and general climatic regime.

2.7 Human Activity and Development

Against a background of dissolved solids from the natural sources of atmospheric and geological environments, solute loads are also generated from human activities in drainage basins. The majority of solutes provided to streams by human activity come via ground, soil and surface waters and a smaller portion is transported through the atmosphere from industrial and urban sources. Thus few portions of inhabited drainage basins escape the effects of human activity. The addition of dissolved solids from human activity can occur in both rural and urban settings. In the rural settings, agricultural wastes and fertilizers, solid waste disposal, septic tank and tile field systems and highways all contribute to the enrichment of stream waters by dissolved constituents.

Farming practices enrich stream waters with both suspended and dissolved solids (Coker, 1968). Apart from the pollutants delivered by poor management of farm soils and animal wastes, stream waters are also enriched by liberal use of fertilizers. Chyurlia (1976) notes the addition of Ca^{++} and K^{+} ions to the solute load of Randboro Brook from fertilizers containing phosphates and carbonates of these metals. In

addition he also notes higher concentrations of chloride and nitrate ions in waters from fertilized portions of the watershed in question. In areas where irrigation is practised, water returned to streams and rivers from irrigation ditching is often more saline than when it entered the irrigation network. Galegar (1969) reports increases in the concentration of minerals in returned irrigation waters from three to ten times the initial concentrations, and Dunne and Leopold (1978) report increases in the order of twenty times in the Sevier River in Utah.

Solid waste (garbage) disposal sites contribute excessive concentrations of solutes to soil and groundwaters and ultimately to streamwaters. Many authors (Anderson and Dornbush, 1967; Schneider, 1970; and Cherry et al., 1980) have reported dramatic increases in the solute content of groundwaters downslope of landfill sites. Pollution potential from such sites is high in permeable soils. Organic matter in the refuse decomposes to produce CO_2 which combines with infiltrating precipitation to produce carbonic acid. The acid acts on refuse, soil and rocks to release cations to the groundwater so that waters from the landfill operation tend to be hard. In addition salts are dissolved and carried to the water table. Schneider (1970) reports Cl^- concentrations of 260 mg/l and hardnesses to 900 mg/l at some sites. Clark (1975) in a survey of 45 landfills in Illinois reports the following values:

	max.	min.		max.	min.
Ca^{++}	2300*	100	Cl^-	1820	75
Na^+	1100	25	SO_4^{--}	2000	0
K	740	2.4	Hardness	6500	430
Mg^{++}	1102	68			

* all values as mg/l.

Parameters deemed sensitive as indicators of landfill leachate contamination have been identified by Anderson and Dornbush (1967). Chloride and Na^+ concentrations prove best with nitrates and specific conductance providing less confident indications of pollution. In their study, hardness did not differ significantly from background due to biological extraction of nutrients and precipitation of carbonates but in other studies (i.e. Schneider, 1970) it has been singled out as a significant indicator. Chloride concentrations in ground waters can be increased fifty times the background values by landfill contamination. Chloride is not readily adsorbed by soil and is not biologically recycled to any extent so it can be expected to travel a considerable distance downstream of landfill operations.

Control on dispersion of solutes from landfill sites are climate, soil permeability, slopes, elevation of water table and permeability of soil cover on the refuse itself. Concentrations of solutes from the refuse seem to depend on the water table elevations. The higher the water table the larger are concentration values (Anderson and Dornbush, 1967). Humid areas also produce greater volumes of leachates and high concentrations of solutes. Generally, pH of groundwater is lowered by leachate through the introduction of carbonic acid, especially during wet conditions when large volumes of leachate are produced (Fungaroli and Steiner, 1971). Conversely pH is higher during dry periods. Thus flow rate of fluids through the refuse is a major factor controlling pH of leachate.

Downslope from landfill sites, leachate concentrations are attenuated to various degrees by soil adsorption, chemical precipitation,

dispersion processes, biological uptake and dilution by recharge. Only Na^+ and Cl^- ions travel the furthest and Anderson and Dornbush (1967) report a return to background values for all but Na^+ and Cl^- for a travel distance of 1200 feet below a landfill site in their study. Thus there is no doubt that landfills offer a source of solutes to groundwaters and ultimately stream waters through the production of leachates from refuse.

Septic tank disposal fields also can contribute solutes to groundwater sources of stream water flow (Leopold, 1968). Often return of waste waters to the drainage basin in this fashion can increase the dissolved load of percolating ground waters dramatically during the early growth of towns and suburban areas. Leopold (1968) reports that although soils may remove over 90 per cent of the bacteria in sewage effluent over the first few feet, dissolved solids such as nitrates, phosphates and chlorides will move easily through the soil to local watercourses.

However more recent work by Brandes (1975) shows that the phosphorous content of effluent (10-20 mg/l in the tank) is reduced to 0.1 mg/l over 10 feet in clay soils and to 0.37 mg/l over 65 feet in sandy soils. Similarly nitrates had little effect on increasing the concentrations of solute in groundwater. On the other hand he found that chlorides (30-80 mg/l in tank) exhibited little attenuation except due to some dilution by recharge. Thus most of the chemical constituents of sewage effluent from septic tanks appear to be reduced to very small concentrations after 60 feet of percolation through the soil except for chloride which moves freely in the soil environment.

McGauhey (1968) notes that ammonia from effluent can displace the Ca^{++}, Mg^{++}, and Na^{+} from soil to be carried away by percolating groundwaters. In fact when sewage is applied to a soil the result is an increase in concentrations of anions and cations normally found in groundwaters such as the SO_4^{--}, HCO_3^{-}, NO_3^{-} and Na^{+}, Ca^{++} and Mg^{++}. It is apparent from the above discussion that septic systems may contribute to groundwater sources of solutes to a maximum distance of about 65 feet.

The final major sources in the rural environment due to human activity are the highway and road systems. Deicing salts are being applied to highways in ever-increasing amounts and such salts find their way into surface and ground waters rather easily. The two salts commonly used are sodium and calcium chlorides. McConnell and Lewis (1972) report that upwards of nine million tons of deicing salts were used in 1970 in the United States alone. These salts are removed from road by infiltration to ground water, by surface runoff and by wind or moving air. Between 25 and 50 per cent of all salts used are said to enter the groundwater often producing "chemical banks" in soil which discharge slowly over the ensuing years (McConnell and Lewis, 1972). The same authors also report chloride concentrations in highway runoff to 10,250 ppm in Wisconsin and as high as 25,000 ppm in Chicago when a major storm required excessive salting. Groundwaters along highways near Boston showed values approaching 250 ppm of chloride. Not only do deicing salts add sodium, calcium and chloride to soil but Na^{+}, being more reactive than other metals, produces ion antagonism in the

soil by saturating the adsorption sites of the soil at the expense of K^+, Ca^{++} and Mg^{++}. Lakes have also suffered the increase in road salting; for example, Lake Ontario has shown a three-fold increase from 9 to 29 mg/l for Cl^- since the turn of the century (Ontario Ministry of the Environment, 1975). Road salt is used universally throughout North America for deicing roads. The rates of application vary and, in Ontario, the Ministry of the Environment suggests an application rate of 400-500 pounds per two lane mile. With such rates in practice, there is no doubt that road salting must ultimately supply Ca^{++}, Na^+, and Cl^- to streamwaters. In the urban setting deicing salts also provide large quantities of these ions to natural waters. Many authors (Wulkowicz and Saleem, 1974; Huling and Hollacher, 1972; Broecker et al., 1971; and others) have researched the effects of salt on stream waters in the urban setting. Wulkowicz and Saleem (1974) report that 55-72 per cent of the 20,260 tonnes of NaCl and the 40 tonnes of $CaCl_2$ applied to the Salt Creek basin of the Chicago metropolitan area were removed by April 30 of the study year. Another 10 per cent was removed in the next six months and the remainder was held due to lag mechanisms. Concentrations of Cl^- depended on the amount of salt applied, the temperature, duration of precipitation events and the dilution capacity of the stream. Removal of Cl^- depended on (1) percentage of area as streets, (2) highway density, (3) population density and (4) road salt application per unit area. Maximum values of Cl^- measured were in the range 600-750 mg/l.

Urban settings provide other sources of solutes to increase streamwater concentration of dissolved solids as well. Several authors (Leopold, 1968; Waller, 1971; Gregory and Walling, 1973; Dunne and Leopold, 1978; and others) have discussed the increase in pollution and dissolved solids generated by urbanization generally. In a more specific study, Koch (1970) reports increases in dissolved solids up to 3-4 times natural concentrations in streams of Nassau County, Long Island. His results are listed in Table 2.4. Obviously urbanization has produced a marked increase in the concentration of ions in local streamwaters. Most of the change he attributes to the thousands of septic tanks and a few industrial sumps that had enriched the soils of the study area for years. A section of the study area which had been sewered since the 1950's still produced high values, in some cases equal to or greater than adjacent areas with active septic tank installations.

TABLE 2.4

CHANGE IN WATER QUALITY DUE TO URBANIZATION

	Ca^{++}	Na^{+}	K^{+}	Mg^{++}	HCO_3^{-}	SO_4^{--}	Cl^{-}	NO_3^{-}	Hardness	pH
Rural *	5.2	5.3	0.7	2.6	14.2	7.8	7.4	1.5	23.5	6.8
Urban	18.5	29.0	4.1	4.2	28.3	38.2	33.3	19.7	71.8	6.4

* average concentrations in mg/l computed from Koch (1970, Table 2, p. c191)

Other studies (Gorham, 1961; Scheidt, 1971; Waller, 1971; and others) have reported on the myriad of chemicals introduced into runoff and streams from the urban environment. Dustfall, street litter, oil and grease, particulate rubber, leached asphalt, sewage and industrial wastes and

contaminants to waters from urban catchments and although the increased runoff from urbanization should normally dilute solute concentrations, often urban sources tend to increase these concentrations to levels greater than background or natural value.

2.8 Summary of Controls

In the last seven sections, it has been shown that the solute load of streamwater at a given point in space and time is a result of a complex interplay of physical, biological and often human influences. Not only do sources of solutes themselves differ but the hydrological and biological pathways by which they reach the stream can also introduce changes to the original concentrations at the soil/groundwater and mineral interface. Within the channel itself further changes can occur due to chemical adjustments of the streamwater to incoming solutions and temperature changes downstream. On top of the biophysical control often the human influence is added and certainly within urbanized areas this aspect often overpowers the "normal" rural variance of solutes in the streamwaters. A brief summary of the controls is outlined below.

Precipitation may introduce both spatial and temporal variance to streamwaters in a watershed. If the watershed is large, the quality and quantity of chemical constituents in the rainfall may vary from site to site or from time to time depending on air mass source and movement. Over smaller watersheds this effect is of little consequence.

The watershed itself by virtue of either its geological, pedological and morphometric heterogeneity can produce spatial variance

in streamwater quality. A heterogeneous geology will produce different amounts and species of dissolved consituents at differing locations in the watershed. The rates of chemical decay of minerals and rocks may vary over the watershed. The morphometry may serve to slow or expedite the precipitation falling over the watershed to the stream channel as runoff interflow, throughflow, or groundwater flow thereby affecting the residence time of solutions in soil, rocks or litter. The CEC of soils may vary from place to place depending on the parent material and local conditions. All of these aspects will condition the amounts of solutes produced, transported and given up to streamwaters.

Chemical changes occurring both in the uplands and in the channels of the watershed can introduce both spatial and temporal variance in solute loads. Temperatures and concentrations of source waters entering along the streams may produce changing equilibria in channel waters and during storms, newly infiltrated waters will cause shifts in equilibria in the solutions attacking mineral faces in soil and rock. The fact that chemical weathering and equilibria are not uniform over a basin preclude spatial variance in solute production and transport. Of course seasonal influence mainly through annual climatic changes will introduce a temporal heterogeneity to chemical process as well.

Biological processes within the watershed will introduce both spatial and temporal variance in solute release to streams as well. Spatial variance will be a function of the presence or absence of the vegetation and of its type and quantity. During the peak growth in the biomass, nutrient uptake will upset the delivery of solutes to

streams and may even affect the concentrations in the streamwater itself; therefore, seasonal and even diurnal cycles may be developed in solute concentrations in streams. During leaf fall increased nutrients are available to stormflow which runs overland through the leaf and forest litter. Thus biological uptake, and restitution can provide strong controls on solute movement to streams.

Hydrologic controls operate throughout the watershed. The movement of water from watershed to channel follows several different pathways overland and through the litter, soil and rock. Thus water is given up to the channel at different rates from different sources and it is the mixing of these waters and their solute loads that determine the ultimate solute load at a point along the stream. Water is not given up uniformly in space or time from the watershed. Thus both spatial and temporal variance can be expected due to these hydrological controls.

Finally anthropogenic influences may produce spatially distinct sources of solutes in the watershed and channel through land use and waste disposal practices. Some of these sources may even introduce a temporal variance; for example, the daily habits of humans may be reflected in sewer outfalls and their concomitant solute loads giving a diurnal variance to streamwater quality.

In the following chapters, a research theme is developed to identify and quantify these controls on solute variation in the waters of Chippewa Creek both in the rural and the urban settings. Spatial and temporal variability are investigated systematically, based on the principles established in this chapter.

CHAPTER III

The Chippewa Watershed

3.1 Location and Extent

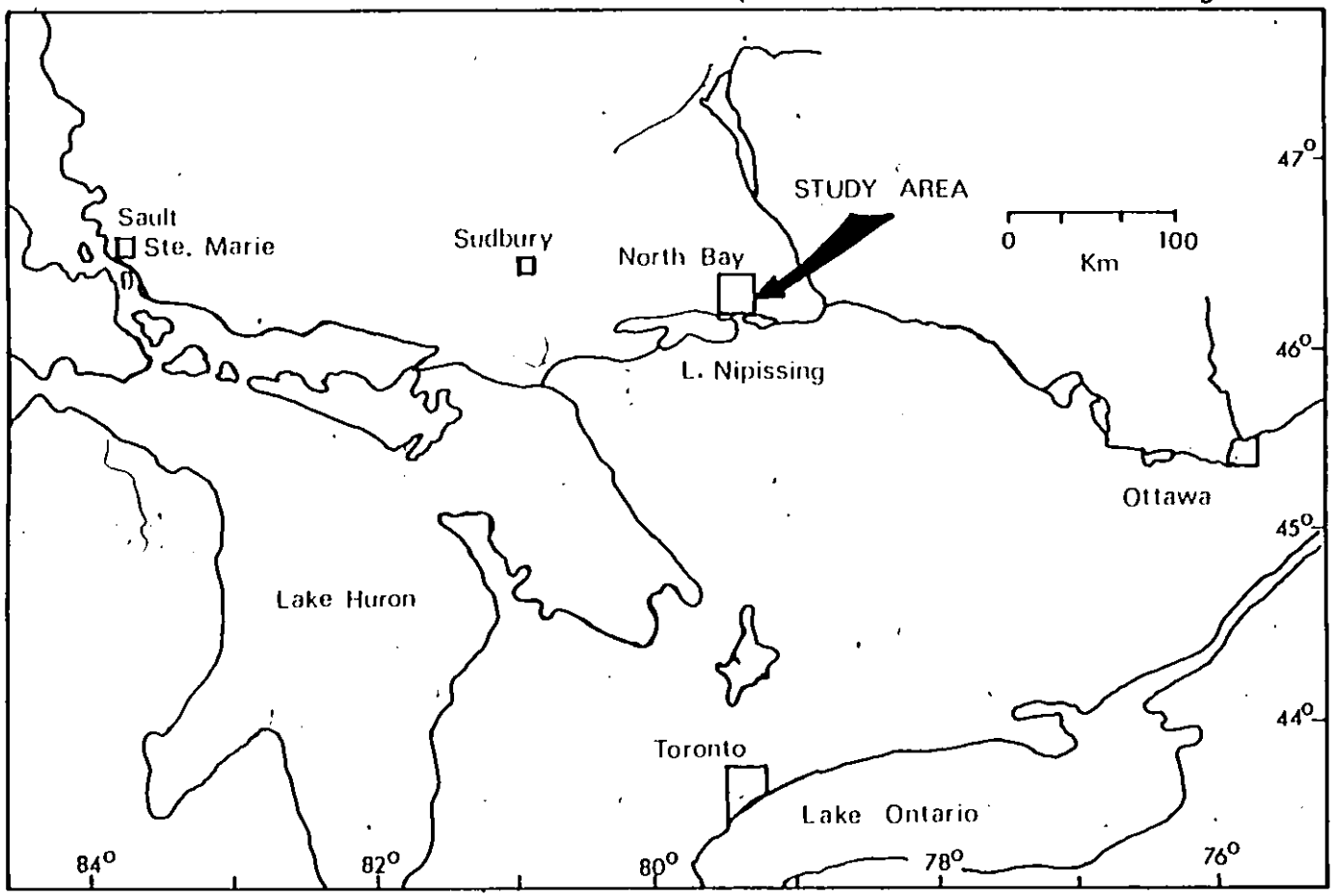
The study area, The Chippewa Watershed, is situated at North Bay, Ontario, approximately 331 km. north of Toronto, Ontario (see Figure 3.1). Chippewa Creek, the principal stream draining the Chippewa watershed, empties into Lake Nipissing situated in the upper reaches of the French River and Georgian Bay watersheds. The stream flows from a predominantly rural setting in the north to an urban setting in the south. Its basin is entirely within the city limits of North Bay, a city of 50,000 people, but only approximately 25 per cent of the watershed was fully urbanized at the time of sampling for this study (Figure 3.2). The areal extent of the basin, 61.23 km^2, falls between Latitude 46°18'N to 46°23'30"N and Longitude 79°28'30".

The areas of both the total watershed and the sub-basins (described later) were calculated from city maps having a scale of 1:4,800 by cumulating the area of a system of grid squares and planimetering oddly shaped areas using a Coradi polar planimeter.

3.2 Physiography

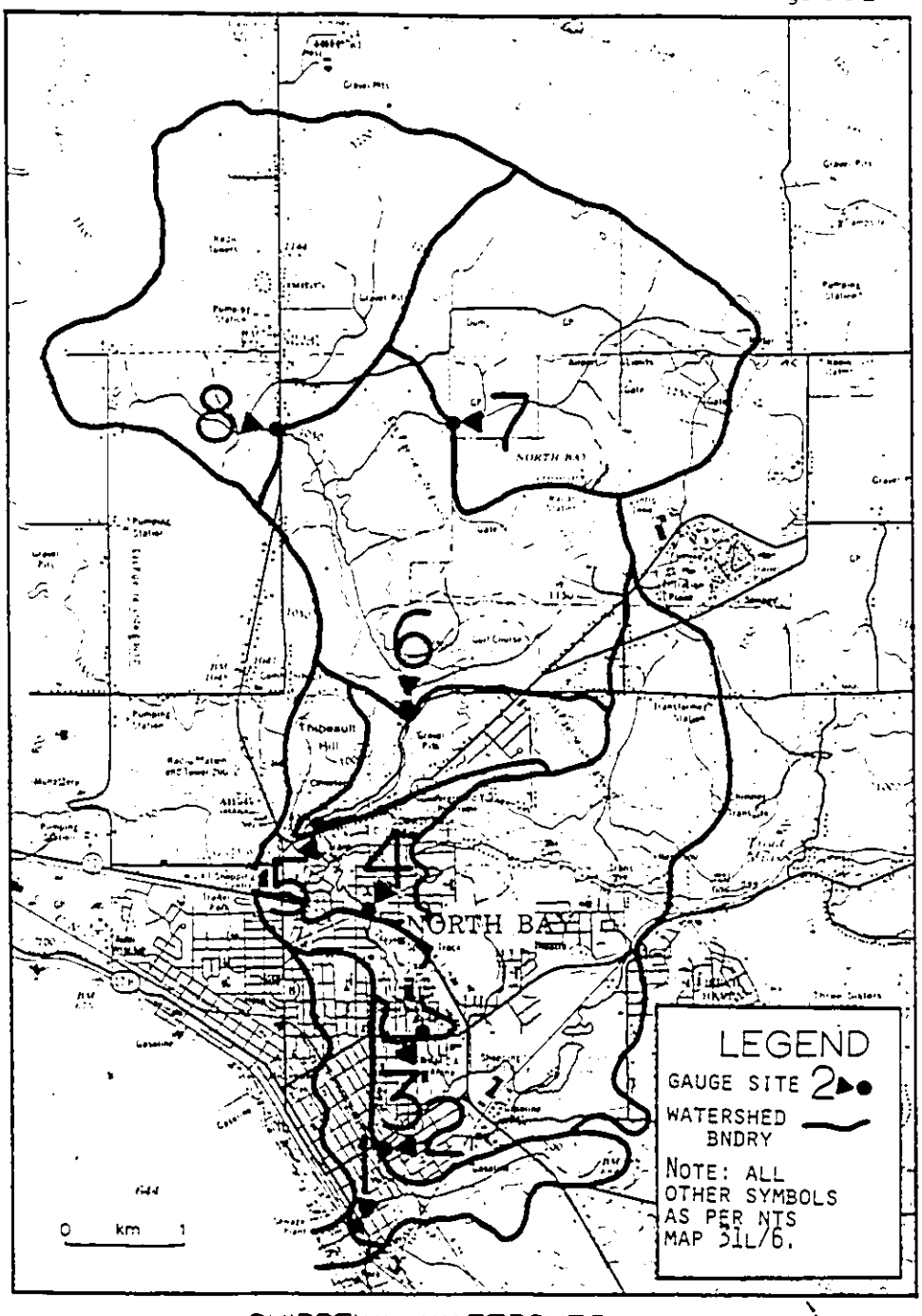
The physiography (Figure 3.2) of the Chippewa Basin varies from a relatively flat lowland area bordering Lake Nipissing to a rugged, upland area in the source regions. The lowland area is characterized

Figure 3.1



LOCATION OF STUDY AREA

Figure 3.2



CHIPPEWA WATERSHED

by subdued topography created by the waning waters of the early stages of the Upper Great Lakes (Prest, 1970; Lumbers, 1971; Harrison, 1972). Elevations range from 196 m. a.s.l. near Lake Nipissing to 229 m. a.s.l. on strand lines associated with the post-glacial development of the Nipissing basin. The strands and old lake-bottom topography have been dissected by present creeks draining from the upland in the north to produce moderate slopes having an average value of 1.6°.

The upland area is separated from the lowland by an escarpment produced by fault activity which began during the late Precambrian and which according to Lumbers (1971), was active to the late Ordovician. This upland area is an old peneplain of Middle Ordovician Age which was subsequently buried by Paleozoic sedimentation and then exhumed by post-Ordovician erosion, Pleistocene glaciation and recent fluvial activity (Lumbers, 1971). Elevations in the upland part of the basin generally range from 229 to 381 m. a.s.l. and the average slope is approximately 3.16°.

Slope values in the watershed and in the sub-basins represent average slopes as calculated per the Wentworth technique (Monkhouse and Wilkinson, 1971, p. 134). Data for the technique was collected from accurate maps of the urban area, having a contour interval of 2.5 feet. Data for some of the rural sections were necessarily taken from smaller scaled maps (1:50,000) due to lack of coverage at larger scales in the upper watershed. Values are presented in Table 3.12 later in Section 3.7 (p. 118).

The Chippewa basin has a length of 11.09 km. from stream mouth to the most distant point on its drainage divide. The basin is somewhat pear-shaped and form factor of $F = \frac{A}{L^2}$ (Gregory and Walling, 1973, p. 51) is used to quantitatively describe its shape. The value of the form factor for the Chippewa basin is 0.35, a low value which predicts quick drainage from the basin and its extremeties to the main channel. The drainage pattern is essentially dendritic and of fourth order as classified by either the Horton or Strahler stream ordering systems (see Gregory and Walling, 1973, p. 43).

The major valley in the basin has been formed by Chippewa Creek and its ancestor. The creek is deeply incised into the glacial sediments of the upland area to create a valley with a maximum depth of about 69 m. where it opens out onto the lowland. The creek apparently has excavated a drift-filled preglacial valley, part of a preglacial topography which was somewhat subdued by deposition of drift. Channel gradients over the 15 km. watercourse average 10.86 m/km. Shallow gradients of 1.91 m/km near the mouth give way to 3.81 m/km up over the escarpment to 11.43 m/km in the upper reaches. The escarpment divides the basin nicely into two sections of differing physical and urban character.

Channel gradients for the total stream length and the reaches in each sub-basin were obtained principally through a levelling survey of the stream thalweg using a Wild N2 level and engineering rod. Some reaches were profiled from maps mentioned above and very accurate flood plain maps made available through the North Bay-Mattawa Conservation

Authority. Channel gradients are summarized in Table 3.12 later in Section 3.7 (p. 118).

3.3 Geology

3.3.1 Bedrock

The bedrock geology of the Chippewa Basin is fairly uniform in composition (see Figure 3.3). The most common rock type is biotite gneiss containing mainly biotite, quartz and feldspar with minor hornblende in several variations (Lumbers, 1971). Minor amounts of migmatitic biotite gneiss occur in the southern portion of the basin along with a single occurrence of migmatitic and gneissic biotite granite.

Modal compositions of the rocks in the Chippewa Basin are summarized in Table 3.1. Principal constituent minerals consist of quartz, plagioclase, K-feldspar, biotite and hornblende and a great deal of overlap appears between the composition of the various biotite gneisses. The relative abundance of these minerals appears to be nearly equal throughout the basin. However rocks above the escarpment are reported to be richer in alkalic feldspar and lower in calcic feldspar than those below the escarpment (Lumbers, 1971). Thus the underlying bedrock can be expected to be a source of the Na^{+}, K^{+}, Mg^{++} and Ca^{++} ions studied in this thesis.

Two fault zones are found in the basin. An east-west trending fault, the Mattawa River Fault, is responsible for the escarpment which divides the basin into north and south portions. A small, NW-SE trending fault above the escarpment, possibly near a shear fault off the main Mattawa River Fault, is the structural control for the Chippewa Creek

Figure 3-3

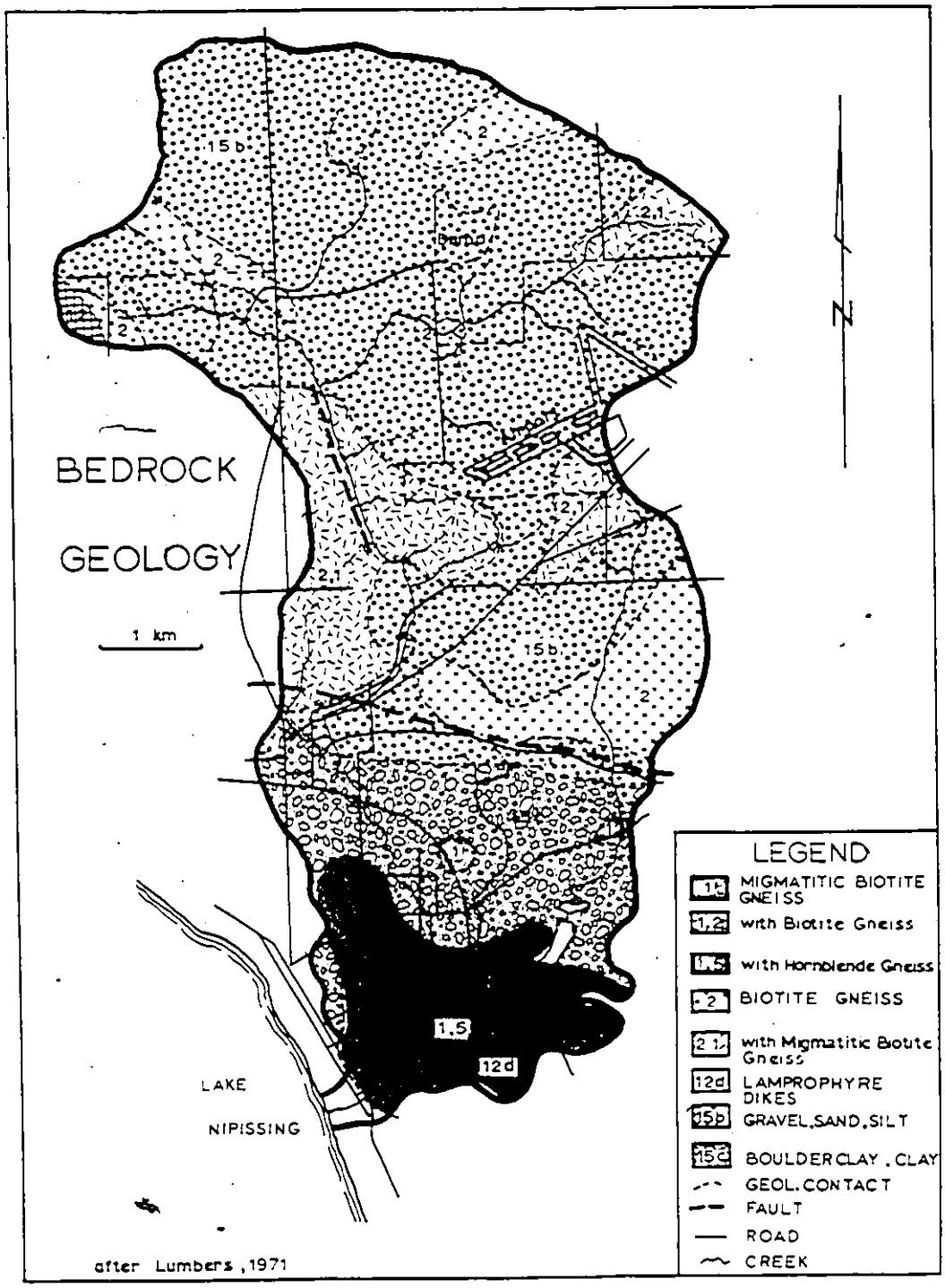

BEDROCK
GEOLOGY
1 km
N
LAKE
NIPISSING
after Lumbers, 1971
LEGEND
1+ MIGMATITIC BIOTITE GNEISS
1,2 with Biotite Gneiss
1,5 with Hornblende Gneiss
2 BIOTITE GNEISS
2,1 with Migmatitic Biotite Gneiss
12d LAMPROPHYRE DIKES
15b GRAVEL, SAND, SILT
15c BOULDER CLAY, CLAY
GEOL. CONTACT
FAULT
ROAD
CREEK

TABLE 3.1

RANGES IN MODAL COMPOSITION OF BIOTITE GNEISS AND MIGMATITIC BIOTITE GNEISS RELEVANT TO THE CHIPPEWA BASIN

VARIETY OF GNEISS	(1)	(2)	(3)	(4)
SAMPLES	21	15	4	5
QUARTZ	*15 - 40	25 - 40	30 - 40	25 - 35
PLAGIOCLASE	30 - 55	25 - 50	15 - 25	30 - 35
PLAGIOCLASE (%An)	17 - 30	10 - 22	17 - 20	10 - 30
K-FELDSPAR	6 - 17	15 - 25	25 - 35	15 - 25
BIOTITE	10 - 20	10 - 15	10 - 15	10 - 15
HORNBLENDE	0 - 3	0 - 1	-	8 - 10
KYANITE	0 - 1	-	-	-
GARNET	0 - 5	0 - 3	0 - 1	0 - 2
MUSCOVITE	0 - 1	0 - 1	0 - 1	-
OPAQUE MINERALS	0 - 4	0 - 2	0.5 - 2	0 - 2
APATITE	0 - 1	0 - 1	0 - 0.5	0.5 - 1
SPHENE	0 - 1	0 - 2	0 - 1	0.5 - 2
SCAPOLITE	-	-	-	0 - 1
OTHERS	1.0 - 2.5	0.5 - 2.0	0.5 - 1.0	0.5 - 1.0

* VALUES IN %

modified from Lumbers, 1971, p. 12, Table 2.

drainage. The channel in the upper middle reach appears to be following this fault or lineament (see Figure 3.3).

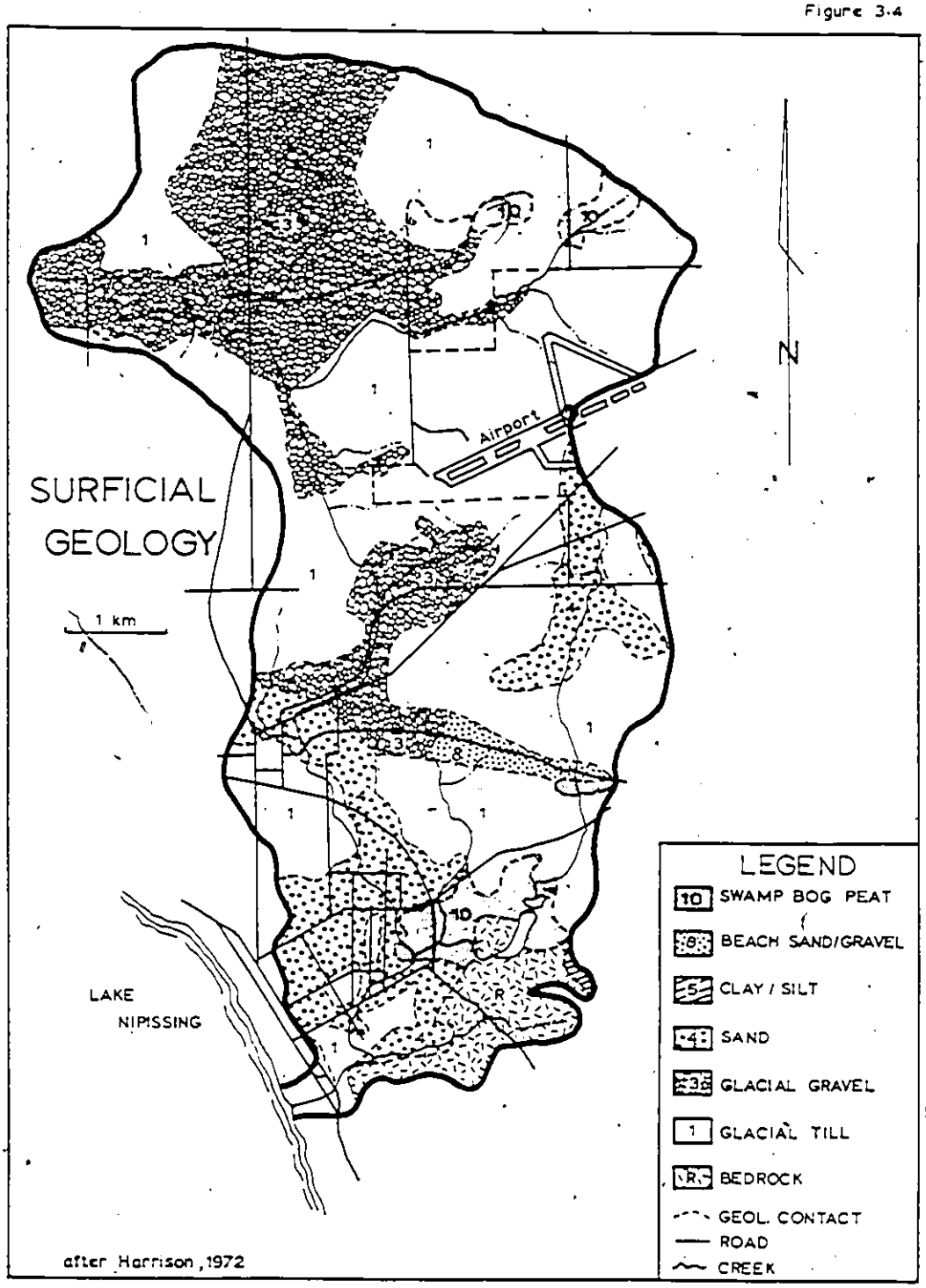
The rocks of the basin seem to be compact with limited fracturing at depth. Drilled water wells on the escarpment tend to be unreliable and many dry wells have been drilled in a major subdivision in the eastern part of the basin.

Above the Nipissing Great Lakes shoreline (about 230 m. present elevation) rocks appear to be deeply weathered, moreso than below this elevation. Reasons for this deep weathering are unclear (Lumbers, 1971); however, it is apparent that the rates of weathering have been greater on and above the escarpment than below.

3.3.2 Surficial Geology

A great deal of the bedrock in the Chippewa Basin is buried beneath thick deposits of locally derived glacial drift (Lumbers, 1971). Harrison (1972) has mapped and classified the drift cover in the North Bay area (see Figure 3.4). His mapping indicates that the upper part of the basin is covered mainly by glacial till and glacial gravel. He describes the till as a heterogenous mixture of non-calcareous materials from silts to large boulders. The gravels, which also contain sand, occur as kames, eskers and undifferentiated outwash deposits. In the lower part of the basin to the south, lacustrine sands and beach sands and gravels are interspersed with the glacial till. Low areas occupied by swamps and peat are underlain by lacustrine silts, a legacy of former elevated lake levels. Lithologic composition of the drift

Figure 3.4


SURFICIAL
GEOLOGY
1 km
N
Airport
LAKE
NIPISSING
after Harrison, 1972
LEGEND
10 SWAMP BOG PEAT
8 BEACH SAND/GRAVEL
5 CLAY / SILT
4 SAND
3G GLACIAL GRAVEL
1 GLACIAL TILL
R BEDROCK
GEOL. CONTACT
ROAD
CREEK

reflects the local bedrock for the most part but some boulders in the drift have been transported from the Huronian Supergroup to the north and west of the North Bay area (Lumbers, 1971).

3.3.3 Geomorphology

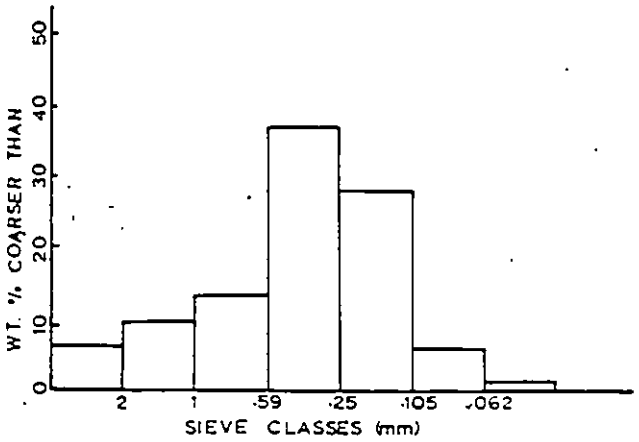
The major feature of the study area is the Chippewa Valley occupied by Chippewa Creek. The creek has cut deeply into the glacial till, sand, and gravel and in some places has eroded to bedrock. Other features include terraces, and terrace remnants, beaches and lake beds which were built by the early proglacial and post-glacial lakes in the Nipissing Basin.

The stream channel itself is floored with materials derived from the local glacial and lacustrine deposits. Thus, differing amounts of sand, gravel and boulders with minor amounts of silt make up the bed material of the creek. Limited size analyses of bed materials are presented in Figure 3.5. At the stream mouth near Oak St. (see Figure 3.17, p. 115 for street index) bed material is principally medium to fine sand; whereas, upstream at the Airport Road, medium sand is secondary to a dominant gravel or larger bed material. Grain size variance is not large and is attributable likely to particle size attrition downstream. However the calibre of the fine bed load is small enough to adsorb ions from stream waters (Kennedy, 1965). Few deep pools exist in the creek channel although many existed prior to Hurricane Hazel, a storm which, in 1954, caused severe flooding and erosion in the watershed. Since that time the channel has shallowed and widened with the influx of sediments.

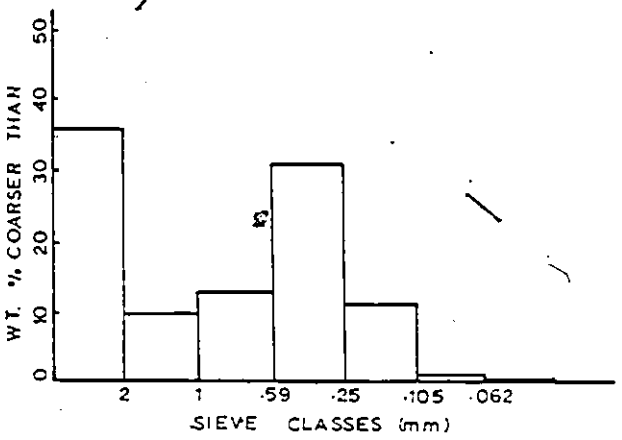
Figure 3-5

CREEK BED SEDIMENT SIZE ANALYSIS

OAK ST.



AIRPORT RD.



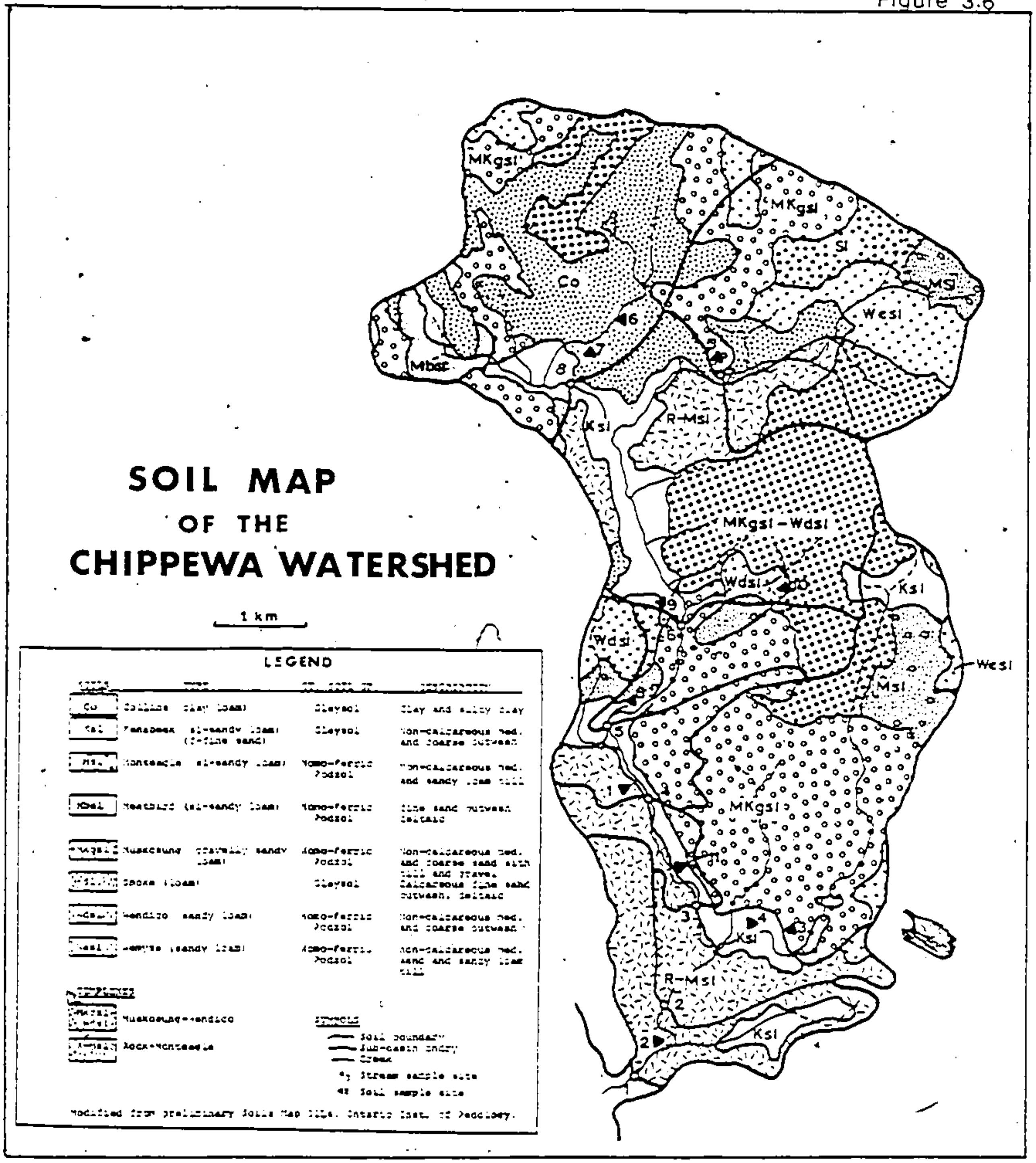
3.4 Soils

3.4.1 Existing Soil Data

Soil maps of the North Bay area and the Chippewa Watershed specifically have yet to be published. However a preliminary map is available through the Ontario Institute of Pedology at Guelph, Ontario. Data taken from this map are displayed for the Chippewa Watershed in Figure 3.6. Generally the soil groups in the watershed are predominately Humoferric podzols and they display physical and chemical characteristics typical of soils developed on the Canadian Shield. They usually have a thin organic L horizon at surface and are underlain in turn by a light grey loamy sand A horizon and a yellowish or reddish brown B horizon, paling at depth into an ill-defined C horizon of parent material (Hoffman, et al., 1962). As well some gleysols exist in poorly-drained areas.

The main soil types are the Muskosung gravelly sandy loam; the Monteagle sandy loam; the Wendigo sandy loam; the Wemys sandy loam; and the Collins loam including also two complexes: The Rock-Monteagle and the Muskosung-Wendigo. Other minor types include the Kenabeek sandy loam; the Meatbird sand; and the Smoke fine sand. Generally the soils in the Chippewa Watershed are sandy and non-calcareous with good drainage except for the Collins, Smoke and Kenabeek soils which tend to be finer, poorly drained and calcareous. However samples taken by this author have not confirmed some of this preliminary soils mapping especially the presence of the Collins soil type over the extent displayed in Figure 3.6 as illustrated by soils described at Sites 6 and 7

Figure 3.6


SOIL MAP
OF THE
CHIPPEWA WATERSHED
1 km
LEGEND
Gleysol
Clay and silty clay
Homo-Ferric Podzol
Soil sample site
MKgsl
Co
Sl
MSl
Wesl
Mbsl
Ksl
R-Msl
MKgsl-Wdsl
Wdsl
Msl

in the next section, 3.4.2. As well no calcareous soils were found, confirming Harrison (1972).

3.4.2 Sampling and Description

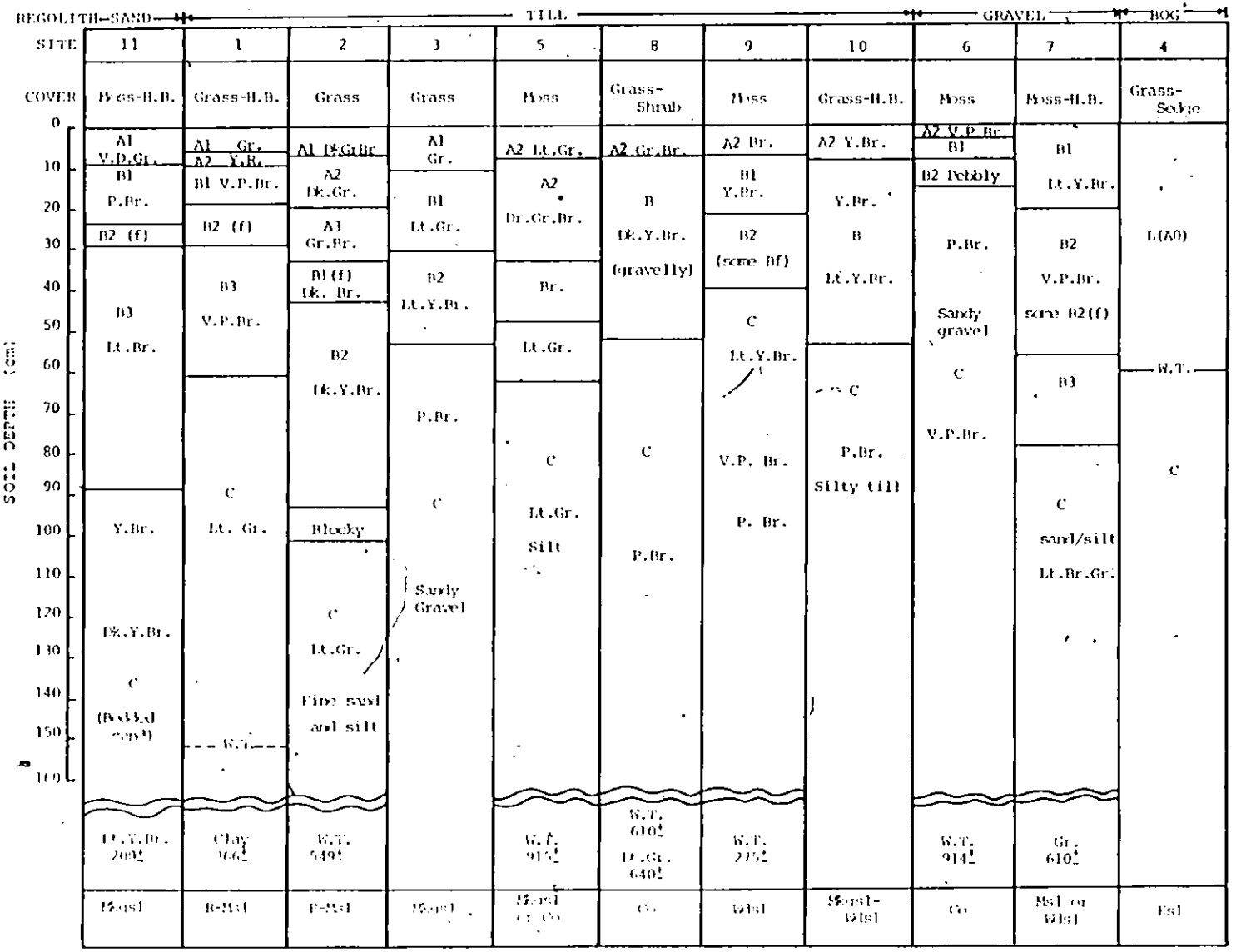
As was discussed earlier in Chapter II, soil physical and chemical character determines the chemical quality of soil water which ultimately contributes to streamflow. Thus some knowledge of the chemical makeup, especially cation exchange capacity and base saturation is necessary to consider the contribution of soils to variation in streamwater quality in the Chippewa Watershed. The dearth of quantitative information about soils in the Chippewa Basin necessitated a sampling and analysis programme to determine the chemical nature of soil cation exchange properties. A limited number of samples were collected as it was not the purpose of the thesis to undertake a comprehensive soils study.

Sampling sites were restricted to open face cuts and pits where horizons could be sampled accurately within their boundaries. A minimum of two sites were located in each of the surficial sedimentary sequences classified and mapped by Harrison (1972). However only one sample was taken from the peat bog (unit 10 in Figure 3.4, p. 66) because of the uniformity of its sediment character and relationship. The sampling sites are located on Figure 3.6, p. 70.

The soil columns at the various sites are displayed in Figure 3.7. With the exception of the peat bog all sites display typical podzolic characteristics of soils developed on the Canadian Shield. Soil horizons are usually readily identifiable on the basis of colour changes from horizon to horizon. The eluviated A horizons tend to grey or

FIGURE 3.7

SOIL PROFILES IN THE CHIPPEWA WATERSHED*



H.B. = hazel brush; V.= very; Gr. = grey; P. = pale; Br. = brown; Lt. = light; R. = red; (f) = ferric; Y. = yellow; Dk. = dark; A0 = Soil Horizon; Msl = Soil type (see Figure 3.6), W.T. = water table.

* classification from Strahler (1975), p. 237.

greyish brown colours and the illuviated B horizons tend to yellowish and reddish browns due to deposition of iron oxide and often the B horizons contain hardpan, a hard compact sandy layer cemented together with ferrous oxide. The presence of this hardpan layer appeared to be restricted to elevations below about 225-230 m. a.s.l. However a more intensive sampling programme is required to determine the universality of this statement. All sites except the peat bog (site 4) display poorly developed organic L horizons of 0-6 cm. depth. The A horizon thickness varies with forest or field, being thicker under the open field areas. Often the B horizons merge into the C horizons with just a paling of colour. Water tables appear at considerable depths near bedrock at most sites and the upper horizons appear to be well drained due to the high permeability of the granular soil materials and regolith.

Thicknesses of the soil horizons vary within the study area but the soils appear to be physically similar throughout with the exception of site 4 and the presence or absence of gravel, a hardpan material in some horizons and not in others. Very little clay exists near surface and only site 1 had clay at depth although not all sites were examined to bedrock. The only really anomalous soil condition occurs at site 4 in a bog formed on the bed of an abandoned channel or lake within the North Bay outlet which functioned in the waning stages of the Nipissing Great Lakes phase of the Great Lakes (Prest, 1970). Here the L horizon is well developed and up to 60 cm. thick and it is underlain by what appears to be silt and fine silt-sized material.

The chemical character of the soils was also investigated. Procedures and methods are discussed in Appendix B and the raw data is compiled in Table B1, also in Appendix B. Several conclusions can be drawn from the soil data with respect to the influence of soils on streamwater quality.

As developed in Chapter II earlier, weathering in soils and the concomitant redistribution of solutes in soil profiles may have a distinct effect on the chemical nature of soil waters and subsequently streamwaters. If the chemical characteristics of soils differ spatially over the watershed then one could expect a corresponding variability in streamwater quality.

Thus the analysis and discussion of the Chippewa soils will be to attempt to establish whether the soils could possibly contribute to spatial variance in streamwater quality.

Perusal of Table B1 reveals several important aspects of the soils in the Chippewa Watershed. First, with the exception of the bog soil of site 4, all soils are acidic and non-calcareous. Base saturation of the soil is for the most part quite low. This fact denotes that the majority of the exchange sites in the soils are occupied by H^+ ions. Calcium seems to be quantitatively the most important ion of the bases measured, and generally its concentrations are low. These relatively low cation exchange capacities, low pH and base saturation levels of the Chippewa Watershed soils can be expected of soil development in such sandy, permeable and well-drained surficial materials. The results obtained here correspond well with results obtained in

similar soils (Monteagle, Wendigo, Kenabeek, etc.) studied in Parry Sound District at sites 50 to 150 km. to the southwest of North Bay (Hoffman, et al., 1962). Rapid infiltration and throughflow of acidic precipitation and soil waters would tend to remove solutes quickly. As well the relatively coarse granular materials do not provide exceptional surface area (as compared to clay) for the adsorption and retention of ions.

The exceptional soil at site 4 is quite different from the others. A thick organic L horizon and an underlying silt provide more adsorption sites and hence the CEC, base saturation and pH are all higher than surrounding soils. This particular soil association is likely the result of soil formation on an old lake or stream bed and its distribution is restricted to sites in the outlet channels of the North Bay outlet of the Nipissing Great Lakes which were active about 4200 years B.P. (Prest, 1970).

Soil chemistry varies with depth in the watershed. Highest base saturation values often occur in the first 5-10 cm. of the soils where organic materials abound and then drop considerably to begin to rise again near the water tables in the C horizons. The greater base saturation levels in the A horizons, principally due to Ca^{++}, are likely the result of the decay of plant and leaf litter (samples were taken after leaf fall). Calcium is slow to be released from tissues, as it forms an integral part of plant structure and is not quickly leached like potassium and magnesium. Thus it seems reasonable that higher values should exist in the upper levels of the A horizon. High values

in the A horizon are explained by the presence of hazel brush leaf litter. Low values occur in the absence of hazel brush litter in the presence of grass or moss. However the universality of this relationship could stand further testing.

Base saturation values in the B horizons are low indicating extreme leaching of soil nutrients from these permeable sandy and gravelly horizons. Values in the C horizons tend to increase close to the soil water table where nutrients are being concentrated and transported in soil water and groundwater from surrounding soils and possibly from bedrock sources as well.

The significance of this vertical variation to streamwater quality is of note. Solutes from the soil enter streams via normal throughflow in low streamflow conditions and via subsurface stormflow during and subsequent to stormflow conditions. Thus these waters will, in times of lowflow, be principally in contact with the lower soil horizons in the watershed and during stormflow will also be in contact with the uppermost horizons. One might expect different solute delivery to streams from these two sources and flow regimes in view of the vertical variation of base saturation levels.

In addition the spatial heterogeneity of the base saturation levels in the soils of the watershed may also produce variable streamwater solute concentrations at various watershed sites. As base saturation levels increase, pH increases and more solutes become available to the soil water system. Therefore large spatial divergences in base saturation should produce similar diversity in streamwater qualities.

Average base saturation values for the A, B and C soil horizons in the watershed are presented in Table 3.2 (p. 78). From the data there appears to be some common relationships albeit in a somewhat limited number of samples. Certainly the largest value for BS in the A horizon occurs at site 4 and is a result of the decay of plant materials leaving a residual of calcium and magnesium to be adsorbed. In the A horizon next highest base saturation values occur generally in the soils developed on urban tills; whereas, values in A horizons of rural tills and rural gravels tend to be lower except at site 5. This site may be artificially high due to gravel and sand pit operations. In the C horizons again site 4 is high and rough groupings appear as urban till, rural tills, rural gravels and urban sand.

The nature of A horizon differences might be expected in light of hydrological environments in the urban and rural settings. In the rural settings infiltration rates are likely higher due to tree cover and a thick litter layer; thus, A horizons tend to be better leached. This fact is also supported by the BS levels in the B horizons.

In terms of solute yields to streamwater, it is apparent that the soils of the Chippewa Watershed are capable of supplying limited solutes (bases) to streamwaters. Generally most adsorption sites are filled with H^+ ions and soils are acidic. Thus few metallic cations would be available for exchange into soil waters. Of course bog soils are the exception where a wealth of adsorbed cations, especially Ca^{++}, are available for exchange. Even so for the generally limited supply it appears that there is a difference in possible solute availability

TABLE 3.2

SUMMARY OF BASE SATURATION VALUES OVER THE CHIPPEWA WATERSHED

HORIZONS			A		B		C	
SITES			% BS	Ca*	% BS	Ca	% BS	Ca
TILL	1	U	21.0	33.6	13.4	0.71	18.0	11.02
	2	U	25.2	40.3	5.9	0.24	10.3	12.22
	3	U	28.7	46.5	21.5	1.56	10.9	12.00
	5	R	22.7	69.5	8.3	0.59	30.9?	68.90?
GRAVEL	6	R	13.6	12.0	30.9	1.65	19.8	18.00
	7	R	10.0	9.8	5.9	0.12	16.8	29.90
TILL	8	R	5.2	3.0	4.2	0.22	20.2?	61.70?
	9	R	4.7	2.0	6.0	0.18	13.3	7.82
	10	R	7.8	3.0	8.1	0.19	12.4	8.42
SAND	11	U	11.3	19.2	1.5	0.06	5.0	18.90
BOG	4	U	57.4	263.9	-	-	97.3	257.90

* concentrations in mg/l
R Rural site
U Urban site
? Doubtful value

from the various soil materials of the watershed. Waters passing laterally through the A horizons of soils into the creek will likely receive more solutes from urban tills than from rural tills, gravels or urban sands. Soil waters at depth tend to be more equal in magnitude of BS; however, it is possible the rural gravels may provide slightly larger solute loads than urban or rural tills and urban sands at depth.

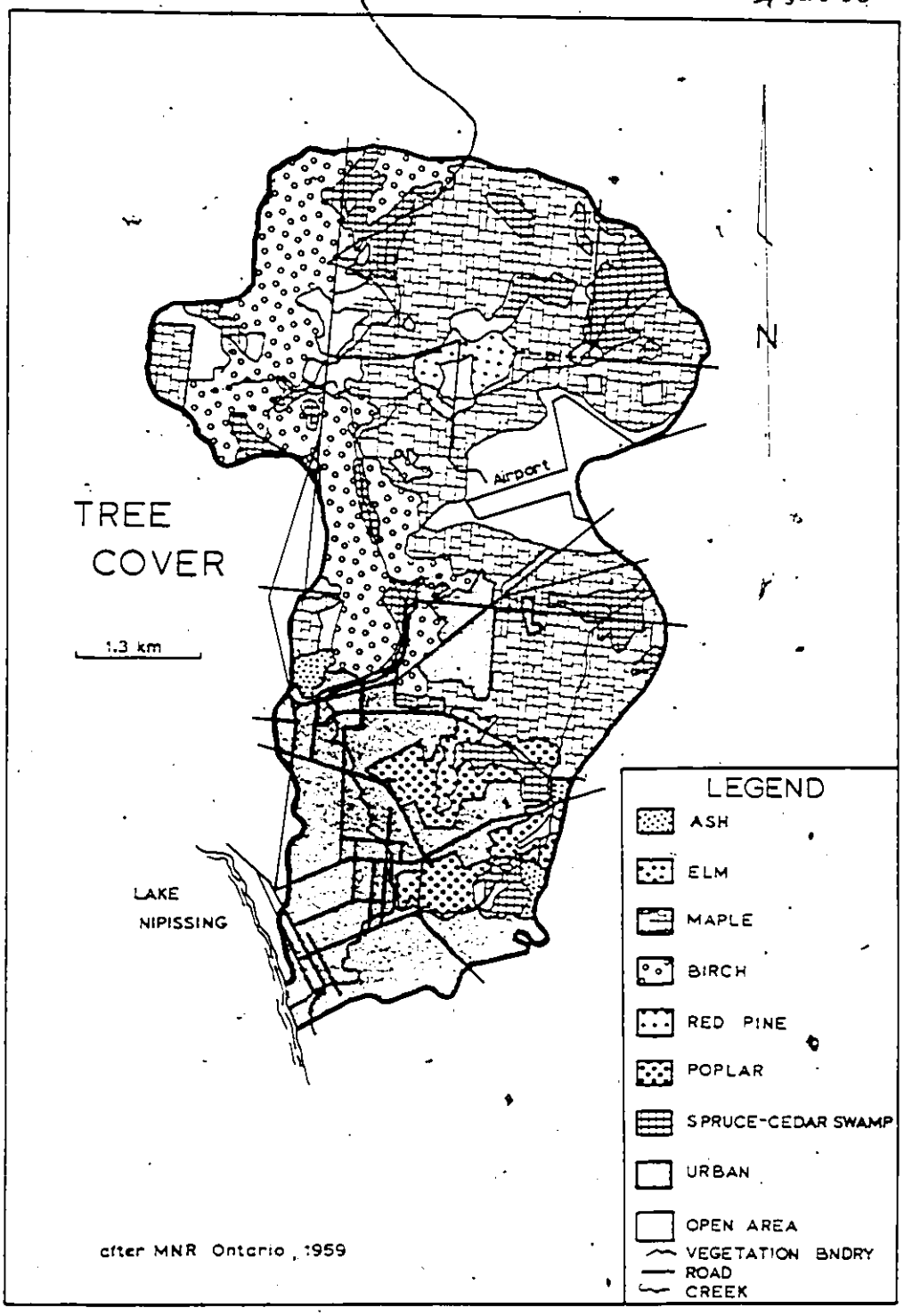
In summary, it appears that the % BS and the amount of exchangeable calcium in Chippewa soils are dependent on the types of parent materials on which the soils have formed. The extent and spatial variability of these parent materials within the watershed and in the subbasins may influence the chemical quality of soil waters which ultimately find their way into stream waters. One might expect this diversity of soil character to produce spatially variable streamwater qualities in the watershed and this contribution should be accounted for in any model or discussion of solute variability within Chippewa Creek.

3.5 Vegetation

The study area is within the northern part of the Great Lakes-St. Lawrence Forest Region in a transitional zone south of the Boreal Forest Region. Thus the flora consists of a mixture of coniferous and deciduous trees typical of these two regions.

Figure 3.8 shows the patterns of tree cover within the watershed. The information was derived from the most recent Ontario Forest Inventory maps (1959) and was modified by information from a report on the proposed Highway 11 Corridor (Proctor and Redfern, 1975) and from recent air photos.

Figure 3-8


TREE
COVER
1.3 km
N
Airport
LAKE
NIPISSING
after MNR Ontario, 1959
LEGEND
ASH
ELM
MAPLE
BIRCH
RED PINE
POPLAR
SPRUCE-CEDAR SWAMP
URBAN
OPEN AREA
VEGETATION BNDRY
ROAD
CREEK

Within the city, trees are limited to isolated clusters or individuals although some lesser vegetation in the form of hazel brush, alders and grass exists along the creek channel itself. The reach from Cassells Street to High Street (see Figure 3.17, p. 115, for street index) has some mature birch, elm and maple close to the channel which in places form a continuous canopy. The reach from High Street to the By-Pass and on to Milani Road is flanked on both banks by areas of fairly dense alder brush with a few elm and birch but, for the most part, vegetation within the urban section of the watershed is sparse and is restricted to a few trees and mostly grass.

North of the Airport Road, the watershed is well vegetated by species of both deciduous and coniferous trees. A densely stocked mature maple-birch association occupies the upper Chippewa Valley above the escarpment. Conifers such as balsam, cedar, hemlock, larch, jack pine and white pine, also populate the rural setting of the upper watershed but not as dominant species. In the extreme upper reaches, black spruce dominate the bogs and swamps which are the source areas for Chippewa Creek.

Generally speaking the forest cover of the watershed is principally deciduous. Thus the biological rhythms of season will likely control to some extent the availability of nutrients to stream water from the biomass. Earlier in Chapter II the biological recycling of nutrients was discussed and in light of the principles included there, solute generation from the biomass in the Chippewa Basin will likely show a great deal of variation, especially between the urban and rural sections and possibly between areas of differing dominant species.

3.6 Hydrology of the Chippewa Basin

3.6.1 Precipitation

The average annual precipitation for the study area as measured at the North Bay Airport at the N.E. edge of the Chippewa Basin is 979.2 mm. Of this total 705.8 mm. falls as rain and 273.4 mm. as snow (Annual Meteorological Summary, 1975, North Bay). Monthly total precipitation averages calculated over the 39-year record kept at North Bay show that summer maxima values for June, July, August, September, October and November tend to be higher than those of January, February, March, April, May and December. Average summer month rainfalls range between 86.4 mm. and 115.8 mm.

Occasional storms have produced heavy rainfalls in the study area and one such storm occurred on July 24-25, 1977. About 98.5 mm. fell in a twelve-hour period. This storm was calculated to be a one in twenty year storm and it produced a one in five year flood in Chippewa Creek (M.M. Dillon, 1977b). Over the years there have been many storms of nearly equal magnitude and these events have choked the creek rapidly with runoff and sediment.

Quantity of precipitation may determine the input of solutes to a drainage basin as well as the rates of chemical weathering of soils and rocks (see Chapter II earlier). Variation in rainfall amounts may ultimately be responsible for variation in streamwater quality over both short and long term bases.

A small survey was conducted to determine the effects of the elevation change introduced by the escarpment on the rainfall quantities in the Chippewa Basin. Data from three permanent gauges at the

Jack Garland Airport, King Street in the city and at Nipissing University and from two other temporary gauges are presented in Table 3.3 (p. 84). On the basis of the data, there appears to be a minor difference between total quantities above and below the escarpment for the periods studied and for storms of different magnitudes. However the differences are small enough to be the result of instrumental error, measurement error or local environmental conditions about the gauges. Thus for the purposes of this study, the rainfall quantities with their resultant solute loads are assumed to be equally dispersed over the watershed and therefore contribute little to spatial variability in solute loads to streamwater in the basin.

3.6.2 Streamflow

Historical runoff and streamflow data were extremely sparse for the Chippewa Basin and the North Bay area as a whole before 1974. In November, 1974, the Inland Waters Directorate of Environment Canada established a continuous stage recorder on Chippewa Creek near the intersection of Fisher and Chippewa Streets (see Figure 3.17 p. 115) and data is now available for flows on a monthly and annual basis. A summary of flow data is given in Table 3.4 (p. 85). Stage recorders used in this study were installed in June, 1975 and up to the establishment of these and the Environment Canada gauges, no continuous monitoring had been undertaken so far as is known.

Gauging of the creek was carried out by the author in the summer of 1973 using staff gauges at sections rated by the float velocity technique (Leopold, et al., 1964, p. 167) for a study concerning the

TABLE 3.3

TEST OF RAINFALL VARIABILITY

(A) PRECIPITATION TOTALS FOR TWO GAUGE SITES, 1973

	STORMS	KING STREET[1]	AIRPORT[2]	VARIATION
JULY	15	97.8*	104.6	6.8 (6.5%)
AUGUST	23	93.7	103.4	9.7 (9.38%)

(B) PRECIPITATION TOTALS FOR TEST GAUGES, 1978

DATE OF STORM	SITE 1[1]	SITE 2[2]	SITE 3[1]
AUGUST 23-24	41.4*	40.9	36.6
AUGUST 28	29.0	26.9	29.7
SEPTEMBER 9-10	6.1	7.4	5.3
SEPTEMBER 10-11	6.9	6.9	7.6
SEPTEMBER 14-15	51.8	54.4	52.6
TOTALS	135.2	136.5	131.8

(C) VARIATION

	SITE 1	SITE 3
SITE 2	1%	3%
SITE 3	3%	

* RAINFALL IN mm.

[1] SITES BELOW THE ESCARPMENT

[2] SITES ABOVE THE ESCARPMENT
(for locations see Figure 3.17, p. 115)

TABLE 3.4

HISTORICAL STREAMFLOW DATA[#]: CHIPPEWA CREEK

CHIPPEWA CREEK AT NORTH BAY - STATION NO. 02DD014

MONTHLY AND ANNUAL MEAN DISCHARGES IN CUBIC METRES PER SECOND FOR THE PERIOD OF RECORD

YEAR	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	MEAN
1974	-	-	-	-	-	-	-	-	-	-	1.15	0.261	-
1975	0.251	0.141	0.209	1.38	0.822	0.499	0.338	0.116	0.241	0.423	0.602	0.528	0.463
1976	0.128	0.088	1.39	1.77	1.03	0.348	0.452	0.166	0.214	0.233	0.298	0.164	0.519
1977	0.118	0.106	1.42	1.71	0.270	0.209	0.527	0.537	0.659	0.563	0.653	0.302	0.591
1978	0.181	0.135	0.146	1.78	0.848	0.290	0.286	0.547	0.916	0.867	0.461	0.235	0.558
1979	0.192	0.209	1.45	2.62	0.935	0.309	0.184	0.344	0.480	0.805	0.968	0.444	0.745
MEAN	0.174	0.136	0.923	1.85	0.781	0.329	0.367	0.342	0.502	0.578	0.680	0.322	0.575

LOCATION - LAT 46 18 38 N DRAINAGE AREA, 37.3 km^2
LONG 79 27 00 W NATURAL FLOW

ANNUAL EXTREMES OF DISCHARGE AND ANNUAL TOTAL DISCHARGE FOR THE PERIOD OF RECORD

YEAR	MAXIMUM INSTANTANEOUS DISCHARGE (m^3/s)	MAXIMUM DAILY DISCHARGE (m^3/s)	MINIMUM DAILY DISCHARGE (m^3/s)	TOTAL DISCHARGE (dam^3)
1974	-	-	-	-
1975	6.63 AT 18:51 EST ON JUL 20	4.02 ON APR 19	0.010E ON AUG 18 [#]	14 600
1976	8.01 AT 19:14 EST ON MAR 27	6.09 ON MAR 27	0.068 ON AUG 30	16 400
1977	9.46 AT 06:24 EST ON JUL 25	6.23 ON JUL 25 [#]	0.059 ON JUL 23	18 600
1978	10.30 AT 03:28 EST ON SEP 15 [#]	5.66 ON SEP 15	0.062 ON JUL 6	17 600
1979	-	5.308 ON MAR 24	0.075 ON JUL 20	23 500
				18 100

B - ICE CONDITIONS
E - ESTIMATED

[#] - EXTREME RECORDED FOR THE PERIOD OF RECORD

[#] from: Environment Canada, Historical Streamflow Survey: Ontario to 1979, Queen's Printer, Ottawa, 1980.

selection of a new by-pass route around North Bay. Values for discharge at these sections are given in Table 3.5 (p. 87). This gauging programme was also carried over into the summer of 1974 when sampling began for the present study.

Information on the hydrological character of the watershed was also almost non-existent at the inception of this study. One study done by the author (Rees, 1974) on the watershed of Trout Lake, a basin lying to the east and adjacent to the Chippewa Watershed, reports a mean annual runoff figure of 35.1 per cent for the year 1972. In view of the proximity of Trout Lake to the study area, it is likely that this figure applies as well to the physiographically similar, undeveloped parts of the Chippewa Watershed.

Because continuous streamflow data was not available, it was therefore necessary to collect such information on Chippewa Creek over the study period. For a series of gauging stations, corresponding to the sub-basins to be studied, sections were surveyed and checked periodically over the study period for changes in cross-sectional area. The sections were subsequently rated with an Ott C1 current meter and rating curves and equations were developed. For each water sample collected, a gauge level was recorded for which a discharge could be derived from the rating equations. Airport Road and Oak Street sites were fitted with continuous stage recorders, an Ott type X and an Ott type XX respectively (see Figure 3.9). All other sites were gauged with staff gauges.

TABLE 3.5

SUMMARY OF MEAN DAILY DISCHARGES FOR CHIPPEWA CREEK

JULY - AUGUST, 1973

		STATIONS			
		A (OAK ST.)	B (THIRD AVE.)	C (AIRPORT RD.)	D (HWY 11N)
DISCHARGES	max.	1.40*	1.32	0.88	-
	mean	0.44	0.41	0.21	0.08
	min.	0.17	0.12	0.07	-

* DISCHARGES IN cu. m./sec.

FIGURE 3.9

RECORDING GAUGES

OAK ST. (Photo A)

AIRPORT RD. (Photo B)

Each gauging site cross-section was surveyed with a wild N2 level and a stadia rod. Elevations were taken to the stream bed at one foot intervals across each section and then plotted to scale on square graph paper. Staff gauges were established at all of the sites and related to temporary benchmarks nearby for relocation purposes if sites were vandalized.

Continuous recording gauges were established at Airport Road and Oak Street in plywood boxes on top of vertical corrugated culverts buried near the bank and connected to the mid-channel by a four-inch plastic pipe (see Figure 3.9 p. 88). These two recorders were calibrated at various intervals with the staff gauges at their respective sections.

An example cross-sectional plot of a gauge site is given in Figure 3.10 (p. 90). Over the study period certain cross-profiles having a mobile bed were checked through a re-levelling programme and the results showed that although there were small changes in configuration of the bed profiles, the net change in cross-sectional area over the study period was extremely small or negligible. Unfortunately there was no way of easily determining possible changes during storm events and their effects on the sectional area and resulting flow calculations. As an example, Figure 3.11 (p. 91), shows the magnitude of the profile changes at Oak Street, one of the sites having a mobile, sandy bed.

For each gauge site an area-depth curve was established by determining the cross-sectional areas from the plots of the sections for increments of depth. A plot of cross-sectional area against gauge height (Figure 3.12, p. 92) allowed the quick determination of area for the

Figure 340

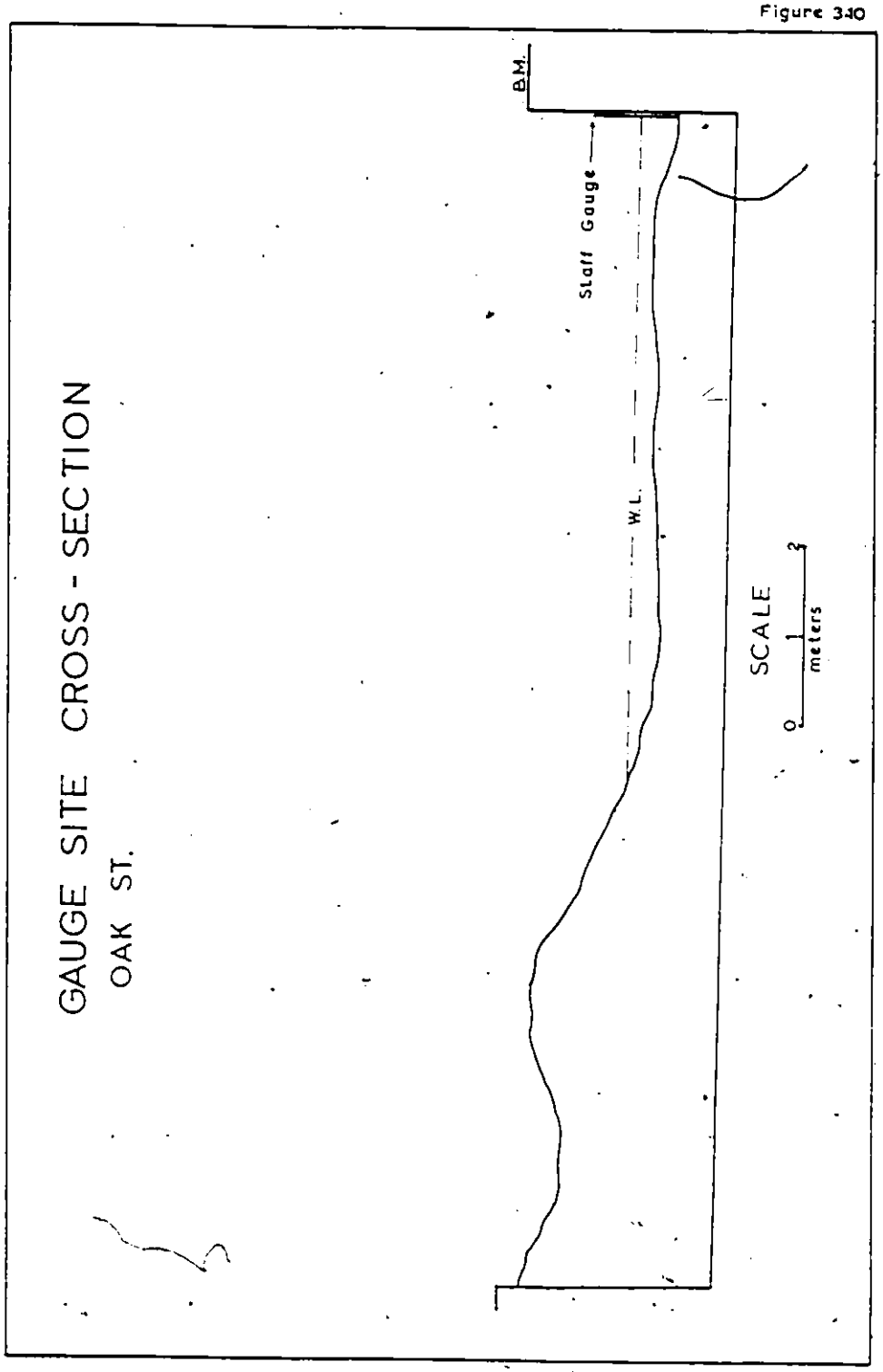

GAUGE SITE CROSS - SECTION
OAK ST.
B.M.
Staff Gauge
W.L.
SCALE
0
1
2
meters

Figure 3-11

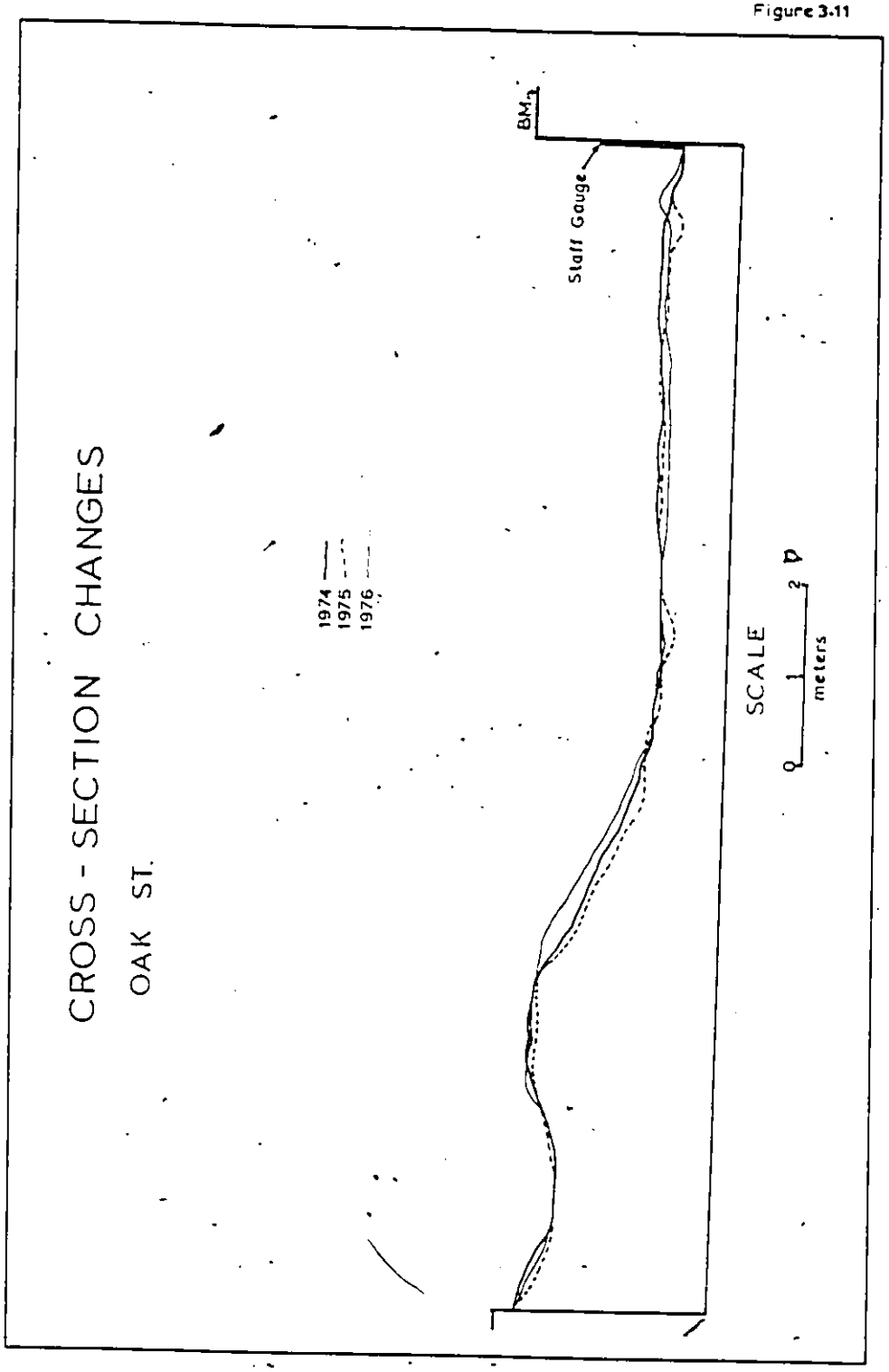
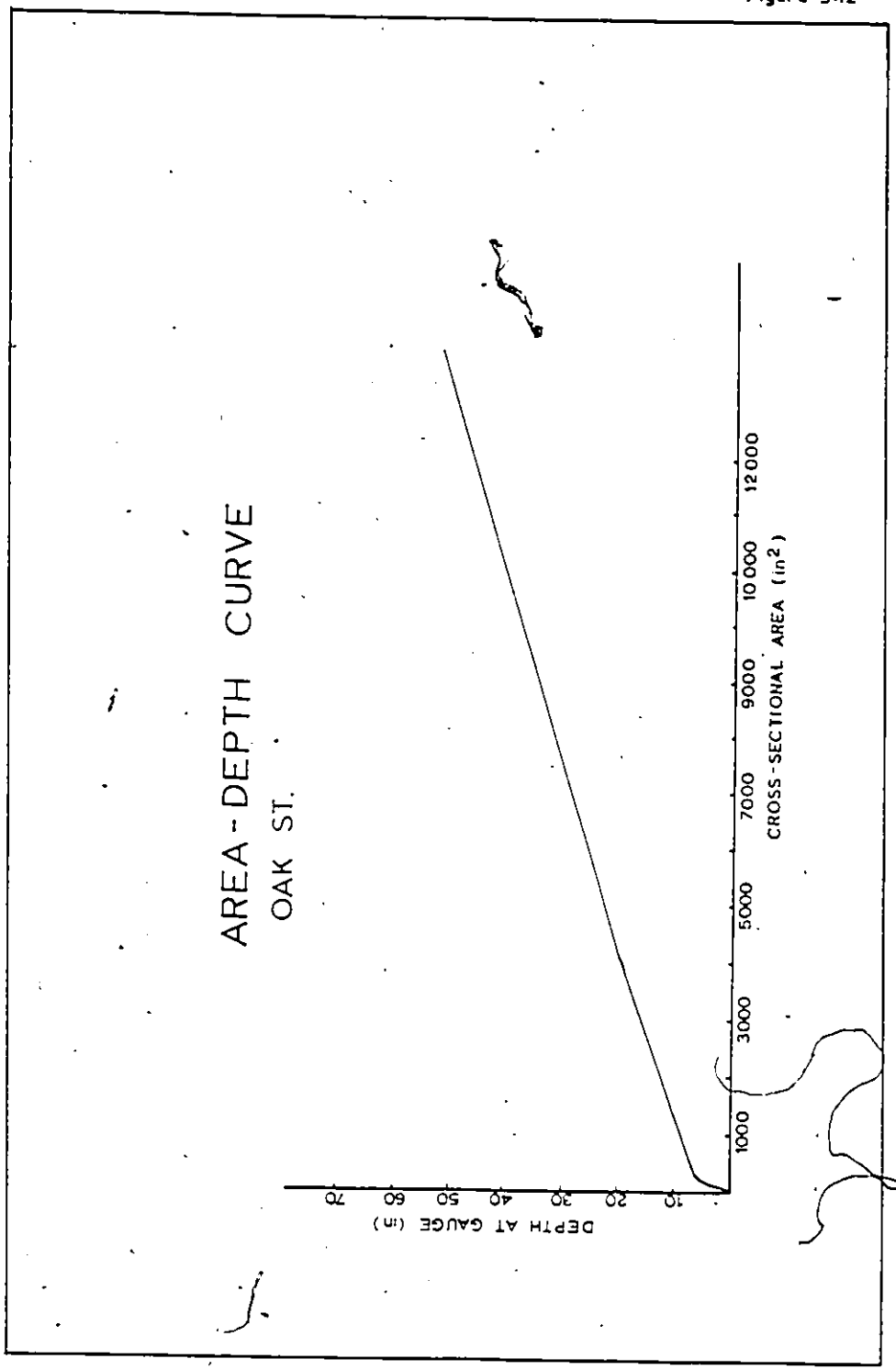

CROSS - SECTION CHANGES
OAK ST.
1974
1975
1976
BM
Staff Gauge
SCALE
0
1
2
meters

Figure 3.12


AREA-DEPTH CURVE
OAK ST.
DEPTH AT GAUGE (in)
10
20
30
40
50
60
70
CROSS-SECTIONAL AREA (in²)
1000
3000
5000
7000
9000
10000
12000

gauge heights associated with later velocity measurements used for the determination of flows.

Each section was rated for flow by measuring the mean water velocities at various gauge heights and then using the formula $Q = A\bar{V}$ where Q = flow in cfs or cumecs and A is the cross-sectional area at the time of velocity sampling determined by using gauge height and area-depth curves mentioned above; and $\bar{V}$ is the average stream velocity across the section.

Velocities were taken at several points across the stream at the sites several times over the study period for as wide a variety of water stages as possible. Most of the velocities were measured with an Ott C1 current meter employing the regular methodology as described in Chow (1964) and Grover and Harrington (1966) but in high flows a float technique had to be used and a small, weighted fishing bobber was used. Float velocities were measured over a specific distance for several runs across the channel and corrected by a multiplier of .8 (Leopold, et al., 1964, p. 167). Thus the upper ends of the rating curves may be questionable as to absolute values of discharge but relatively (from site to site), there seemed to be good correspondence of discharge values downstream.

Rating equations were developed by the regression of flows (Q) and gauge levels (d). Power functions of the form $y = m(x)^n$ seemed to produce the best fit and gave the best significant R^2 values. The results are in keeping with the relationships between stage and discharge reported in the literature (Chow, 1964; Gregory and Walling, 1973; Dunne and Leopold, 1978; and others).

The results from the regressions were graphed and an example plot is given in Figure 3.13 (p. 95). The rating equations are summarized in Table 3.6 (p. 96). These rating equations have been used to determine the values of discharge for the stage at which each sample was collected at the sampling sites.

The character of stream flow in Chippewa Creek is variable depending on the quantity and quality of rainfall from storms and on the character of snowmelt in the spring (see Table 3.4 p. 85). Several storm hydrographs were constructed from the continuous gauge data at both Oak Street and Airport Road. The precipitation character and resultant hydrographs are shown in Figures 3.14 and 3.15 (p. 98 and p. 99).

Flows from the urbanized part of the watershed (Oak Street gauge) build to peak more quickly and with greater volume under all watershed and storm conditions than at Airport Road. This is a result of the greater impervious area and lower infiltration rates in the city. With dry antecedent conditions and a low intensity storm (Figure 3.14 p. 98) lag times are approximately five times smaller at Oak Street than at Airport Road but under wet antecedent conditions, the rural part of the watershed loses some of its storage capacity and the Oak Street lag time is only about one-half of that at Airport Road.

During high intensity storms and dry conditions (Figure 3.15, p. 99), Oak Street flows peak again much more quickly than Airport Road flows. Oak Street lag time is about seven times shorter than at Airport Road and of course volumes are significantly larger at Oak Street even though its watershed area is by far smaller.

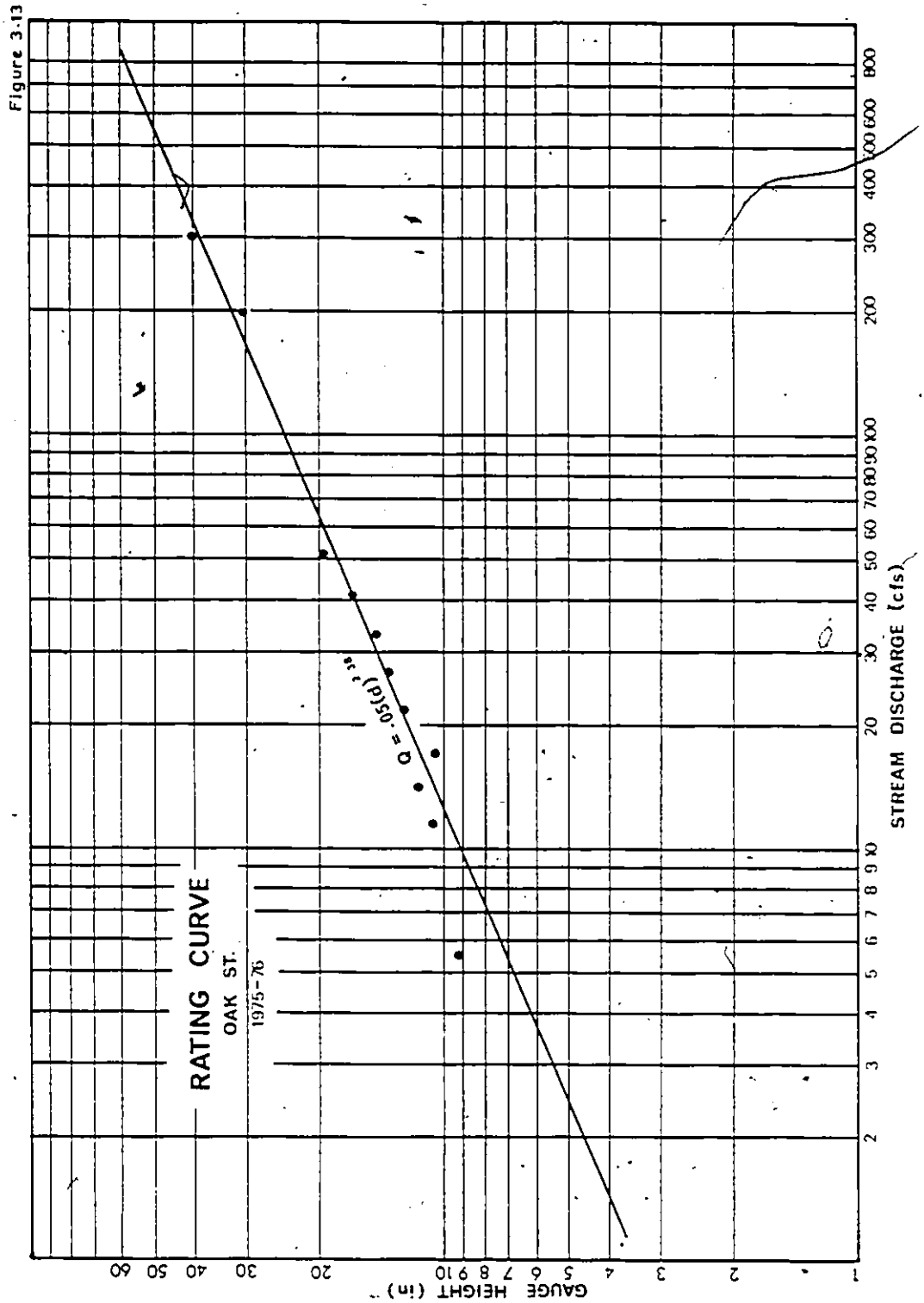

RATING CURVE
OAK ST.
1975-76
Q = .05(d)^2.5
GAUGE HEIGHT (in.)
STREAM DISCHARGE (cfs)
1 2 3 4 5 6 7 8 9 10 20 30 40 50 60
1 2 3 4 5 6 7 8 9 10 20 30 40 50 60 70 80 90 100 200 300 400 500 600 800

Figure 3.13

TABLE 3.6

SUMMARY OF RATING EQUATIONS

SITES	EQUATIONS	
OAK ST.	$Q = 0.06\ d^{2.24}$	(1974)
	$Q = 0.05\ d^{2.38}$	(1975 ON)
THIRD AVE.	$Q = 0.11\ d^{2.17}$	
CASSELLS ST.	$Q = 0.17 \times 10^{-3}\ d^{3.88}$	
BY-PASS	$Q = 0.64\ d^{1.62}$	
AIRPORT RD.	$Q = 2.87\ d^{1.38}$	
GOLF CLUB RD.	$Q = 1.18\ d^{1.54}$	
MARSH DR.	$Q = 0.15\ d^{2.38}$	
HWY. 11 N	$Q = 0.27\ d^{1.53}$	

Note: Q is in cfs
d is in inches

The Oak Street flows show a sensitivity to the variations in rainfall intensity during storm events and small peaks occur both before and after the main peak flow. Those before can be equated to the variations in rainfall intensity (Figure 3.14, p. 98) with each peak occurring from 1.4 to 2.0 hours after its corresponding burst of rain under dry watershed conditions and about 2.8 hours after rainfall bursts under wet watershed conditions.

The minor peaks occurring after the main peak at Oak Street are attributed to the arrival of peak flows from the rural sector upstream of Airport Road. Under wet and dry watershed conditions the rural peak passes from Airport Road to Oak Street in 2.0 to 3.0 hours respectively but apparently can take 7.4 hours after intense rainfall (Figure 3.15 p. 99).

The Airport Road flows also display multiple peaks of a more subdued nature than those at Oak Street under low intensity storms. However with high intensity storms Airport Road flows display a sharp peak immediately (within one hour) after peak rainfall. This peak is likely the result of runoff from roads and ditches in the first 1.5 km. upstream of Airport Road. It takes about three hours for this peak to reach Oak Street below.

In summary, then, Chippewa Creek appears to be a relatively flashy stream in its urbanized reach in both low and high intensity storms. In its rural reach, the stream is flashy for high intensity storms and accumulates runoff relatively slowly under low intensity storms. Overall the surface storm runoff tends to reach the channel

Figure 3.14

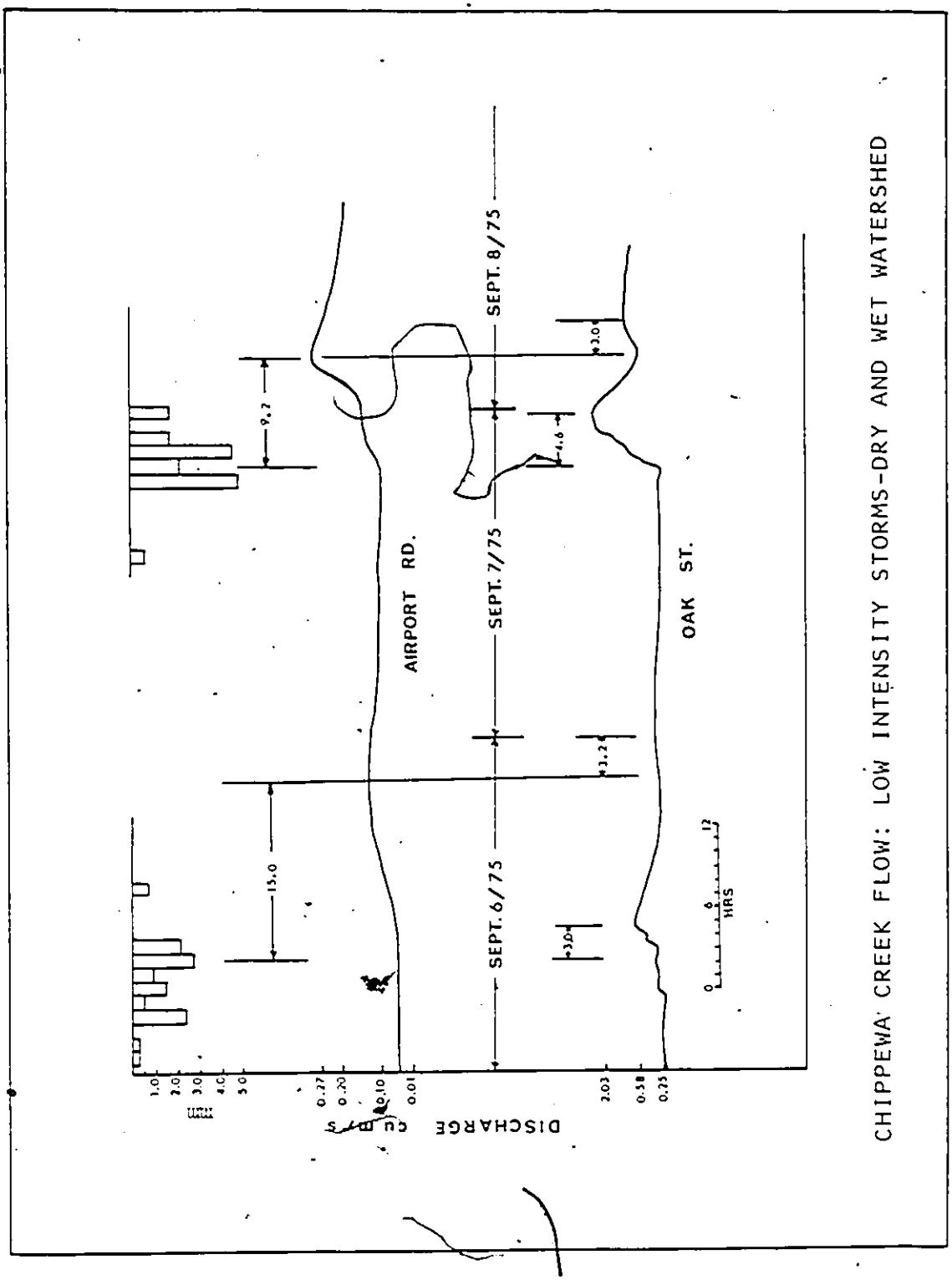
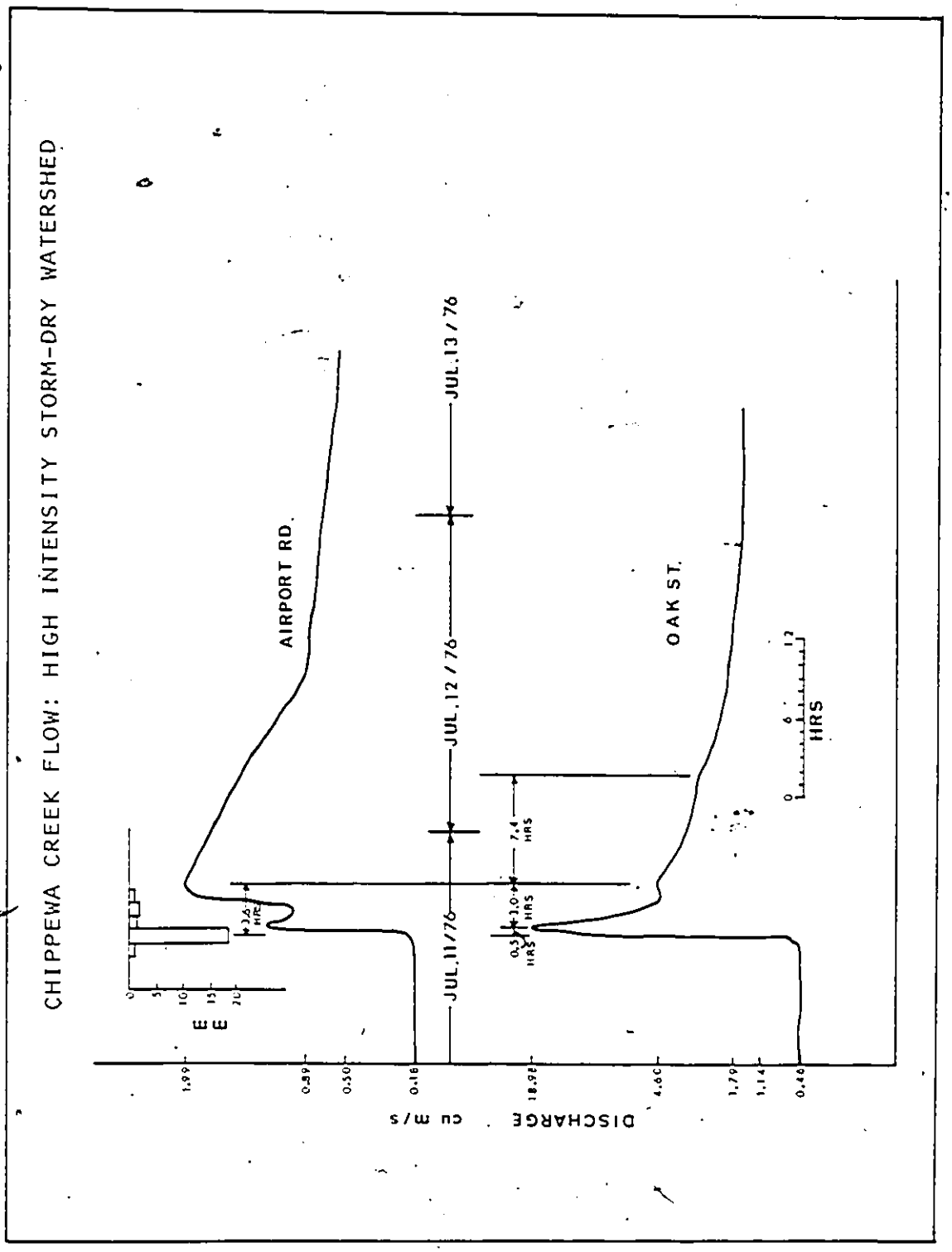

CHIPPEWA CREEK FLOW: LOW INTENSITY STORMS-DRY AND WET WATERSHED
SEPT. 8/75
SEPT. 7/75
SEPT. 6/75
AIRPORT RD.
OAK ST.
9.2
15.0
4.6
3.0
3.2
3.0
0
6
12
HRS
DISCHARGE
1.0
2.0
3.0
4.0
5.0
0.27
0.20
0.10
0.01
2.03
0.58
0.25

Figure 3.15


CHIPPEWA CREEK FLOW: HIGH INTENSITY STORM-DRY WATERSHED
AIRPORT RD.
OAK ST.
JUL.11/76
JUL.12/76
JUL.13/76
DISCHARGE cu m/s
1.99
0.99
0.50
0.16
18.98
4.60
1.79
1.14
0.46
HRS
7.4 HRS
3.0 HRS
0.5 HRS
2.6 HRS
mm

rather quickly from basin extremeties and this action will have ramifications with regard to the concentrations of solutes in channel waters. It is obvious that waters in the main channel are a mixture from different runoff and throughflow sources. Areas close to the channel will yield waters quickly while areas further away will yield waters more slowly. Residence times of soil and surface waters will vary throughout the basin thus causing variability in solute accumulation and transport. In the urbanized sector, surface runoff is primarily the way in which storm waters reach the channel as shown by short lag times. These waters can be expected to be dilute and thus will likely tend to dilute streamwater solute concentrations. Water which enters the stream channel more slowly by way of throughflow through the A, B and C horizons of the soil will likely be more concentrated than surface runoff and may slightly dilute streamwater concentrations or in fact increase them. Thus stormwater by arriving at the channel through different spatial and temporal pathways in the Chippewa Watershed, will likely cause variance in solute loads within Chippewa Creek water.

The rate at which sub-surface stormflow reaches the channel is more difficult to estimate. A close scrutiny of the continuous gauge records at Oak Street revealed that two minor, subdued peaks in streamflow occur on the average at 40 hours (S.D. 4.45) and 67 hours (S.D. 21.49) after major storm peaks. After consideration of possible causes, it is concluded that these hydrograph rises are due to sub-surface stormflow from the very granular and permeable sands and gravels of the watershed. Again it is also likely that the first peak is due to increased sub-surface stormflow from the surficial materials of the urbanized

watershed sector and the second due to increased sub-surface stormflow from those above the escarpment and Airport Road. Although not quite so prominent because of gauging scale, similar peaks follow major storms on the continuous gauge sheets at Airport Road. However only a single subdued peak is present at about 55 hours (S.D. 5.2) after most major storms. This fact seems to lend support to the above statements concerning the sources of flow producing these peaks.

Hewlett and Nutter (1970), Dunne and Leopold, (1978), and Freeze and Cherry (1979) discuss the phenomena of sub-surface stormflow at length and they note several points of interest to this study. Flow rates for sub-surface stormflow are much slower than Hortonian overland flow rates and peak sub-surface flows will arrive at the channel with considerable lag relative to surface storm runoff. In fact lag times often exhibit values from 1-30 hours or more in permeable materials. As infiltrated waters percolate downward, the slope of the water table increases toward the channel and with a concomitant increase in sub-surface flow rate to the channel. Some well log data is available for the upper part of the Chippewa Watershed and groundwater contours have been interpolated into this data (Gore and Storrie, 1977; Shrubsole and Desjardins, 1981; and Cherry et al., 1981). Hydraulic gradients were determined from these contours and the average gradient was in the order of 20.6 m/km. This gradient is relatively steep and a high throughflow rate can be expected if permeabilities are high. However, these gradients will necessarily be somewhat less in the lower reaches of the watershed.

The surficial materials in the watershed are described in Section 3.3.2 (p. 65). They consist mainly of clean sands and gravels with some silty till, all very permeable materials. Permeabilities in m/day for such materials are reported by Dunne and Leopold (1978, p. 206) as follows:

1.	medium to coarse sand	10 - 3,000
2.	sand and gravel	0.3 - 10
3.	gravels	1000 - 10,000
4.	glacial till	0.001 - 10

Thus the length of time required for throughflow to reach the Chippewa Channel will vary depending on the materials present. Generally, the distances of travel from divides to channels in the Chippewa system are from 300 to 2000 m. and from 100 to 1000 m. in the rural and urban settings respectively.

Thus in view of these distances and permeabilities, the hydrograph peaks discussed above could very well represent the arrival of the sub-surface stormflow peak and the consequent flow increase in the channel. As well, these lag times give good approximation of the time required for all infiltrated waters to reach the channel from more distant parts of the watershed. Waters arriving in this fashion would have travelled through and contacted several different soil types and horizons. Thus it could be expected to be more concentrated in solutes than surface runoff.

3.6.3 Chemical Quality of Precipitation

The chemistry of precipitation in the North Bay area has been researched by Kramer (1973, 1975, 1976) as part of a larger study dealing with Northern Ontario. His investigation of the chemical character of bulk precipitation extended over a period from December 1972 to March 1976, a period which partially coincides with the sampling period of this study. Data selected from Kramer's summaries are presented in Table 3.7 (p. 104) for the North Bay area from December 1, 1972 to October 25, 1975.

Generally, most parameters are of very low concentrations and have small standard deviations. The largest means are total P, HCO_3^- and SO_4^{--}. These parameters have terrestrial sources from dust (collector was near to agricultural area) in the case of P and HCO_3^- and smelter activity in the case of sulphate and from data at another site near Sudbury (130 km. distant) display a seasonal variance with summer maxima (Kramer, 1975). Other parameters are generally low reflecting the inland location of the North Bay area.

The mean pH of precipitation is 4.86 which is considerably lower than the 5.6 value representing equilibrium with atmospheric CO_2. The presence of SO_4^{--} and to a minor extent other acid radicals tend to produce pH values lower than CO_2 equilibrium value. The pH maximum of 7.60 is likely the result of buffering during periods of increased atmospheric alkalinity provided by air-borne dusts and particulate matter. However, for greater than 68 per cent of the samples, pH values lie below natural precipitation acidity levels.

TABLE 3.7

PRECIPITATION CHEMISTRY, NORTH BAY AREA

(DEC. 1/72 TO OCT. 25/75) +

	MAX.	MEAN	MIN.	DEV.
pH	3.75	4.86	7.60	0.97
Cl	5.77*	0.46	0.06	0.48 E-03
Total Particulates	0.13	0.02	0.003	0.38
Na	3.75	0.14	0.10 E-01	0.56
K	3.70	0.31	0.05	0.49
Mg	0.40	0.10	0.10 E-01	0.40
Ca	6.60	0.50	0.13	0.37
Alk.	103.10	7.70	2.40	0.40
SiO_2	0.21	0.05	0.10 E-01	0.30
P (total)	235.0	46.0	6.0	0.40 E+00
NO_3	0.83	0.66	0.26	0.55
NH_3	14.70	0.42	0.01	0.78
SO_4	13.65	3.60	1.80	0.24
Sp. Cond. (umhos)	168.0	22.0	1.0	0.43 E+00

* all parameters in mg/l except pH and Sp. Cond.

+ Data summarized from Kramer (1976).

The pH of the snowpack also has an influence on the pH of streamwaters in springflow periods. Jeffries et al. (1979) found pH values of 4.0 to 4.5 for the snowpack of Central Ontario in 1977-78. They estimated that a 2-13 fold increase in H^+ occurred during melt conditions and that between 36 and 77 per cent of the year's export of H^+ from the study watersheds occurred in April alone.

The significance of precipitation chemical quality to streamwater quality has been discussed generally earlier in Chapter II, Section 2.2 (pp. 12-15). Certainly at the Chippewa Watershed location, concentations of dissolved constituents in the precipitation are low except for HCO_3^-, P and SO_4^{--}. Even maximum values are small for most solutes and it appears that rainfall does not account for much of the solute load in streamwaters of Chippewa Creek. The contribution of rainfall chemistry to solute concentrations are variability is discussed again in detail in Chapter V.

3.6.4 Groundwater Quality

Background data on groundwater quality is virtually non-existent for the Chippewa Watershed except for a few isolated test samples taken by the Ontario Ministry of the Environment and a series of tests on the leachate from the landfill in sub-basin 7. One such set was taken and analysed for several wells in the vicinity of Sunshine Lane in the extreme north end of the watershed (see Figure 3.17 in Section 3.7 p. 115) Average values are given in Table 3.8 (p. 106) (Mr. Ray Banach M.O.E., North Bay, personal communication). These values represent background

TABLE 3.8

EXAMPLES OF GROUNDWATER SOLUTE VALUES

	SUNSHINE LANE*	LANDFILL***
pH	5.83	6.3
HCO_3^-	9.33 !	155.0
HD	22.67	-
Cl^-	4.33	36.0
Ca^{++}	-	31.0
Na^+	-	60.0
K^+	-	5.0

! Values in mg/l

* From M.O.E. Ontario, personal communication

*** From Cherry et al. (1981).

Note: Sunshine Lane data is considered to represent background concentrations in the groundwater.

groundwater concentrations developed in the glacial gravels of sub-basin 8. Values of chemical species in groundwater along the main flow path from the city landfill site (see Figure 3.17 in Section 3.7, p. 115) are also presented in Table 3.8 (Cherry et al., 1981). It is obvious from Table 3.8 that the landfill site is an important source of solutes to the north-east branch of Chippewa Creek.

3.6.5 Streamwater Quality

Very little previous data existed on solute concentrations in Chippewa Creek prior to 1974. Some water quality data were available for the years 1970-73 as published by Environment Ontario but the data were limited to occasional samples at the mouth of the creek and were reported mainly from a pollution perspective.

Limited water quality data were also obtained during a study done to determine the best route for a new, enlarged By-Pass around North Bay in the summer of 1973. The author was involved as part of the team investigating the natural environment and was responsible for determining stream discharges and to some extent water quality.

Another study carried out by students at Nipissing University as a course project produced a range of values for water quality parameters, HCO_2^-, pH, total hardness, and Cl^- for winter flows. Their results, although not related in any way to discharge, are tabulated in Table 3.9.

Water quality data on Chippewa Creek from 1970 to the present (1981) as reported by Environment Ontario in annual publications, are summarized in Table 3.10 and Figure 3.16 for some of the major cations

TABLE 3.9

WATER QUALITY DATA CHIPPEWA CREEK, WINTER, 1973

DATE	STATION A					STATION B					STATION C				
	Golf Club & O'Brien Sts.					Princess & Fisher Sts.					Monk St. (Oak St.)				
Day	Hour	pH	Alk.	Ca	Cl	Hour	pH	Alk.	Ca	Cl	Hour	pH	Alk.	Ca	Cl
JAN 24	1330	7.3	21	30	29*	1400	7.0	18	48	60	1420	7.1	19	54	93
28	1330	7.2	19	32	26	1400	6.8	22	50	59	1415	7.0	22	54	92
31	1320	7.6	20	35	24	1325	7.2	21	45	48	1415	7.1	23	53	53
FEB 04	1350	7.6	20	35	42	1325	7.2	21	55	73	1310	7.2	23	56	134
07	1310	7.1	19	36	47	1330	6.8	21	58	87	1345	6.9	24	53	165
18	1235	7.0	19	49	25	1255	6.8	22	60	43	1315	6.7	23	67	84
14	1325	7.0	18	40	21	1350	6.8	19	57	45	1405	6.8	22	60	71
11	1310	7.0	16	46	22	1330	6.7	21	63	47	1350	6.6	22	68	71
21	-	7.4	19	46	23	-	7.0	23	56	47	-	7.1	24	69	87
25	1310	7.4	20	44	26	1330	7.1	23	67	49	1345	7.1	25	63	76

* concentrations are in mg/l.

and anions analyzed. The data are sketchy and consist of spot samples at two sites, at the mouth near Oak Street and at Golf Club Road just upstream of Airport Road (see street reference map, Figure 3.17, p. 115). Some ions have been consistently monitored while others have not. In addition Table 3.11 lists some background values for the various ions studied in this thesis. These data were collected from several small streams draining natural and undeveloped watersheds flowing off the escarpment into Trout Lake just east of the Chippewa Watershed.

Within the Chippewa Creek data, mean values at both Golf Club Road and Oak Street tend to be higher than background values from undeveloped sites indicating the influence of human activity. Values for HCO_3^-, hardness and Cl^- at Oak Street tend to be about double the background values (compare Table 3.10 p. 110 to Table 3.11, p. 112). Values for Ca^{++}, Na^+, K^+ and Mg^{++} are lacking in the Ministry of the Environment data but the winter data presented in Table 3.9 (p. 108) indicate that these ions (especially Ca^{++}) will also likely have considerably higher concentrations than background. In all cases values tend to be greater at Oak Street than at Golf Club Road, likely a result of the influence of urbanization. Specifically temperatures, Cl^- and total TDS are considerably higher and SO_4^{--} only slightly higher.

The historical water quality data also show considerable variability (see Figure 3.16, p. 111). Values differ from the rural site, Golf Club Road, to the urban site near Oak Street; thus, it appears that degree or quality of urbanization will likely introduce spatial variation to streamwater quality. Obvious seasonal variance occurs from winter

TABLE 3.10

SUMMARY OF HISTORICAL WATER QUALITY DATA ON CHIPPEWA CREEK

	SITE	WATER TEMP. °C		pH		HARDNESS		CALCIUM		POTASSIUM		SODIUM		MAGNESIUM		CHLORIDE		ALKALINITY		SULPHATE		SILICA		N		P		T.D.S.	
		$\bar{X}$	SD	$\bar{X}$	SD	$\bar{X}$	SD	$\bar{X}$	SD	$\bar{X}$	SD	$\bar{X}$	SD	$\bar{X}$	SD	$\bar{X}$	SD	$\bar{X}$	SD	$\bar{X}$	SD	$\bar{X}$	SD	$\bar{X}$	SD	$\bar{X}$	SD	$\bar{X}$	SD
MARCH	1	0.72	0.92	7.23	0.36	76.0	-	-	-	-	-	-	-	-	-	186.00	241.00	37.0	-	17.50	3.11	-	-	2.40	1.06	0.10	0.030	289	119
	6	1.00	1.73	-	-	-	-	-	-	-	-	-	-	-	-	23.00	10.68	-	-	9.00	-	-	-	1.67	0.44	0.13	-	-	-
APRIL	1	2.85	2.40	6.95	0.35	86.0	-	-	-	-	-	-	-	-	-	47.71	39.90	11.0	-	16.00	-	1.45	-	1.44	0.40	0.20	0.230	176	68
	6	2.40	1.67	-	-	-	-	-	-	-	-	-	-	-	-	22.20	11.61	-	-	14.00	-	-	-	1.58	0.49	0.05	0.060	90	35
MAY	1	14.50	3.91	6.75	0.21	70.5	27.6	-	-	0.4	-	-	-	-	-	52.80	12.68	27.0	1.41	10.00	-	-	-	1.33	0.29	0.09	0.050	194	19
	6	10.50	2.89	-	-	-	-	-	-	-	-	-	-	-	-	16.50	1.29	-	-	-	-	-	-	0.98	0.32	0.04	0.030	75	16
JUNE	1	18.56	1.95	6.88	0.41	60.0	-	-	-	-	-	-	-	-	-	102.13	125.22	33.0	1.41	12.50	3.54	-	-	1.25	0.55	0.11	0.070	195	40
	6	18.25	2.50	-	-	-	-	-	-	-	-	-	-	-	-	18.33	2.08	-	-	-	-	-	-	0.76	0.29	0.03	0.020	112	68
JULY	1	20.44	1.84	6.80	0.26	-	-	-	-	-	-	-	-	-	-	46.50	16.94	-	-	-	-	-	-	1.46	1.21	0.21	0.340	173	46
	6	20.50	3.11	-	-	-	-	-	-	-	-	-	-	-	-	14.80	7.66	-	-	-	-	-	-	0.74	0.18	0.03	0.003	96	20
AUG.	1	20.17	2.48	7.15	0.21	52.0	-	-	-	-	-	-	-	-	-	52.14	14.46	32.0	-	-	-	-	-	1.43	1.32	0.21	0.340	185	37
	6	18.60	2.07	-	-	-	-	-	-	-	-	-	-	-	-	13.00	6.16	-	-	-	-	-	-	0.59	0.22	0.02	0.010	80	13
SEPT.	1	15.75	3.15	7.45	0.07	44.0	-	-	-	-	-	-	-	-	-	40.17	12.78	38.0	8.49	14.00	0.00	-	-	0.98	0.32	0.12	0.120	170	30
	6	10.40	1.82	-	-	-	-	-	-	-	-	-	-	-	-	15.75	1.71	28.0	-	13.00	-	-	-	0.60	0.14	0.06	0.070	85	13
OCT.	1	8.10	2.96	7.10	0.30	50.0	-	-	-	-	-	-	-	-	-	38.88	11.33	31.0	1.41	10.50	2.12	-	-	1.01	0.50	0.06	0.030	140	37
	6	7.00	3.22	-	-	-	-	-	-	-	-	-	-	-	-	12.67	7.31	-	-	16.00	-	-	-	0.61	0.21	0.02	0.010	81	27

Notes: 1. Means and standard deviations have been calculated from MOE Summaries 1970-78.

2. All data except temp. and pH are in units of mg/l.

3. Site 1 is OAK ST. and Site 6 is GOLF CLUB RD.

HISTORICAL WATER QUALITY GRAPH

Figure 3.16

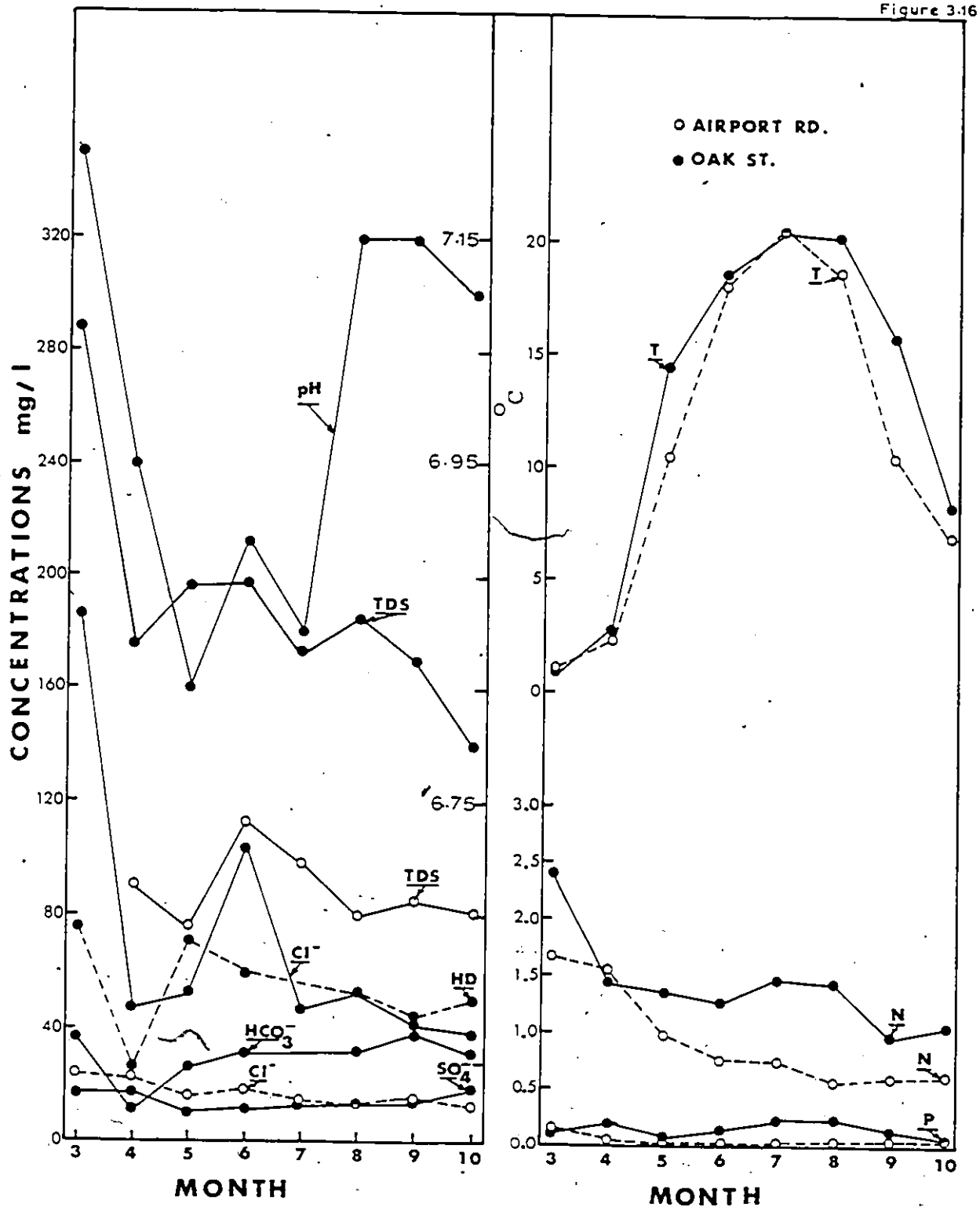


TABLE 3.11

SELECTED TROUT LAKE INFLOW WATER QUALITIES

VARIABLE	HIGH LAKE CK.	HOGAN CK. (above Rwy.)	UNNAMED CK.	means
Hardness	17/15*	16***	17/21*	17.20
Alkalinity	9/8	-	12/12	10.25
Chloride	3.1/3.4	0.4	3.1/7.8	3.56
Calcium	4.8/4.2	5.0	4.6/5.4	4.80
Magnesium	1.15/1.15	0.95	1.45/2.00	1.34
Sodium	-	1.6+	-	1.60
Potassium	-	0.95+	-	0.95
Suspended	-	0.3	-	0.30
Dissolved	-	33.0	-	33.00

* June/July, 1979 in mg/l

*** August, 1978 in mg/l

\+ June, 1978 in mg/l

Adapted from Myslik et al. (1979).

through spring, summer and fall. The large standard deviation on some parameters indicates additional controls, likely discharge, operating within the seasonal influence; whereas, other parameters such as the SO_4^{--} concentrations appear to vary little over both the seasons and the two sites.

The major parameters influencing the character of water quality in Chippewa Creek appear to be hardness, alkalinity and chloride. They appear to dominate in terms of magnitudes and variance both spatially and temporally. Sulphates, nitrates, phosphates and silica appear to be of minor importance as constituents making up the solute load of Chippewa Creek.

3.7 Landuse and Development

About 25 per cent of the areal extent of the Chippewa Creek Watershed is urbanized. Basically all of the urbanization occurs below the escarpment (see Figure 3.2, p. 59) with minor amounts of the residential, commercial and light industrial development occurring along major arteries extending from the city. Few major developments occurred in the watershed within the city or on the escarpment for at least five years prior to the beginning of this study. Single unit and small multiple unit dwellings were erected sporadically throughout the area especially in a low swampy area just south of the Ski Club (see Figure 3.2, p. 59).

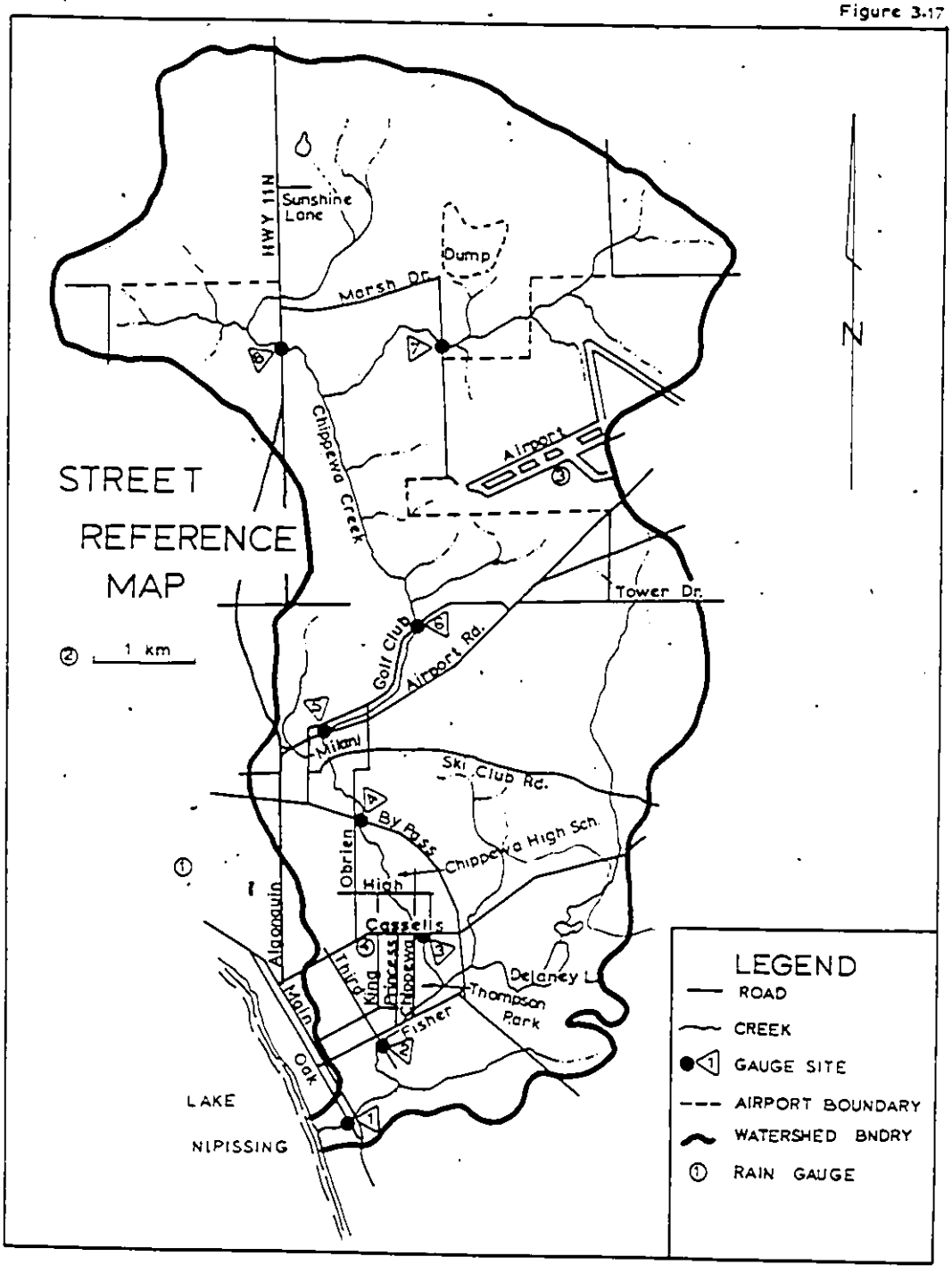
All of the roads within the urban sector of the watershed are paved or black-topped and a great many contribute their runoff via ditches

or storm sewers to the channel of Chippewa Creek. Most of the storm sewers are restricted to the lower reaches of Chippewa Creek from the By-Pass south and some combined storm and sanitary sewers exist in the downtown area as well. In the past, the creek has been used as an open sewer in a limited capacity but few, if any, sanitary sewers flow into the creek now except for occasional anomalous situations where gates have to be opened for purposes of repair or in extreme flood events. Even so, one sewer draining Oak Street (see street references in Figure 3.17, p. 115) near the mouth of the creek is very suspect and may be the last sanitary sewer to contaminate the creek.

The core of urban development is situated adjacent to the lake front and the rail yards with major, core arteries travelling NW-SE. Development behind the three principal downtown arteries quickly merges into residential area. The urban section of the watershed also contains a park and several institutional developments such as schools, sports facilities and a home for the aged.

From the Airport Road (Hwy. 123) up the escarpment, numerous large but presently inactive gravel pits are found. Between these pits and the headwaters is a relatively rural, undeveloped section which merges again with gravel pit development and an active landfill site in the headwater regions. Except for the gravel pits and erosion sites along the channel, most of the watershed has a good vegetative cover of grass in the city and forest in the rural areas. Thus, from mouth to source the watershed presents a variety of physical and human landscapes.

Figure 3.17


STREET
REFERENCE
MAP
1 km
HWY 11N
Sunshine Lane
Dump
Marsh Dr.
Chippewa Creek
Airport
Tower Dr.
Golf Club
Airport Rd.
Milani
Ski Club Rd.
By Pass
Chippewa High Sch.
Obrien
High
Cassells
Algonquin
Third
King
Princess
Chippewa
Main
Fisher
Delaney L.
Thompson Park
Oak
LAKE
NIPISSING
N
LEGEND
ROAD
CREEK
GAUGE SITE
AIRPORT BOUNDARY
WATERSHED BNDRY
RAIN GAUGE

In order to try to determine the effect of various urban environments on water quality, a multiple-watershed approach was adopted and the city was divided into sub-basins or sub-watersheds of the larger Chippewa Creek Watershed (see Figure 3.2, p. 59). A reconnaissance survey of the creek and its watershed showed that there were obvious points on the creek which could be selected as sample sites for flow determinations and water sampling and which collected runoff from differing urban watershed environments.

The first and most obvious choices were to sample the creek at the Airport Road or Golf Club Road sites and at Oak Street to try to determine the "rural" (rural is used throughout to mean undeveloped land within the city limits) and urban solute outputs and flows respectively. From there, additional sites were selected to look at intra-urban and intra-rural situations (see Figure 3.2, p. 59).

Site 1 (Oak St.) while draining part of the central business district would likely display the effects of railroad development and commercial areas; Site 2 (Third Ave.) the effects from an older residential section of the city; Site 3 (Cassells St.) the effects from an institutionalized and residential part of the city (schools, etc.); Site 4 (By-Pass) likely the effects of the highway setting and newer residential areas; and finally Site 5 (Airport Rd.) the effects of the rural setting. The rural Site 6, Golf Club Rd., would likely show the effects of a well vegetated and sparsely developed section of the watershed, and Site 7, Marsh Dr., the effects of an open, sand pit area abutting a city landfill site and finally Site 8, Hwy. 11 N., the effects

of the highway, sparse development, and the source wetland of this northwest branch of the creek. In addition to their relevance to the study, the sites also presented good, stable cross-sections which could be gauged to yield reliable flow and water quality data.

The human and physical characters of the sub-basins are described by the data in Table 3.12 (p. 118). The parameters used to describe the sub-basins have been selected with relevance to their possible control or relationship to water quality. Their choice is rationalized later in Section 5.42 (p. 211); however, a brief comment is made below on their deprivations, magnitudes and variance for each of the sub-basins.

Deprivation of many of the physical variables have been explained already or are self-explanatory. Urban variables such as building densities, impervious areas, road lengths, street crossings and ends, and sewer densities were all measured from large scale aerial photos and city maps of recent age. Population densities were derived using enumeration area statistics. Enumeration area data were cumulated for each sub-basin and where enumeration area boundaries cross over a sub-basin divide adjustments were made on an areal basis; that is, the population density for the whole enumeration area was apportioned to the parts within the sub-basin on the basis of the area of the enumeration area lying within the sub-basin.

Basically the values of the parameters of Table 3.12 (p. 118) separate into two groups, the urban and rural sub-basins. Values of most parameters are quite different for Sites 1 to 4 and Sites 5 to 8.

TABLE 3.12

VALUES OF URBAN GEOMORPHIC VARIABLES

	BASIN AREA (km^2)	BASIN SLOPE ($avs\phi^o$)	FORM RATIO (A/L^2)	FOREST COVER (km^2)	GRAVEL %	TILL %	BS SOIL (%) (A HORIZON)	BS SOIL (%) (A + B HORIZON)	BS SOIL (%) (C HORIZON)	BUILDINGS (10's)	IMPERVIOUS AREA ($1000's\ m^2$)	ROAD LENGTH (km)	STREET CROSSING AND ROAD ENDS	SEWER LENGTH (km)	POPULATION (100 's)	MEAN SPRING Q (l/s)	MEAN STORM Q (l/s)	MEAN LOW FLOW Q (l/s)
1. OAK	2.55	2.50	0.35	0.10	0.1	22.0	25.2	7.60	12.6	224.53	49.77	21.20	8.0	3.76	131.92	1439.51	883.30	26.34
2. THIRD	9.55	1.72	0.28	2.48	3.0	47.0	25.1	14.40	10.9	216.12	65.42	30.94	5.0	6.49	47.56	834.83	579.99	95.44
3. CASSELLS	0.74	5.58	0.07	0.03	0.1	64.5	11.3	4.15	5.0	52.53	16.11	7.21	7.0	1.96	37.03	635.78	203.05	74.76
4. BYPASS	1.95	3.76	0.42	0.61	14.0	50.0	21.7	19.58	38.2	86.99	24.80	12.87	5.0	3.00	26.73	113.56	73.92	52.11
5. AIRPORT	1.41	7.02	0.17	1.18	42.0	53.0	5.2	13.78	20.2	5.51	5.99	6.20	2.0	1.54	10.08	367.31	151.23	26.34
6. GOLF CLUB	9.01	3.30	0.78	7.94	25.0	74.0	5.9	8.68	12.9	3.06	2.34	4.78	1.0	0.10	1.67	619.08	8.21	30.87
7. MARSH	5.95	2.14	0.65	5.53	13.0	82.0	22.7	13.95	30.9	0.42	0.36	0.18	1.0	0.10	0.18	501.26	517.12	17.56
8. HWY 11 N.	8.29	1.48	0.91	8.24	70.0	30.0	11.8	12.50	18.3	5.72	4.89	1.16	3.0	0.10	2.40	358.53	209.57	12.46

Most, also display a dramatic change in value from sub-basin 4 to sub-basin 5 indicating the boundary between the rural and urban settings.

More specifically slopes tend to be steeper, forest cover greater (except for sub-basin 2), and channel gradients more severe in the rural sub-basins. Form ratio s of urban sub-basins are smaller than the rural and are indicative of narrow basin geometry; whereas, the rural sub-basins tend to display wider and fuller geometries. Thus the urban sub-basins will likely give up their water to the main channel quickly compared to the delivery from the rural sub-basins. Gravel sediments appear to be in larger quantities in the rural sub-basins than in the urban. Whereas till dominates other sediment in both environments, it appears to be in greater quantities in the rural setting as well.

Human parameters also accentuate the boundary between urban and rural at Site 5. Numbers of buildings, impervious areas, and street crossings of the creek channel, are considerably lower for the rural basins. In addition, population, road density and sewer density also diminish in value beyond Airport Road and it is apparent that human activity is much more limited to the north than to the south of Airport Road in the Chippewa Watershed.

Of special note is sub-basin 7. Even though it appears the most rural and is apparently undeveloped as noted in Table 3.12 (p. 118), it has within its boundaries a sanitary landfill operation (see Figure 3.2, p. 59). The landfill has been studied by several agencies and authors (Gore and Storrie, 1977; and Cherry, 1980). The operation has been in existence since 1962 and accumulates the domestic and commercial refuse and sewage sludge from the city of North Bay.

The landfill has been constructed on sandy tills and gravels which vary in thickness from 3 to 30 meters (Gore and Storrie, 1977). Extensive leachate migration down-gradient from the landfill has occurred in these highly permeable materials and the leachates exit via seeps and springs into Chippewa Creek about 800 m. to the southwest. Major inorganic constituents in the leachate are Cl^-, HCO_3^-, Na^+, Ca^{++}, Mg^{++} and Fe (Cherry, 1980). All occur at concentrations above background levels but are not presently toxic and they also are attenuated towards the creek. Values at about 200 m. from the creek are given earlier in Table 3.8 (p. 106) and it is a certainty that the landfill is an important source of solutes to the northwest branch of Chippewa Creek and should contribute to spatial variability of solute loads in the creek waters.

Thus the environments through which Chippewa Creek flows and from which it derives its flow are diverse and varied in physical and human character. This diversity can be expected to produce concomitant spatial diversity in solute loads in Chippewa Creek waters and it is important then that the parameters of Table 3.12 (p. 118) be considered in any model attempting to explain the solute variability of Chippewa Creek.

CHAPTER IV

Water Quality Data Collection

4.1 Introduction

The various spatial and temporal controls on streamwater solute load variability have been discussed in Chapter II earlier. Any sampling programme must be biased towards gathering samples in concert with such controls in order to determine their magnitudes and effects. The short-term controls such as storm events require frequent sampling on a short-term basis; whereas, long-term seasonal controls require a lengthy systematic sampling frequency and duration. Truly random sampling in space and time would therefore be of limited use in this study.

Sampling practices in geographical research are discussed by many authors (for example, Gregory, 1963; Hammond and McCullagh, 1974; Yeates, 1974; Lounsbury and Aldrich, 1979). Sampling involves the choice of a framework and a procedure. The framework can be spatial where the location is an essential part of the variability and therefore is a variable itself or the framework can be non-spatial where the locational variability is not a consideration (Hammond and McCullagh, 1974). Spatial frameworks can include grids on which point or areal sampling can be done or they can be transects or traverses on which linear sampling can occur. Temporal frameworks include point sampling or continuous sampling over time.

Sampling procedure can be random where a given member of the population studied has the same likelihood of being included in the sample as any other member or sampling procedure can be systematic where samples are taken at regular intervals (Hammond and McCullagh, 1974). Systematic samples are biased by their very nature unless the population is randomly distributed. Often the random and systematic procedures must be modified by stratification, especially where an area has two or more environments affecting the properties or values of the parameter being sampled (Yeates, 1974). Stratification involves selecting additional samples from data subsets within the general data which would mean the sampling of both environments of the example above.

Yeates (1974) also outlines some problems of sampling spatial and serial data. Spatial and temporal autocorrelation are often problems in geographical sampling. They occur when the position of one observation is such that the value is influenced by the nearby presence of another. Thus the sample values are not spatially independent. This problem occurs frequently in geographical research and in fact most geographic data is spatially autocorrelated or serially correlated (Curry, 1966 in Yeates, 1974). The major problem introduced to analyses of and conclusions about spatial or temporal variability by autocorrelation and serial correlation is that of double counting from sample site to sample site. For example, a portion of the concentrations of solutes measured at a downstream site in a river may have been measured once already at an upstream site. Thus values at the downstream site are not truly indicative of the solute delivery from the watershed between the two sites, and comparisons must account for the influence of the upstream site on the downstream site.

Another aspect of sampling, especially for water quality, is the assumption of a representative sample. Hem (1970) notes the presence of locally poor, lateral and vertical mixing of streamwaters in many streams as a factor which may produce samples not representative of the total solute load at a given time. He suggests a series of samples spatially integrated both vertically and laterally in the channel section at the sampling site to test out the problem. He also recommends selection of sites at which waters are well mixed to get around this problem and to reduce the number of samples required to get a good measure of solute load at the site. Even when streamwater is chemically homogeneous at a site, there may be changes with time on a yearly, seasonal, weekly, diurnal, or hourly scale depending on the degree of control or human impact on the waters. Thus sampling programmes for natural waters must take into account possible short-term and long-term effects.

4.2 Sampling Design

4.2.1 Ion Selections

The chemical quality of streamwaters is a result of the mixing of water from various sources in the watershed. However in most natural watersheds the bulk of the solute yield is generated through the weathering of rocks and soils. Exceptions occur, of course, where precipitation sources predominate (Gorham, 1961). In urban settings additional dissolved constituents may take on more importance (Waller, 1971, etc.).

Garrels and MacKenzie (1967, p. 231) list the solutes to be expected in an idealized water from a typical felsic rock. The chief cations

produced should be Ca^{++} and Na^{+} in the same ratio as in the plagioclase of the felsic bedrock. Potassium and Mg^{++} should be secondary at less than about 20 per cent of the total Ca^{++} and Na^{+}. When the rocks contain higher percentages of mafic minerals, Mg^{++} should become more dominant over K^{+} and if K-feldspar is abundant then K^{+} becomes more important quantitatively. Other cations will be of minor importance except in areas of industrial pollution where heavy metals become a greater part of the solute load.

Ideally the principal or even sole anion should be HCO_3^{-}. Occasionally small concentrations of Cl^{-} and SO_4^{--} may be present derived from rainfall and oxidation of pyrite or other sources. Thus the alkalinity of these waters is primarily a function of the concentration of the anion, HCO_3^{-}, and the hardness a function of Ca^{++} and Mg^{++} cations.

A perusal of the background data collected from previous studies on the water quality of Chippewa Creek (see Tables 3.8 and 3.9 p. 106 and p. 108) confirms this discussion. Alkalinity (HCO_3^{-}) and hardness (Ca^{++} and Mg^{++}) appear to be quantitatively important parameters in Chippewa Creek water. In addition chloride values are extremely large and one would expect high values for Na as well. These latter anomalous values are likely the influence of urban development and land use practice. In contrast other chemical constituents are relatively minor in quantity. Thus the ions selected for this study constitute, quantitatively the most important ions in Chippewa Creek waters, most of which derive from groundwater in contact with the bedrock or soils. Variability of these ions due to spatial and temporal controls will be easily detected

because of their magnitudes. They are listed below.

TABLE 4.1

SOLUTE PARAMETERS STUDIED

A. cations	B. anions
1. Hardness $-Ca^{++}$ $-Mg^{++}$	1. Alkalinity $-HCO_3^-$
2. Na^+	2. Cl^-
3. K^+	

C. other chemical and physical parameters

1. pH
2. TDS
3. water temperature

These ions have also been shown to respond to urbanization (see Chapter II, Section 2.7, p. 45). For example, chloride concentrations can be closely related to volumes of deicing salts dumped on roads and hardness can be related to leachate production from landfill operations.

4.2.2 Site Selections

Site selections were made on a non-spatial basis (as defined by Hammond and McCullagh, 1974). The locations of sampling sites do not vary in the watershed over the study period and presumably neither do the physical and human characteristics of the sites to any significant extent. However the water quality did vary at each site. The rationale

for the selection of the sites has already been discussed in Chapter III, Section 3.7 (p. 113) and will not be repeated here except to say that the selection of the eight sites allows for the investigation of the spatial variation of solute loads in the watershed.

Selection of the parameters used to describe the sub-basin represented at the sampling site was done with regard to the ultimate effect of these parameters on solute yields from the sub-basins. The values and character of these parameters have been discussed previously in Chapter III, Section 3.7 (p. 113) and they are rationalized later in Section 5.2 of Chapter V (p. 135).

4.2.3 Sampling Frequency

Discussion in Chapter II has shown that the chemical quality of streamwater can vary over the short term (hours and days) or over the long term (weeks, months and years) in response to the various controls in the watershed. A random sampling design would undoubtedly fail to sample all of the possible variations unless it was in place for a long time. Thus the nature of solute variation demands a stratified systematic sampling design. A systematic design of reasonable interval would allow the sampling of long-term variation. Such a design could then be stratified by sampling more frequently at shorter intervals during periods of short-term solute variation, such as those introduced by storms and sporadic human activity.

In this study, data collection began in 1974 and continued throughout 1975, 1976 and parts of 1977, 1979 and 1981. Such a long record was deemed necessary to statistically analyze solute loads and water discharges

from the Chippewa Watershed with some degree of reliability. In 1974 sampling occurred approximately every four days. In 1975 and 1976 samples were collected every two to four days and more frequently for storm events in summer periods. More sporadic sampling was carried out in the springs and autumns of 1975 and 1976, and some special event sampling was done in 1979 and 1981. No sampling was undertaken in winter although some sketchy data is available (Table 3.10, Section 3.6.5 p. 108).

Samples were taken in blocks of eight; that is, all sites were sampled on each sample day. Thus, the samples for the eight sites were more or less contemporaneous within one and one-half to two hours, the time required to sample from site eight to site one, about 11-12 km. distance. This practice ensured that the samples at the eight sites were collected under similar climatic and temporal conditions for later comparison. This systematic sampling programme was further stratified with respect to the time of day at which samples were collected. An attempt was made to vary the sampling time in order to try to sample possible diurnal variation.

A total of 617 samples were collected at eight gauging sites and were analyzed for all or many of the solute variables mentioned above. Peripheral information gathered included site, date, time, gauge level, flow, suspended solids and temperature; variables which might be used in future studies. The matrix containing all data holds some 7,000 pieces of information on the solute loads (and sediment loads) and related data on Chippewa Creek.

Not all samples have a complete set of solute values. Due to lengthy storage, broken sample bottles or other mishaps many samples were rejected. The research requires the comparison of sets of samples which are all collected contemporaneously over the eight sites. So, if on a given sample day, a sample at any site is lost or destroyed, then the sample data for the other sites may have to be removed as well. Discussion of these problems is undertaken more fully in Section 5.1 of Chapter V (p. 130). The total matrix of sample data is available in original records held by the author.

4.2.4 Sampling Methods

As mentioned earlier (Section 4.1 p. 121) often solutes are not uniformly mixed in a stream cross-section. To overcome this possible problem, samples were taken with the use of a U.S. Geological Survey DH 59 type depth-integrating sampler. Although the suspended load is stressed more than the solute load, the theory behind depth-integrated sampling is well discussed by Nelson and Benedict (1951); Leopold, Wolman and Miller (1964); Chow (1964); Leliavsky (1966); Guy (1970); and others. Other more sophisticated but somewhat costly and/or impractical methods are available and have been discussed by Brown et al. (1970); Walling and Teed (1971); Carson and Kirkby (1972); and Bennett (1973). Basically the depth-integrating sampler fulfills the requirements for obtaining an accurate, average sample of solute load.

The sampling was conducted by lowering and raising the DH 59 through the depth of the stream ensuring a mean sample in the vertical. Several verticals across the channel at the sampling sites were initially

sampled, cumulated and averaged. On inspection, each vertical produced very close to equal values for the solute parameters indicating that the streamwaters were well mixed; therefore, subsequent sampling was conducted in only a single vertical in approximately mid-channel whenever possible.

Samples were transferred from the sampler to well-washed, brown, glass bottles to minimize photo-chemical activity and capped to prevent contact with air while in storage. Before use, the bottles were cleaned with laboratory soap, rinsed in distilled water, rinsed in dilute HCl and rinsed a final time with distilled water. In the field, the bottles were rinsed with creek water before being filled with the sample. Field data such as water temperature, gauge level, date, time and site were recorded on the bottles.

4.3 Chemical Analyses

Chemical analyses were done as quickly as possible after samples were collected. Even so some sample storage was necessary, the details of which are documented in Appendix A. Samples were filtered to remove suspended material using Whatman #50 filter paper and a vacuum system. Total dissolved solids concentrations were determined by drying and weighing a portion of the filtrate. Cations such as Na^{+}, Ca^{++}, Mg^{++} and K^{+} were determined by atomic absorption. Anions were determined by titrametric means and pH was determined by use of a Corning dual electrode pH meter. Attention was paid to detail in doing the analyses to prevent contamination and problems of interference from dissolved constituents not under study. Details of discussions of procedures, effects of storage and reproducibility can be found in Appendix A.

CHAPTER V

Solute Variations in Chippewa Creek

5.1 Methodology of Analysis

5.1.1 Partitioning of the Data

In order to fulfill the purpose of this thesis set out in Chapter I, it has been necessary to partition the data in several ways. The data were collected by a sampling design described in Chapter IV earlier. By its very nature the design introduces spatial and to a lesser extent serial autocorrelation into the data. Essentially this fact means that values at Site 1 (at the stream mouth) will be influenced by values at all sites upstream. Thus it becomes difficult to determine the effects of the sub-basins behind each sampling site on the water quality at the site. The presence of such autocorrelation also introduces problems to the interpretation of the results of statistical methods used in this thesis.

To remove this problematical aspect from most geographical data is often difficult or nearly impossible; however, in the case of time series or flowing systems, the problem is most easily solved by determining the difference score, between adjacent, downstream sample sites (Johnston, 1978). This operation can be performed because time, as it influences geographical events, goes in only a forward direction and streams flow in one direction from source to mouth, making it conceptually

easy to rationalize the removal of upstream effects by simple subtraction. However, not all effects are removed because the parcel of water sampled at a downstream site may not be exactly the same parcel sampled at the upstream site. To sample the exact effect of each sub-basin on the streamwater quality, it would be necessary to follow a parcel of water from site to site taking samples at each site and the subtractions made. The differences measured would be the net result of the effects of the sub-basins on the water passing through. In this study time-of-travel for water passing from Airport Road to Oak Street has been estimated earlier in Chapter III as being from 2-3 hours. Sampling time is somewhat less so that the exact same parcel of water is not sampled at each site. This problem is most accute during periods (i.e. storms) when water quality parameters are changing rapidly but is of little consequence during more stable lowflow periods. The magnitude of the problem is assessed later in the storm data analysis.

The data for this research were also taken over different flow regimes and seasons. Samples were taken in the spring and summer for lowflow and storm events. In Chapter II it was shown that solute variability is very much influenced by hydrological parameters. Thus in order to better investigate the relationships between solute data and hydrological variables, the data were further partitioned into sample subsets of springflow, summer flow including stormflow and lowflow and autumn samples over the eight sites. During each of these flow regimes solutes react differently due to changing sources and varying degrees of concentration or dilution and therefore can be expected to show different variance patterns amongst the sub-basins.

The data file containing all samples over the eight sites was partitioned through removal of the spring samples by date and through sorting the remaining samples, on the basis of gauge level by use of a computer programme. The default date for spring was chosen as the date on which significant diurnal variation in water stage ceased to appear on the continuous recorders. This event occurred at the end of April during the study period.

Similarly the gauge level used to sort stormflow from lowflow in the creek was decided by study of the continuous gauging records. Lowflow was defined by a flat gauge record and hence a flat hydrograph. Some samples had to be subsequently classified individually, for in the lee of storm events high stage records often degrade to a flat and steady configuration and yet water levels are at a greater elevation than those of true lowflow conditions. However, all samples were checked and the files edited to package samples into springflow, stormflow and lowflow data subsets.

5.1.2 Modelling of Solute Variability

Most water quality parameters vary as a trend over time and space with stochastic variation about that trend (Yevjevich, 1979). In addition water quality is a function of many chemical, biological, geological, hydrological and human factors some of which are often difficult to measure. Thus modelling of water quality is a very complex process and a multi-variate model may be required to explain the variance in a given water quality parameter. The model to be used in this thesis is the regression model.

Many researchers have used the regression model to explain variance in both suspended sediment and solute concentrations (for example, Pionke and Nicks, 1970; Edwards, 1973; Wulkowicz and Saleem, 1974; and Walling and Foster, 1975). Even so the model is not without requirements; Johnston (1978), nicely summarizes these requirements. Input data must be free of autocorrelation to prevent "double counting" and resultant spurious correlations amongst variables. Input data must be linear and if not it can be transformed by logarithms or some other suitable means. As well, the use of the regression model assumes that the input variables are normally distributed. Variances of the conditional distributions or the residual variance should be nearly equal for all values of the dependent variable(s); a situation producing homoscedascity. When one or two values of x in a relationship $y = f(x)$ are very large relative to the others, heteroscedascity results and the regression coefficients become severely biased. This condition can again be eliminated by using logarithmic transformations of x. When the regression is multivariate, collinearity may exist when the independent variables are highly interdependent. This condition generates biased regression coefficients which are difficult to interpret and hence it becomes difficult to determine the contribution of each independent variable to the explanation of the variance in the dependent variable. In most cases the regression coefficients of the independent variables which do not explain much variance in the dependent but are highly correlated with another independent that does, will not be significant and will have small beta weights. A small beta weight indicates little contribution to the explanation of the

variance in the dependent variable. Therefore offending independent variables can be detected easily and can be either removed from the regression or discounted as major explanatory variables.

5.1.3 Method of Approach

In the following sections the relationships between the solute parameters (see Table 4.1, p. 125) in Chippewa Creek and sets of hydrological, temporal and spatial variables are investigated by regression and other statistical techniques. First of all, the data means are presented graphically in "raw" form over the eight sampling sites to display the magnitudes and general character of the solutes in Chippewa Creek. This discussion leads into a display and analysis of all samples collected at Airport Road and Oak Street as a comparison between the "rural" part and the "urban" part of the watershed. Subsequently, obvious variabilities in the solute parameters are analyzed by statistical methods.

The within-site variance is analyzed by a series of bivariate regressions between the solute parameters and a set of hydro-temporal variables for each flow regimen (spring, storm and low). Only Site 1 (Oak St.) and Site 5 (Airport Rd.) are analyzed in this fashion because continuous hydrological data are restricted to these two sites; therefore, only the urban and the rural responses of solutes to these variables are determined. Problems of statistical multicollinearity amongst the hydro-temporal variables are dealt with by factor-analysis and subsequent stepwise multivariate regressions.

Between-site variance is similarly analyzed for each flow regimen by a series of bivariate regressions between the solute parameters and

a set of geo-urban variables describing the character of the sub-basins behind each sampling site. Again problems of interdependence of these spatial (geo-urban) variables are analyzed and dealt with by multivariate techniques. All of the statistical relationships are interpreted as to their physical meaning with respect to watershed characteristics and processes and their ultimate effect on the solute parameters studied in this thesis. Finally the export rates of the various solutes are calculated and compared for the urban and rural sites of Oak Street and Airport Road thus determining the net yields from the urbanized and from the rural portions of the Chippewa Watershed.

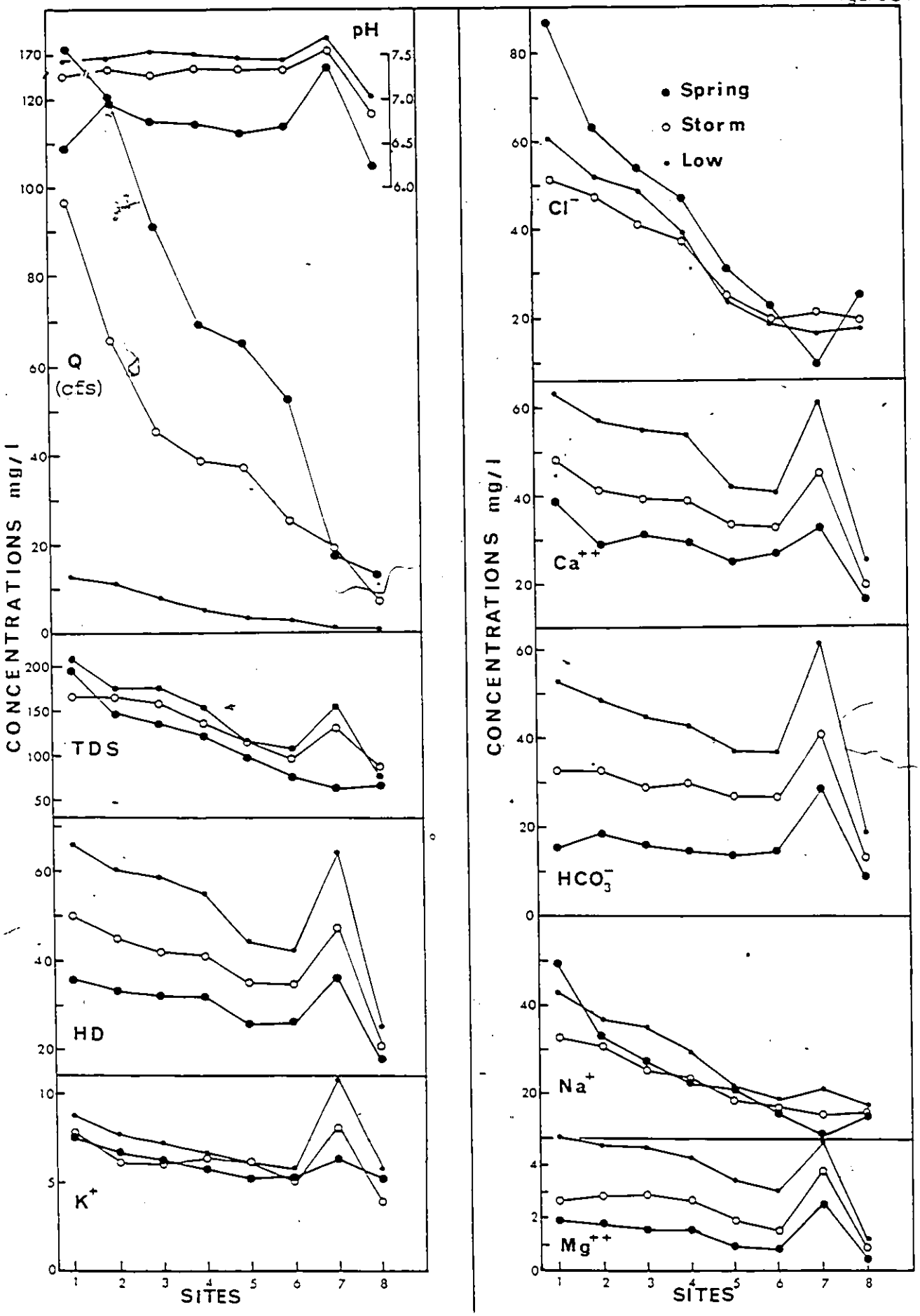
5.2 Magnitude and Character of Solute Load

5.2.1 Site Means

A complete data summary is given in Appendix C for temperature, discharge, pH and the solute parameters measured at each of eight sample sites during spring, storm and lowflow conditions. These data are those actually measured at the sites and have not been adjusted for further analysis. The means of these data have been graphed and the results are presented in Figure 5.1. A brief analysis of Figure 5.1 shows that generally Site 7 stands out from the others as an anomalous contributor of solutes to the creek. Clearly the city landfill site contributes high concentrations of Ca^{++}, K^{+}, Mg^{++} and HCO_3^{-} for spring, storm, and lowflow conditions. Sodium and Cl^{-} are exceptions having relatively low concentrations in spring especially and to some extent for stormflow and lowflow conditions as well.

PLOTS OF DATA MEANS AT SAMPLING SITES

Figure 5.1



The high concentrations of Site 7 are diluted by Site 6. The large volumes of relatively dilute water from sub-basins 8 and 6 generally tend to reduce concentrations of all of the solutes except Na^+ and Cl^- during spring and storm events. Downstream from Site 6 solutes are accumulated through the city to eventually build back up to relatively high levels again at Site 1 (Oak St.).

Quantitatively Ca^{++}, Na^+, Cl^- and HCO_3^- are the most important ions of those studied for this thesis in Chippewa Creek waters; whereas, K^+ and Mg^{++} exist in relatively minor amounts. Calcium, K^+ and Mg^{++} appear to have similar variation to HCO_3^- and overall water hardness (Hd) suggesting that these ions form ion pairs. On the other hand, Na^+ and Cl^- vary in similar fashion suggesting that these two form an important ion pair also. Ionic balances were determined between the cations and anions of springflow, stormflow and lowflow. Using the means (converted to epm values) of Table C1, Appendix C in a charge-balance equation (Freeze and Cherry, 1978, p. 96) charge-balance errors were derived for the data at Sites 1 and 5 over the three flow regimes. Results are tabulated below.

	Springflow	Stormflow	Lowflow
Site 1 (Oak St.)	24%	36%	37%
Site 5 (Airport Rd.)	37%	42%	45%

These figures indicate that the anions studied here are not completely balancing the cations with respect to ionic charge. Thus other anions are present which have not been measured (i.e. SO_4^{--}, OH^- and negative complexes).

The greatest mean values occur during the lowflow periods at all sites except for Cl^- and Na^+ at Site 1. This fact suggests a large part of the solute load contributing to water hardness and alkalinity is derived from groundwater and that the chemical disintegration of minerals within the rock and regolith is at the expense of rainfall acidity or seepage from waste disposal. During stormflow conditions the concentrated groundwater discharge is reduced by more dilute rain and runoff. The pH reflects this trend as well with highest pH values (more basic) occurring during lowflow and lower pH values (more acidic) during the influx of acid rain (see Table 3.7, p. 104) and more acidic runoff.

High spring and storm values of Cl^- and Na^+ illustrate that these two ions are derived principally from surficial sources of road salt. As well relatively high lowflow values indicate that the road salt may be lingering in the watershed as soil contaminant along roadways or that other sources such as septic systems may be active.

Thus in Figure 5.1 the solutes display considerable variance amongst the sampling sites and the flow regimes. The effect of the landfill on Site 7 is obvious but the effects of discharge and the city are less obvious. Additional data values in Appendix C further qualify the means plotted above. Standard deviations of spring and stormflow data generally tend to be greater than those for lowflow data showing that variance is large within the data subsets as well. In the following sections, this variance, both within-site and between-site, is addressed and analyzed.

5.3 Temporal Variations: Within-Site Variance

5.3.1 Introduction

As discussed earlier in Chapter II, solutes can be controlled by discharge, seasonal and diurnal cycles in biological nutrient uptake, chemical activity, climate and changing landuse patterns. All of these factors can introduce changes over time in streamwater solute concentrations at a site or in the within-site data. Thus, they generate temporal variations which produce within-site variance of solute concentrations in Chippewa Creek.

In this study, however, little temporal variance is introduced by changing landuse patterns. Over the study period, little change in landuse occurred in the sub-basins behind each of the sites. Thus the between-site variance (analyzed later) is a function of landuse differences from site to site rather than changes within, although strictly speaking there is some variation over time here as well because the sites and their respective sub-basins generate different solute responses for spring, storm and lowflow conditions. Thus in the study of between-site variance the site data are partitioned into flow regimes later.

Within-site solute response is analyzed for two sites--Site 1 (Oak St.) and Site 5 (Airport Rd.). These sites display the solute response of the urbanized and the rural sectors respectively of the Chippewa Watershed (see Chapter III, Section 3.7, p. 113). Urban values used in this section, are the difference scores generated by subtraction of the Airport Road from the Oak Street concentration values, as outlined earlier in Section 5.1.1 (p. 130); therefore, the data analyzed are representative of the actual contribution by the rural and

urbanized sectors of the watershed. As well it is at these two sites that continuous hydrological data is available making it possible to analyze solute variations relative to time-dependent hydrological parameters.

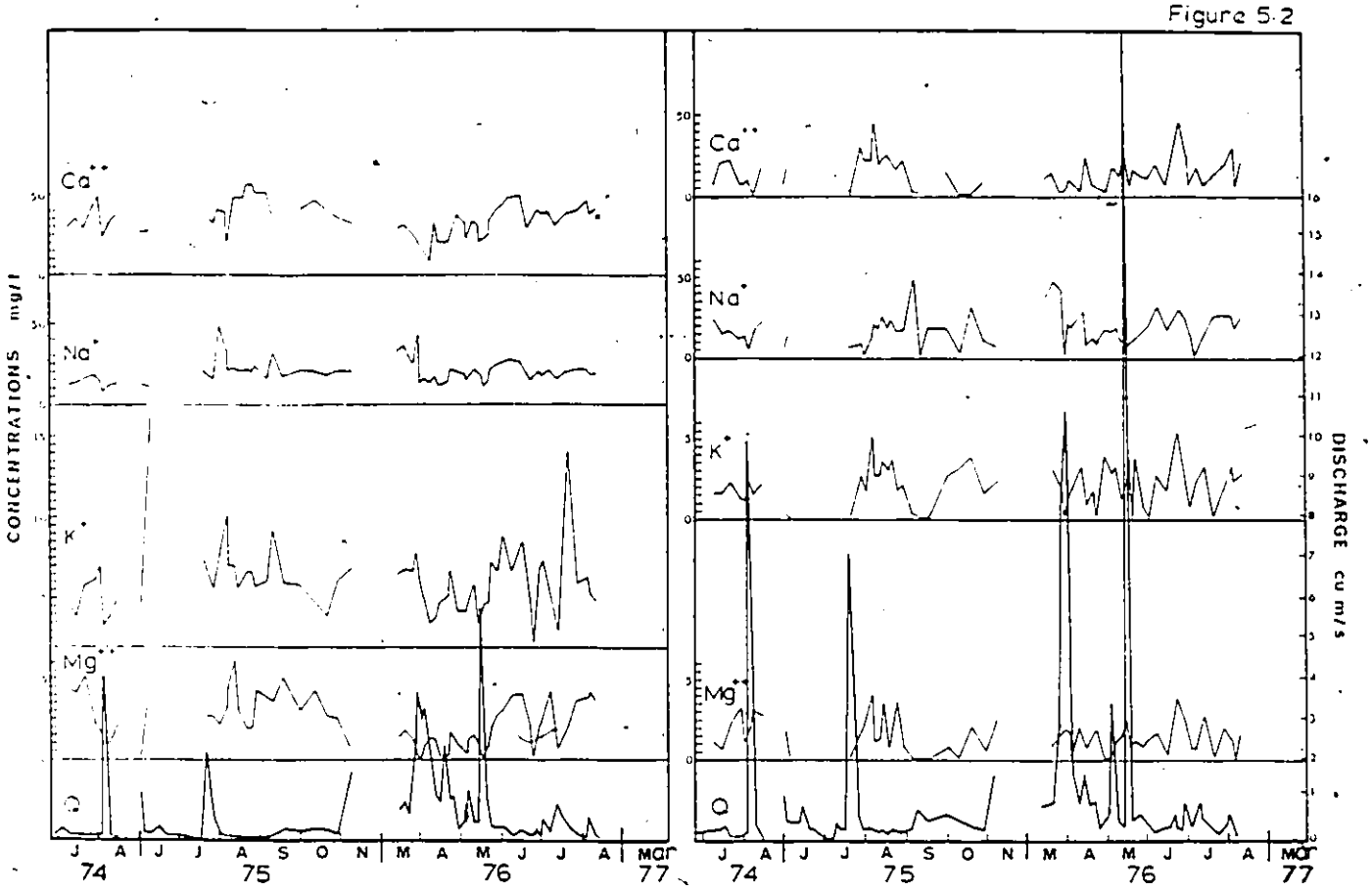
Data are graphed in Figure 5.2 for Oak Street and Airport Road sites over the study period to show the extent and nature of variability of the solute parameters studied. A generalized appraisal (from the plots) of the relative magnitude of the solute parameters between the urban and rural sites and the extents of their variabilities are given below:

Rural values of pH, TDS (total dissolved solids), HCO_3^-, Hd (hardness), Ca^{++}, K^+ and Mg^{++} are all greater in magnitude than urban values. Only Na^+ and Cl^- exhibit greater concentration values for the urban sector of the watershed. The extent of variability is also different in some cases. Calcium, Na^+, Cl^- and pH all display greater variance in the urban setting; whereas, K^+ and HCO_3^- display greater variation in the rural environment. Total dissolved solids and overall hardness appear to have relatively equal variation in both urban and rural environments.

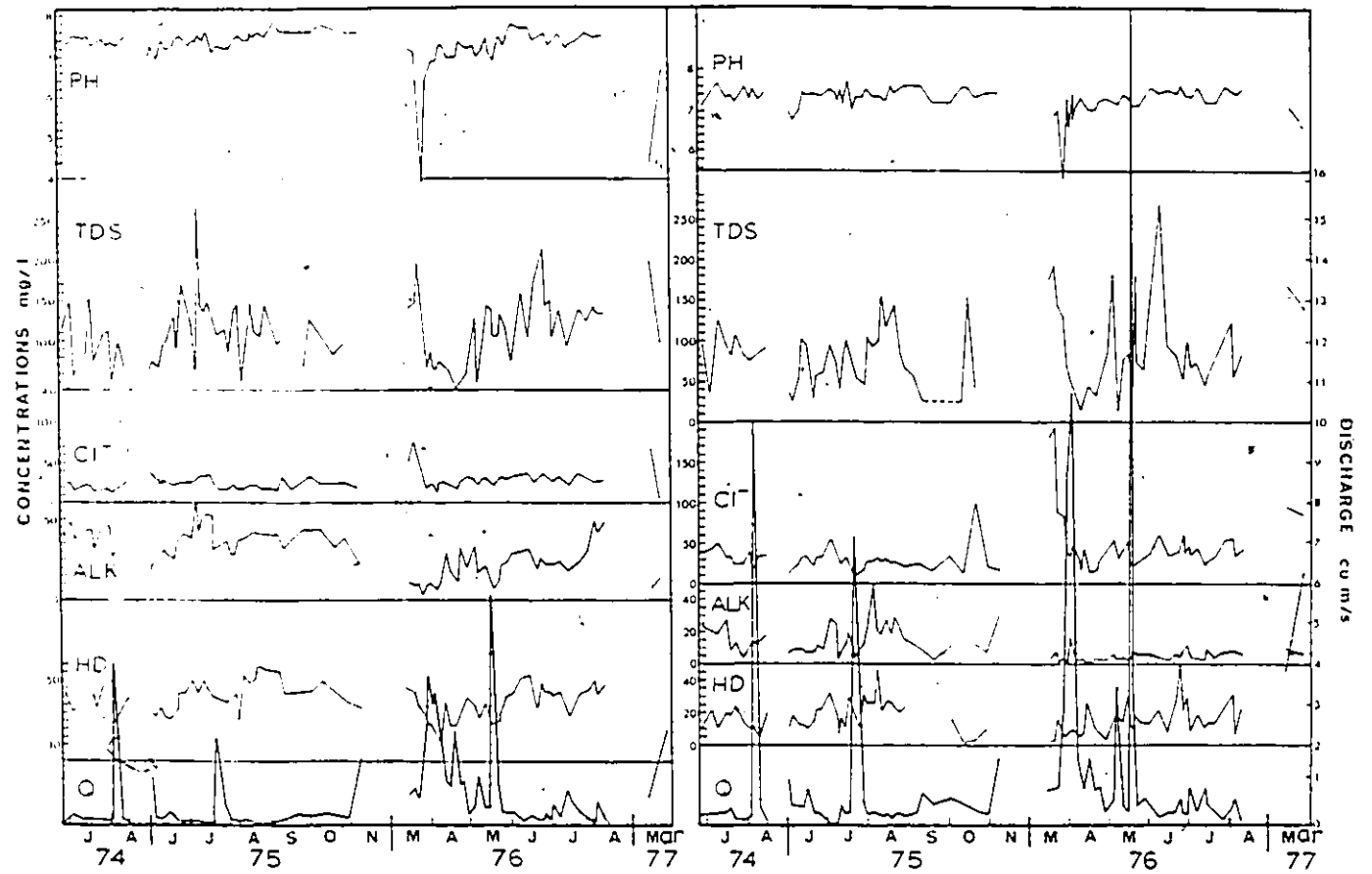
Seasonal trends are also evident but are often difficult to appraise apart from the effects of discharge. Calcium, Mg^{++} and, of course, hardness all tend to build in concentration through the summer months to peak in late September and to drop off in the autumn in the rural setting; however, in the urban setting, values increase in late fall. Magnesium concentrations build over the summer to decline in the autumn

DATA PLOTS FOR URBAN AND RURAL COMPARISON

Figure 5.2



RURAL URBAN



in the rural setting and to decline in September then recover in the urban setting. Sodium concentrations begin very high in the spring and generally decline in the early summer to build slightly in late summer in both urban and rural settings. Chloride concentrations and TDS show a similar pattern. Finally pH displays very low values (acidic conditions) during the spring breakup but recovers to build to more basic levels over the summer, in effect reflecting the buildup of bases such as Ca^{++}, Mg^{++} and K^{+} in the creek waters.

On top of these broad seasonal trends there is apparent variability due to changing discharge. Many of the solute variables show the expected decrease with increasing discharge or dilution effect. In certain cases positive relationships occur but from these plots it is difficult to tell whether these are real or spurious relationships introduced by chemograph lag as described by Walling and Foster (1975).

In summary, a quick perusal of the data plots in Figure 5.2 has revealed extensive variability in solute concentrations at the urban site, Oak Street and the rural site, Airport Road. The response of the solutes to season and discharge events appears to be different for the rural and urban settings in most cases. This fact would suggest that the urban and rural sectors of the Chippewa Watershed are behaving differently with respect to the generation and/or control of solutes delivered to the stream.

5.3.2 Selection of Hydro-Temporal Variables

In order to seek out explanatory relationships for the solute variance, noted within the data in the last section (5.3.1), several hydrological and temporal variables have been selected for use in regression analyses. In Chapter II earlier, the meteorological, hydrological and temporal controls on solute variability have been thoroughly detailed. The selection of explanatory variables must reflect these controls so that environmentally sound interpretations of solute variance can be made. The variables selected are listed and discussed below.

1. Q = discharge per unit area ($l/s/km^2$)
2. QP = magnitude of last peak flow (c.f.s.)
3. TQP = time to last peak flow (hours)
4. TS = time since spring breakup (days)
5. TD = time after 6:00 a.m. (hours)
6. PT = total rainfall in previous 48 hours (mm.)
7. API = antecedent precipitation index (mm.)

Discharge has been shown to be a very important control of solute concentrations in streamflow principally through dilution mechanisms. The effects of Q should be different amongst the flow regimes into which the data has been partitioned principally because source areas are different for spring, stormflow and lowflows. In this case Q has been divided by the area of each sub-basin so that comparisons can be made between the two sites, Oak Street and Airport Road. It is well known that basin area has a major effect on discharge and if comparisons are

to be made between sites the discharge should be area-weighted to remove this effect because area is not at this point going to be used as one of the explanatory variables. Discharge values were determined from flow rating curves (see Section 3.6.2, p. 83) using the stream-gauge record taken with each water sample.

Another effect which creates temporal variance is the flushing or exhaustion of solutes in a watershed which produces chemograph lag and variation in solute magnitudes (Walling and Foster, 1975). Storm events severely alter solute concentrations in streamwaters by flushing and dilution and a recovery period is needed to build the solutes back up to pre-storm levels. This recovery is evident in the storm data discussed later in Section 5.3.3. The exhaustion or the buildup of solutes would necessarily depend on the magnitude of the flushing or diluting action which could be equated to the magnitude of the peak storm flow (QP) and to the time elapsed since the peak flow (TQP). A greater QP should produce larger solute variances through concentration, flushing or dilution of the ions in question. Likewise as time from the last peak flow increases, solute concentrations should also change either due to rebuilding to former levels or diminishing from peak flow levels depending on how they relate to discharge. Values for QP and TQP were extracted for each sample from the continuous stream gauge records collected at Oak Street and Airport Road (see Section 3.6, p. 82).

During winter months the roads within the Chippewa Watershed are well salted with deicing salts containing principally NaCl and a minor amount of $CaCl_2$. When the spring melt occurs, these salts are released

to the ground, soil and surface waters to ultimately find their way into the streams. As time progresses from spring breakup, such salts should decline as the meltwaters, subsequent storm events and groundwater flows flush them from the watershed. Thus behaviour of these and possibly other solutes will likely change as a function of time from the spring breakup because of diminishing supply and delivery rates of solutes and runoff to the streamwaters of Chippewa Creek. As well, other solutes, which have built up in the groundwater flow through the lowflows of winter, will undergo severe dilution in the spring melt and then tend to recover as the watershed dries out. Thus time from spring breakup (TS) should be an important variable in the explanation of solute behaviours over the period studied within all flow regimes. Time from spring (TS) was calculated for each sample by simply cumulating the days from the date of spring breakup (established by observation) to the date recorded when each sample was taken.

Other temporal aspects are introduced by the diurnal changes in watershed processes. Biotic, hydrologic and anthropometric changes occur which control solute variation. The effects of these changes may be examined by relating the time of day of sampling (TD) to the magnitude of solutes at the sites. In this case TD represents the number of hours after 6:00 a.m. and should explain the biologic influence (i.e. photosynthetic effects in streamwaters or biologic uptake of nutrients) and the human influence (human activity begins at about 6:00 a.m. as evidenced by increasing volumes at the city sewage disposal plant). The explanation by TD should be best in lowflow conditions and is likely to

be masked by hydrological effects in stormflow conditions. In spring-flow any diurnal effects will likely be related to solar energy input and the resulting increased discharge provided by meltwaters.

Watershed wetness also influences the delivery and behaviour of solutes to streamwaters. In Chapter II this control has been discussed from the point of view of rock and mineral dissolution, equilibria, dilution, and transport. The measures of watershed wetness chosen here to explain solute variability are total precipitation (rain) in the previous 48 hours (PT) and the antecedent precipitation index API. The variable, PT, not only denotes wetness but to some degree, storm intensities as well. The period, 48 hours, was chosen to mirror both the duration of storm periods and the approximate time after which the stream begins to experience the throughflow effects as determined earlier in Section 3.6.2 (p. 83). The value of PT was determined for each sample from traces taken from the precipitation recorder at the weather office of the M.O.T. at the North Bay airport.

The API has been derived for each sample beginning at April 1 of each sampling year by use of the method outlined in Dunne and Leopold (1978, p. 366). A decay function is employed to estimate the API or soil wetness index for each successive day. The function is as below.

$$I_t = I_o K^t \qquad 5.1$$

where I_t is the API on day in question

I_o is the API in day 1

t is the time in days since the last rainfall

K is the average rate of soil water reduction

April 1 is chosen as a start date for the function because by this date soils are becoming unfrozen and infiltrating meltwaters are saturating the soil horizons. Thus decay begins from a saturated or nearly saturated watershed condition. An initial API was determined by selecting a field capacity of 0.13 for the soil of the watershed by using an average soil depth of 8.20 m., determined from field study and well records of the watershed (M.O.E., North Bay) and by selecting an average decay rate of 0.90 from Dunne and Leopold (1978, p. 366). Rainfalls were then taken from precipitation records and added into the API in the appropriate manner as the API was developed over the study period.

To some extent the above variables are measuring similar controlling influences on solute variability. For example, discharge (Q) will relate to solute concentration but will likely be related to many of the other independent variables such as TS, PT, and API. As TS gets larger, Q will get smaller especially during the springflow period. If PT is a large value then both Q and API must also show increases. When these variables are used to explain solute variation in a multivariate model, they introduce multicollinearity (as seen later in Section 5.3.3, p. 152); in that, because of their common variance, they will explain similar variance in the solute parameters. Thus the common variance of the temporal variables has been investigated using a factor analysis technique.

Factor analysis has been used extensively in geological and geographical research (for example, see Kloven, 1966; Harbaugh and Merriam, 1968; Yeates, 1974; and Johnston, 1980) and several authors have used

the technique to sort out the interdependence of explanatory variables for regression analyses of watershed relationships (for example, Pionke and Nicks, 1970). Principally the procedure organizes or groups a series of variables on the basis of their common variance. Input to the process is the correlation coefficient matrix of the variables in question. Even though it is possible to determine the interrelationships of the variables from this matrix, there is some difficulty in detecting common variance when large numbers of variables are involved. Thus factor analysis is able to expedite the search for common variance within the group of variables under study.

In this study an R-mode factor analysis was run on the hydro-temporal variables for each of the flow regimes on both Oak Street and Airport Road values. Factor loadings were determined for factors having eigenvalues greater than 1.0. The results are given in Table 5.1. It is apparent from the factor loadings of the variables on the factors across the two sites during different flow regimes that the variables behave somewhat differently under different spatial and hydrological conditions. Interrelationships (defined by high factor loadings on the same factor) amongst the variables are present but are not always consistent in magnitude or direction from flow to flow or site to site.

The grouping of the variables by factor analysis can have environmental significance or can occur due to chance statistical correlations. Thus it is often difficult to interpret the physical meaning of each of the factors identified. In this study the technique has been used primarily to identify intercorrelated temporal variables for use

TABLE 5.1

SUMMARY OF FACTOR LOADINGS ON HYDRO-TEMPORAL VARIABLES

FLOW	RURAL (AIRPORT RD.)	URBAN (OAK ST.)
SPRING FLOWS	INSUFFICIENT DATA ON ALL VARIABLES	FACTOR 1 (Discharge) / FACTOR 2 (Time?) Q .93408 / .33366 QP -.44427 / -.35510 TQP -.08091 / .92007 TS -.84534 / .44988 TD -.06197 / -.82311 PT .96626 / .13637 API .95471 / -.24228 % Var. explained = 81.2
STORM FLOWS	FACTOR 1 (Discharge) / FACTOR 2 (Storm Magnitude) Q .84940 / .32407 QP .04790 / .84336 TQP -.69486 / .29324 TS .10976 / -.80277 TD -.05804 / -.62842 PT .97199 / .03109 API .62293 / .70195 % Var. explained = 71.3	FACTOR 1 (Discharge) / FACTOR 2 (Time?) / FACTOR 3 (Watershed wetness) / FACTOR 4 (Storm Magnitude) Q .88224 / -.13327 / .15950 / -.19443 QP -.00991 / -.09104 / .12542 / .95126 TQP -.14632 / -.86741 / .22978 / -.15665 TS -.00995 / .21275 / -.91909 / .01508 TD -.09271 / .86194 / .13805 / -.35792 PT .90807 / .19668 / .07378 / .20208 API .39212 / .19619 / .78481 / .27029 % Var. explained = 88.8
LOW FLOWS	FACTOR 1 (Discharge) / FACTOR 2 (Rainfall Timing?) / FACTOR 3 (Time from Spring) Q .93277 / .10880 / -.05666 QP .80070 / -.00283 / -.45795 TQP -.52727 / -.54894 / .07419 TS -.06867 / -.06442 / .97414 TD -.08829 / .83588 / -.01135 PT -.05070 / .93412 / -.06013 API .84273 / -.33682 / .14228 % Var. explained = 81.5	FACTOR 1 (Discharge from Groundwater) / FACTOR 2 (Discharge from Minor Rainfall) / FACTOR 3 (Time from Spring) Q .50263 / .60216 / .43308 QP .89954 / .10830 / -.05101 TQP -.17846 / -.65413 / .02765 TS -.13413 / -.05921 / .91287 TD -.18131 / .77351 / -.32451 PT -.31250 / .65103 / .21569 API .85975 / -.20369 / -.09742 % Var. explained = 71.9

in the interpretation of regressions later. However some obvious relationships exist and are mentioned below.

In springflow conditions Factor 1 is obviously discharge-related. During the spring melt PT and API would relate highly to discharge under saturated watershed conditions. As spring passes, however, the influences of PT and API become less as evidenced by the negative loading of TS. Factor 2 is not so easily interpreted but seems somehow related to time.

For stormflow at Airport Road, two factors have again been extracted. Factor 1 still displays a discharge function but now API is less influential and PT more influential suggesting that during storm events discharge values are primarily a function of the magnitude of the rainfall event rather than API (watershed wetness) which contributes groundwater flow. This discharge interpretation is strengthened by the negative loading of TQP suggesting that discharge diminishes as time from peak Q increases. Factor 2 appears to define storm magnitude. Apart from a high, positive loading on QP, other loadings suggest a similar interpretation. A high, negative TS loading denotes smaller peak flows as time from spring increases and a positive loading for API suggests that larger peak flows occur with a wetter watershed. Both seem congruous with expected relationships in a "real-world" situation. TD is not easily explained and may be another chance correlation.

For stormflow data at Oak Street, four factors are defined by the temporal variables. Factor 1 again appears to be discharge-related having high loadings from Q and PT. Interestingly, API has a very low loading on Factor 1 suggesting that groundwater flow in the city has

less influence on stream discharge. Factor 2 defines a time function which is again difficult to interpret. Factor 3 could represent a groundwater or soil water contribution factor with a high positive loading by API and a large negative loading from TS which indicates a drying out of the watershed as summer progresses. Finally Factor 4 represents a storm magnitude factor.

In lowflow conditions at Airport Road, Factor 1 again strongly denotes discharge. During lowflow, groundwater becomes the source sustaining streamflow and thus QP and API become important for their magnitudes will govern the volumes of baseflow. The greater the QP of the last storm, the greater will be the API, the elevation of the water table, and the resulting Q. Factor 2 takes on some sort of time connotation once again with high loadings from TQP and TD. Included in this case, however, is PT which might suggest some relationship between time of day and rainfall events. In any event the physical meaning of the relationship is not readily apparent and it may be once again a chance correlation introduced by the sampling schedule. Factor 3 is isolated and defined by TS alone. Thus TS is independent from discharge and event timing as defined by Factors 1 and 2.

Finally, in lowflow conditions within the city, three factors are isolated. Factor 1 appears to represent discharge, fed primarily by ground and soil water. Factor 2 also appears related to discharge but may be discharge resulting from minor rainfall events, large enough to increase Q but too small to drive the gauge levels beyond the lowflow cutoff level discussed earlier in Section 5.1.1 (p. 130). Factor 3 is again defined by TS.

In summary then, a factor analysis of the temporal variables has isolated from two to four groups of variables for the two sites and three flow regimes. Each group defining a factor in most cases appears to have physical or environmental meaning in light of actual hydrological conditions expected during each of the flow regimes at the rural and urban sampling sites. Factors have been labelled according to the environmental relationships between variables which define the factors. Discharge appears to be the dominant factor in all conditions, while storm magnitude, watershed wetness, time from spring factors and a possible event timing factor all contribute under one condition or another.

Also it is apparent that several of the variables are interrelated for various conditions of flow at Oak Street and Airport Road. In effect these variables are describing the same hydrological conditions and use will be made of this information later in this chapter.

5.3.3 Results

For all three flow regimes the values of solute concentrations and the hydro-temporal variables for the samples of streamwater were entered into bivariate regressions in order to determine if the hydrological and temporal watershed processes could be related to solute variance. Only the best fit relationships, statistically significant at the .05 level, are reported and analyzed. Results of these regressions are listed in Table D1 of Appendix D. It is apparent from studying this table that there are complex relationships amongst the solutes and the hydrological and temporal variables. Several types of mathematical

functions are needed to describe all of the relationships. They are listed below.

1.	Linear:	$C = a + bV$	5.2
2.	Reciprocal:	$C = a + bV^{-1}$	5.3
3.	Power:	$C = aV^{b}$	5.4
4.	Logarithmic:	$C = a + b\log V$	5.5

where C is the concentration or value of the solute parameter

V is the hydro-temporal variable

a is the regression intercept (i.e. the value of C for V = 0)

b is the slope of the regression

Relationships defined by Equations 5.3, 5.4 and 5.5 above indicate complex changing rates of variation of the solute parameters. These complex relationships are entirely expected. For example, often solutes are diluted or concentrated very rapidly with increasing discharge, then because of the changing character of supply and delivery or some other control, concentrations stabilize to minima or maxima even though discharge continues to build. Such relationships are parabolic or hyperbolic in configuration and hence must be described by functions other than linear. In addition, the relationships vary over the different flow regimes sampled and they also vary over the two sampling sites at Airport Road and Oak Street. Thus it appears that both within-site (hydro-temporal) variance and between-site (spatial) variance exist in the data.

Within-site solute variance results from the changing hydrologic regimes and the changing watershed supply and delivery of solutes at the sites with the passage of time. The between-site variance is

reflected in the difference in direction and magnitude of solute relationships with the hydro-temporal variables between the Oak Street (urban) and the Airport Road (rural) sites. Often the variance of individual ions or solute parameters is explained by several of the hydrological and temporal variables. At first glance this fact suggests very complex multivariate explanation of the solute variation. However, the total of the R^2 values for these hydro-temporal variables for a given ion is often greater than 1.0 (or 100 per cent explanation). Obviously, there is common variance amongst the hydro-temporal or predictor variables so that they are to some extent explaining similar variance in the solute parameter. The factor analysis of Section 5.3.2 (p. 143) uncovered this common variance within the predictor variables and it is confirmed here by the R^2 values of the bivariate relationships of Table D1. Thus, where several variables are involved in similar explanation of a solute parameter, a stepwise multiple regression has been used to sort out the best explanatory relationships.

In stepwise multiple regression each independent variable is entered into the regression separately, and both its contribution to the dependent and its common variance to the other predictors assessed (Johnston, 1978). If the independent variable is significantly related to the dependent (i.e. the statistic for the regression coefficient for the null hypothesis is significant at the .05 level) then it remains in the equation. Ultimately a multivariate equation is generated containing only significant predictors of solute variance. Results of the stepwise regressions are presented in Tables 5.2, 5.4, and 5.6 in the following sections. These results are discussed in turn in the following pages.

5.3.4 Springflow Relationships

Springflow stepwise regression relationships for the solute parameters investigated in this study are listed in Table 5.2 below. The degree of explanation by the significant hydro-temporal variables is generally low for both the rural and urban settings suggesting that either additional within-site controls are operating or that stochastic events take place to randomize solute variance to some extent. In Figure 5.2 (p. 141) certain short period fluctuations in solute concentrations are evident and would reduce the linearity of the trends of solute concentrations. Initial flushing of solutes in the early spring runoff is one such perturbation which introduces additional variance into the trends of concentration of several solutes. These situations are discussed in turn later. Nevertheless, a portion of the variance in the solute parameters is explained by the variation in one of TS or Q. Both of these variables have been identified as contributing to a discharge-related factor in the factor analysis of springflow data for Oak Street discussed earlier. Thus it would seem that discharge or some expression of discharge is the major control on springflow solutes and solute parameters.

The direction and magnitudes of the relationships differ between solutes and between sites suggesting variable behaviours of the solutes in the hydrological environment of springflow in the rural and urban settings. In order to get a better appreciation of the orders of magnitudes and intensitites of change between similar solute parameters at the two sites, sample calculations have been done for selected intervals

TABLE 5.2

SUMMARY OF SPRINGFLOW RELATIONSHIPS WITH HYDRO-TEMPORAL VARIABLES

DEPENDENT VARIABLE	RURAL (AIRPORT RD.)			URBAN (OAK ST.)		
	EQUATIONS	SIG.	R^2	EQUATIONS	SIG.	R^2
pH	$pH = 5.94 + 0.043\ TS$	*	0.19	$pH = 7.32 - 4.78\ TS^{-1}$	*	0.15
TDS	$TDS = 203.36 - 104.18\ \log TS$	***	0.66	$TDS = 19.36 + 663.33\ TS^{-1}$	**	0.54
Cl^-	$CL = 21.54 + 47.98\ TS^{-1}$	***	0.56	$CL = 11.50 + 401.66\ TS^{-1}$	***	0.63
Na^+	$NA = 35.51 - 13.07\ \log TS$	*	0.28	$NA = 13.15 + 1035.45\ Q^{-1}$	*	0.22
K^+	$K = 7.12 - 1.71\ \log TS$	*	0.18	$K = 1.00 + 79.16\ Q^{-1}$	*	0.31
HCO_3^-	$ALK = 5.98 + 0.48\ TS$	**	0.40	$ALK = -0.48 + 0.02\ Q$	*	0.19
Hd	$HD = 19.08 + 289.57\ Q^{-1}$	*	0.43	-	-	-
Ca^{++}	$CA = 18.36 + 280.51\ Q^{-1}$	*	0.39	-	-	-
Mg^{++}	-	-	-	$MG = 1.45 - 0.001\ Q$	*	0.38

* significant to .05 ** significant to .01 *** significant to .001

on the curves described by the regression relationships. Springflow calculations are presented in Table 5.3 below.

Where urban and rural solute variances are explained by a similar hydro-temporal variable, direct comparisons can be made between the sites at the low and high ranges of the relationship for solute concentration magnitudes and the rates of change (slope) by selecting low and high values of the explanatory variable. However, when two different hydro-temporal variables explain the variance in a given solute parameter at the rural and urban sites (for example, HCO_3^-, Na^+, and K^+ in Table 5.2), the choice of intervals for comparison is more difficult to make. Low and high values for the two explanatory variables must be selected in a rational way according to how they relate within the hydrological regime and within the original data. For example, in Table 5.2, Na^+ relates to TS in the rural sub-basin and to Q in the urban sub-basin. These explanatory variables have different units and therefore their regression intercepts and slopes will not be directly comparable. Thus it is necessary to sample the slopes of both the relationships for high and low values of TS and Q. However to be able to compare rural to urban, the values of TS and Q selected must somehow relate to each other in a rational way. The procedure followed is explained below.

In Table 5.3, the rural relationship is analyzed for a short interval close to the beginning of spring and for one near the end of spring. The original data is used to estimate two corresponding intervals of Q for the urban setting during these two intervals of

TABLE 5.3

COMPARISON OF MAGNITUDES OF RURAL-URBAN RELATIONSHIPS--SPRINGFLOW

SOLUTE PARAMETER	RURAL (AIRPORT RD.) VALUE INDEP. VAR.	VALUE DEP. VAR.	SLOPE	URBAN (OAK ST.) VALUE INDEP. VAR.	VALUE DEP. VAR.	SLOPE	DIFFERENTIAL
pH	TS = 3.0	6.07		TS = 3.0	5.73		
	TS = 3.3	6.08	+0.03	TS = 3.3	5.87	+0.47	U = 15.7R
	TS = 37.0	7.53		TS = 37.0	7.19		
	TS = 40.7	7.69	+0.04	TS = 40.7	7.20	+0.03	R = 1:30
TDS	TS = 3.0	153.65		TS = 3.0	240.47		
	TS = 3.3	149.34	-14.37	TS = 3.3	220.37	-20.10	U = 1.4R
	TS = 37.0	39.98		TS = 37.0	37.29		
	TS = 40.7	35.67	-1.16	TS = 40.7	35.66	-1.63	U = 1.4R
Cl^-	TS = 3.0	37.53		TS = 3.0	145.39		
	TS = 3.3	36.08	-4.83	TS = 3.3	133.22	-40.57	U = 8.4R
	TS = 37.0	22.84		TS = 37.0	22.36		
	TS = 40.7	22.72	-0.03	TS = 40.7	21.37	-0.27	U = 9.0R
Na^+	TS = 3.0	29.27		Q = 770.0	14.49		
	TS = 3.3	28.73	-1.80	Q = 700.0	14.65	-0.20×10^{-2}	R = 900.0U
	TS = 37.0	15.01		Q = 28.6	49.35		
	TS = 40.7	14.47	-0.15	Q = 26.0	52.98	-1.40	U = 9.3R
K^+	TS = 3.0	6.30		Q = 700.0	1.11		
	TS = 3.3	6.23	-0.23	Q = 770.0	1.10	-0.01×10^{-2}	R = 2300.0
	TS = 37.0	4.44		Q = 26.0	4.04		
	TS = 40.7	4.37	-0.02	Q = 28.6	3.77	-0.10	U = 5.0R
HCO_3^-	TS = 3.0	7.42		Q = 770.0	14.92		
	TS = 3.3	7.56	+0.47	Q = 700.0	13.52	+.02	R = 23.5U
	TS = 37.0	23.74		Q = 28.6	0.09		
	TS = 40.7	25.52	+0.48	Q = 26.0	0.04	+.02	R = 24.0U
HO^-	Q = 140.0	21.05					
	Q = 154.0	20.96	-0.01				
	Q = 15.0	38.38					
	Q = 16.5	36.36	-1.53				
Ca^{++}	Q = 140.0	20.36					
	Q = 154.0	20.18	-0.01				
	Q = 15.0	37.06					
	Q = 16.5	35.36	-0.70				
Mg^{++}				Q = 700.0	0.75		
				Q = 770.0	0.66	-0.10×10^{-2}	
				Q = 26.0	1.42		
				Q = 28.6	1.42	-0.10×10^{-2}	

springflow. In this way TS and Q are related, in that, early spring and late spring values of Q are selected for Oak Street to match the early and late spring values for TS. The two variables are now linked in time. Thus for the interval TS = 3.0 to 3.3 for the rural site, the corresponding Q interval for the urban site is 700.0 to 770.0 and for TS = 37.0 to 40.7, Q is 26.0 to 28.6 which is a reasonable selection because Q must decline as spring progresses. Therefore, urban values of Q have been chosen from the original data in a way which makes hydrological and temporal sense vis a vis the progression of events and processes in the watershed. To allow comparisons, these intervals have been standardized by generating a ten per cent increase or decline about the magnitudes selected for each of the variables for both early and late spring at the two sites. Then slope values (difference in solute value divided by difference in hydro-temporal value) are calculated for these ten per cent intervals selected at the extremeties of the relationships. For example, for rural Na^+ in Table 5.3, the slope for the low interval of TS is -1.80 and it is calculated by dividing the difference in the dependent or Na^+ values (i.e. 29.27 - 28.73 = 0.54) by the difference in the independent or explanatory variable TS (i.e. 3.3 - 3.0 = 0.3). The result is the slope value, -1.80, (i.e. 0.54 ÷ 0.3 = 1.80) for this interval in the relationship.

These slope values indicate the steepness of the regression relationships in the selected intervals and because they are non-dimensional and occur over standardized intervals related in time,

they can be compared for the two explanatory variables at the Oak Street and Airport Road sites. These slope values express the rate of change in the solute variables over the intervals chosen and thus in effect they describe the intensity of the process causing the change under differing hydro-temporal conditions. Thus the magnitude of the concentration values as well as the rates of change within various selected intervals in the relationships can be compared for the rural and urban sub-basins. Using the rural Na^+ example from Table 5.3 again, it can be seen that the rural flushing of Na^+ is much greater than the urban rate of increase in Na^+ during early spring by a factor of 900x. However, the absolute accuracy of the values of the solute parameter and the differentials generated will be relected by the R^2 values. Where a good fit and accurate relationship exists, R^2 values will approach 1.0 in value. Under this condition predicted values will approach real values in the watershed and magnitudes of differentials become significant. To minimize inaccuracies in predicted solute values from relationships of low explanation, values for the independent variables were selected within the range of data used to create the regression relationships.

In spring the principal sources of discharge are from spring melt of snow and ice in the watershed. The behaviour of solutes carried to the stream will be determined by these large volumes of water of low pH (Jeffries et al., 1979). Surficial sources of solutes from deicing salts, from the snowpack and from the leaf litter of the previous autumn should be operative. Solute from these sources should

exhibit the flushing and exhaustion trends discussed earlier in Chapter II. On the other hand, solutes which are primarily generated in the soils and rocks and transported to the stream via ground or soil water, will exhibit typical dilution behaviour. As well, pH values will reflect these trends, being very low in early spring meltwaters but increasing towards basic values as meltwaters recede and subsurface waters become more important in supplying discharge. In light of these expectations, the springflow relationships are analyzed below, using the information in Table 5.2 and Table 5.3.

(a) Total Dissolved Solids and Chloride

Total dissolved solids (TDS) and Cl^- exhibit behaviour consistent with a flushing response in both the rural and urban sub-basins. From initial, high concentrations they decline as spring progresses due to exhaustion of surface supplies. Chloride values indicate that this ion is quantitatively the most abundant in early spring and makes up a large portion of the TDS. As expected urban Cl^- values are greater than rural, confirming the source of this ion as being deicing salts. However, in late spring the concentrations of both Cl^- and TDS approach equality for the urban and rural sub-basins. Chloride values are still relatively high even at the end of spring suggesting that this ion also is present in baseflow, a reasonable conclusion in light of reports by other authors that 25 to 50 per cent of deicing salts applied to roads eventually find their way into soil horizons (McConnell and Lewis, 1972).

Flush rates for both TDS and Cl^- are very high in early spring indicating quick removal of solutes, especially Cl^-. By late spring the rates of removal in both rural and urban settings have diminished by about 12.5 times (i.e. comparing slopes from Table 5.3, 14.37 + 1.16 = 12.50) for TDS and 150 to 160 times for Cl^-. Thus by the late spring, TDS and Cl^- concentrations are stabilizing, likely because of the increasing influence of soil and groundwaters as a source of streamflow and due to the exhaustion of surface salt supply and spring runoff. Urban flush rates (slopes in the ten per cent intervals) are greater for both TDS and Cl^- in both early and late springflow. TDS are flushed from the urban watershed at a rate 1.4 times greater than the rural rate and Cl^- is removed from the city at a rate 8.4 to 9.0 times greater than the rural rate. These trends are reasonable in view of the greater magnitude and rates of runoff produced from the largely impervious urban surface as seen in the example storms discussed earlier in Section 3.6.2 (p. 83). The intensity of process, in this case the flushing of surficial salts, is greater in the urban setting and reflects in the slopes of the regression relationships.

(b) Sodium and Potassium

Sodium and K^+ also exhibit negative relationships with their explanatory variables in the rural data which can be explained by a flushing response in the rural environment. The solute variance explained by the regression in each case is not great, likely in part due to the extreme dilution and slight recovery which occurs in the first meltwaters (see Figure 5.2, p. 141). From large concentrations

in springflow, rural Na^+ and K^+ diminish to lower values in late spring. Rural flush rates diminish from early to late spring by about twelve times for both Na^+ and K^+. In early spring, meltwaters could produce the observed response in K^+. Potassium has been shown to peak from leaf litter during spring melt in studies by Gosz et al. (1973) and such a response is seen here in Figure 5.2D. From this peak, K^+ values decline as supply becomes exhausted and dilution becomes dominant. In the urban setting these two ions show reverse trends to those in the rural setting. They are both inversely related to Q and show an increase as Q decreases over the spring melt. This behaviour suggests that sources other than those directly connected with spring runoff are involved. Urban Na^+ experiences a slight first-flush effect (see Figure 5.2 again) then experiences a degree of dilution in early spring and an increase in concentration as the spring passes and values of Q become lower. This behaviour is very suggestive of a subsurface source for Na^+ within the city. Potassium levels in the soils of the urban sector (see Table B1, Appendix B) are well within the magnitudes found in the streamwaters and may be the principal source of K^+ in the urban streamwaters during springflow. The lack of a distinct peak in early spring seems to support this source rather than a flushing of the leaf litter. However, it is possible that the peak occurred earlier than the first sample date in the sporadic melt-freeze cycles which occur in the city prior to the major spring runoff. Also K^+ levels in the urban soils appear to be highest in the A horizons (see Table B1 again) and one would expect a flushing of these horizons in early spring.

Possibly the large runoff volumes from impervious areas tend to mask out the flushing of K^+ from the litter and upper soil horizons.

Sodium levels are generally low in the city soils but at the sample sites close to human activity they exhibit relatively large values even in the autumn when the soil sampling was undertaken (see Table B1, Appendix B, Sites 3 and 4). Thus it is also probable that road salts infiltrating the urban soil horizons could readily be a source of Na^+ during wet, spring conditions.

The increase in the rate of recovery in urban Na^+ concentrations is a phenomenal 700 times from early to late spring; whereas, for K^+, it is 50 times. Thus in late spring urban Na^+ and K^+ levels increase dramatically as the watershed dries out. These late spring rates of increase in both Na^+ and K^+ are greater in the city (by 9.3 and 5.0 times respectively) but during early spring, rural rates of decrease are greater (by 900 and 2300 times respectively) again emphasizing the divergent behaviours of these two solutes in the rural and urban environments.

(c) Magnesium

Magnesium displays a negative, linear relationship to Q in the urban setting and exhibits a buildup over spring similar to Na^+ and K^+ as discussed above. However in this case Mg^{++} increases at a constant rate. The relationship is apparently weakened (low R^2) as well by the first-flush phenomena so that in early spring Mg^{++} values rise with increasing Q for a short period then display a negative relationship to Q (see Figure 5.2D, p. 141). No significant relationships

exist in the rural setting, although from Figure 5.2D it appears that the Mg^{++} concentrations in the rural sub-basin also respond in a negative fashion to Q. As argued above for Na^{+} and K^{+}, this behaviour of Mg^{++} suggests a source other than spring meltwaters for this ion, possibly from ground or soil waters, sources discussed more fully later. Because highest values of Mg^{++} occur in the A horizon of the soils in the watershed (see Table B1, Appendix B), it is likely that Mg^{++} suffers the same fate as K^{+} above. However, in the rural data this effect is difficult to explain because snowmelt should flush the litter and produce rising Mg^{++} values instead of the dilution pattern seen in Figure 5.2C (p. 141).

(d) Calcium and Hardness

Calcium and therefore hardness (Hd) values display negative relationships with Q as well but only for the rural data. From relatively high concentrations in winter months (see Table 3.9, p. 107), these two parameters drop dramatically in the initial springmelt and then recover as time passes. An apparent lag between peak flow and maximum dilution (see Figure 5.2A) again tends to reduce the degree of explanation by discharge. However, the relationships for the rural data are significant and strongly suggest that Ca^{++} and Hd are derived principally from ground and soil water sources. Large winter and low-flow summer values (discussed later) tend to confirm this conclusion. Rates of increase are minimal in early spring but by late spring, they are 135 times greater for Hd and 70 times greater for Ca^{++}. No significant relationships exist for the urban data but from Figure 5.2B

and 5.2D, it is apparent that these two parameters behave in a complex fashion in the spring period. Hardness rises with increasing Q in early spring, apparently due to an increase in Mg^{++} (since Ca^{++} declines), then displays classical dilution, after which it again assumes a positive relationship to Q. Calcium reacts in a similar complex fashion but does not build up in concentration during initial flood.

(e) pH

Streamwater acidity tends to reflect these relationships in Hd and Ca^{++}. The values of pH are positively related to TS for both rural and urban settings, which is to say, as spring progresses and runoff recedes, pH trends to more basic values. The complexity of the "first flush" is also seen in pH (in Figure 5.2, p. 141) and as a result explanation by the relationships in Table 5.2 are also low. With the first of the spring runoff, a rapid depression of pH occurs at both sites. The depression is lowest at the rural site, even though normally the pH values tend to be higher (more basic) in the rural setting. This depression is consistent with the results of Jeffries et al. (1979) where it was found that the first 30 per cent of meltwaters from snow packs in Central Ontario (Muskoka Region) contained 70 to 80 per cent of H^+, SO_4^{--}, and NO_3^- ions held in the snow and about 36 to 77 per cent of the yearly export of H^+ from watersheds occurred in April. The urban setting again displays the most rapid recovery to more basic values with a return rate of 15.7 times the rural value for early spring, indicating a faster release and runoff of acidic snowmelt waters in the urban setting. As spring progresses

and runoff declines, ground and soil waters become quantitatively more important in supplying streamflow and pH rises in sympathy with the increasing concentrations of Ca^{++}, Mg^{++} and HCO_3^-.

(f) Alkalinity

Alkalinity (HCO_3^-) also reflects the behaviour of pH and the bases Ca^{++} and Mg^{++} in the rural setting, exhibiting a linear increase as spring progresses and discharges diminish. However, this relationship only applies for the rural data. The urban HCO_3^- behaves in an opposite fashion declining linearly towards the end of springflow. The reason for this decline is not readily apparent because the cations which usually combine with HCO_3^- are seen to increase with the passage of spring in the urban sub-basin. Bicarbonate alkalinity (HCO_3^-) is provided to streamflow primarily from ground and soil waters (Freeze and Cherry, 1979). Thus the decline of HCO_3^- in late spring suggests a surficial source for this ion, or a low rate of soil weathering beneath the city and the presence of another anion (SO_4^{--}) to balance the increased cation concentrations. In addition, pH values in the urban sub-basin are generally lower than the rural so that the HCO_3^- may be expended in buffering urban discharge.

(g) Springflow Hydro-Temporal Variance: A Summary

In summation, during the springflow period, the magnitudes and responses of the solute parameters studied show definite differences in variance over the spring period within and between the two sites, Oak Street and Airport Road. In terms of magnitudes, Cl^- and Na^+

dominate in the urban setting; whereas, Ca^{++}, Mg^{++}, HCO_3^- and K^+ dominate in the rural setting. The variations of these ions over the springflow period appears to be in response to the flushing and diluting action of spring runoff. Where solutes are derived from surface sources (i.e. Cl^-, Na^+, K^+) the magnitude of their response to flushing is greatest in early spring and least in late spring. Conversely, solutes derived from subsurface sources (Ca^{++}, Mg^{++}, HCO_3^-) exhibit maximum dilution in early spring. Exceptions to these general relationships occur in the urban setting for Na^+, K^+ and HCO_3^-, which exhibit responses reversed from those in the rural setting.

The strength of the explanations by the hydro-temporal variables, Q and TS, is overall relatively low indicating other possible variables involved or other sources of variation. Explanations are marginally better in the rural data suggesting more controlled and orderly solute responses than those in the urban setting. The low degree explanation may be related to the dramatic "first flush" of many of the solutes with the initial dilute meltwaters of the spring thaw and the resultant chemograph lags. Certainly this lack of symmetry between peaks and troughs of hydrological and solute responses to springflow conditions, introduces problems to the explanation of solute response by hydrological variables.

Major differences occur in both the magnitudes and behaviour of ions between the rural and urban sub-basins. Concentrations of Cl^- and TDS are generally larger for the urban environment and intensities of process are greater in the urban setting especially for ions exhibiting flushing behaviour in early spring. However, Na^+ and K^+ are again

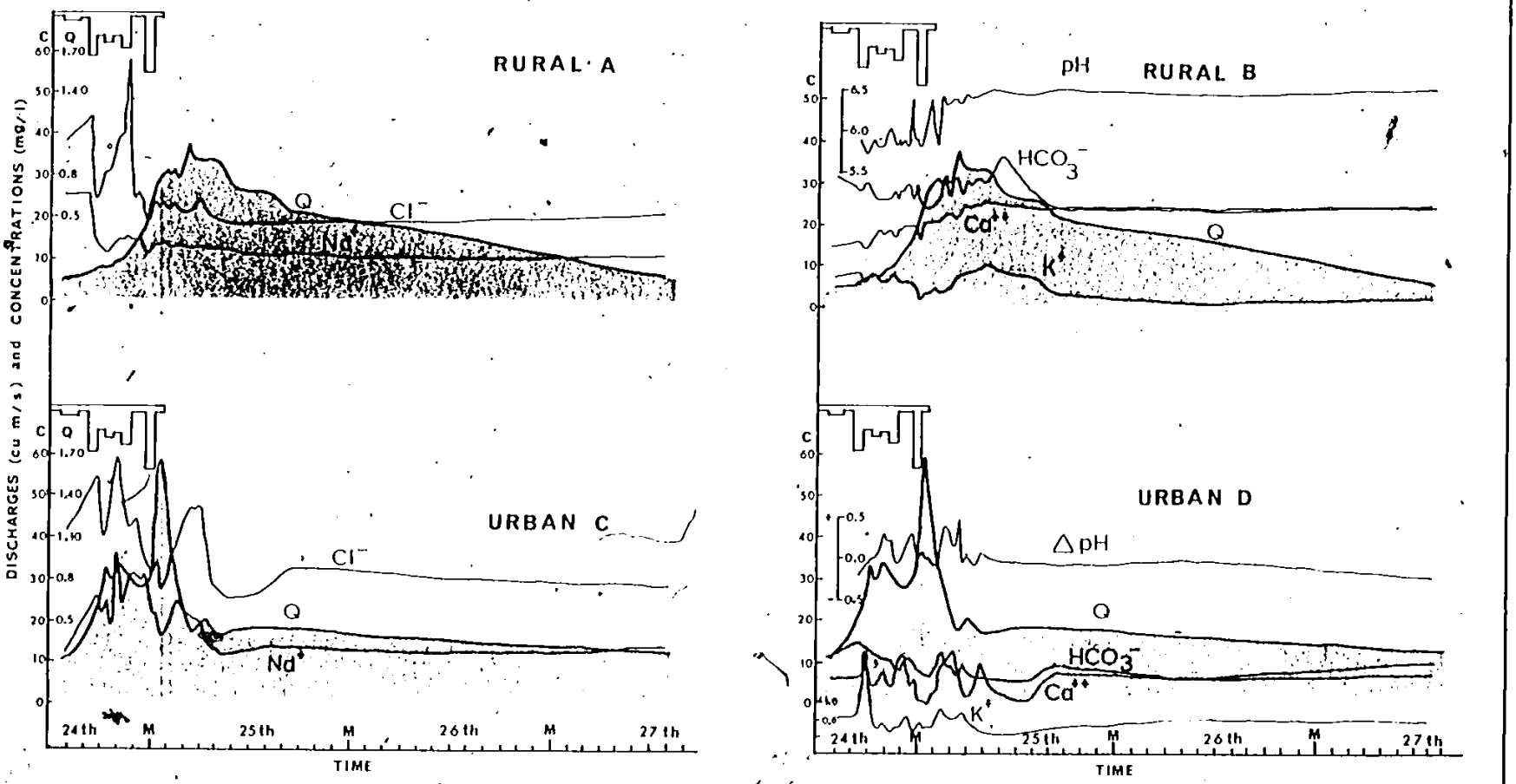
exceptions in the early spring. Ions diluted in early spring (HCO_3^-, urban K^+ and urban Na^+) all show greater magnitudes of dilution in the rural sub-basin. Thus, based on an analysis of the variance within the springflow data at Oak Street and at Airport Road, there are apparent differences in the magnitudes of solute concentrations, and the strength of their responses to hydrologic controls both over the springflow period and between the urban and rural sites.

5.3.5 Stormflow Relationships

During stormflow conditions water is supplied to the creek from rainfall, surface runoff, throughflow and baseflow. Each of these sources of discharge travels through different chemical environments and therefore may contain different solute magnitudes. Mixing of these variable sources results in the chemical character and patterns of solute response of streamwaters. Rainfall is on the average, more acidic than creek water; thus, direct precipitation into the creek can be expected to lower pH values and contribute only minor amounts of solutes. Surface runoff from storm events will likely be variable in solute content, although it is generally more dilute compared to baseflow solute concentrations (see Figure 5.1, p. 136). The magnitudes and behaviours of the solutes will depend on antecedent conditions such as time since last storm, magnitude of last storm and the general wetness of the watershed. Lengthy dry periods will allow the buildup of solutes in dust and litter in the city and in the biomass of the rural environment. Conversely, lengthy wet periods tend to exhaust surface supplies and solute response is quite different from

Figure 5.3

SOLUTE RESPONSE IN A STORM EVENT ON CHIPPEWA CREEK: JUNE 24-25, 1981.



that found after the dry period. The solute content of throughflow will depend on the ability of the upper soil horizons and leaf litter to provide soluble ions. Supply from leaf litter peaks in the spring and late autumn (see Section 2.5 p. 32) so that generally low concentrations might be expected from this source during summer storm events. Soils with large base saturation will supply the greatest amounts of solutes and in the Chippewa Watershed the % BS of the A horizons are variable over the area (see Table B1, Appendix B). Baseflow is expected to be the most concentrated because of its lengthy contact with soil horizons and mineral surfaces. During storm events the concentrations of solutes delivered by baseflow generally will display an initial dilution response then a recovery to pre-storm values. In summary, negative relationships with Q are generally expected during storm events. As well storm magnitude, QP, will likely be negatively related to solute concentration in most cases. As time from peak flow (TQP) increases solute concentrations should increase; however, exceptions to this and the above expectations can occur due to flushing and exhaustion of surficial solute species from the biomass and city streets. Thus with these principles in mind the solute variance in stormflow events is analyzed below.

5.3.5.1 Storm Period Variation

First of all the storm period variations in the solutes being studied here are based on the relationships of Figure 5.3 below. The storm depicted here occurred on June 24 and 25, 1981. Although by area standards it is not a large storm, the effects

on solute response are substantial in that a long dry spell preceded the storm. The solute data displayed were collected manually at the two sites (Oak Street and Airport Road) at regular, synchronized intervals of 0.25 hours for periods of rapidly changing discharge. Samples were subsequently analyzed using the techniques outlined in Appendix A. Values plotted for Oak Street were derived by subtracting the corresponding Airport Road values of three hours previous, (the time of travel for water between the two sites) thus removing spatial autocorrelation in the data at Oak Street. As a result the curves presented represent the relative urban and rural contributions to Chippewa Creek solute loads during the storm.

In terms of magnitudes of concentrations during the storm of June 24-25, there appear to be some similarities and differences between the solute loads at the rural and urban sites. Generally for the urban site the order of quantitative importance is $Cl^- > Na^+ > HCO_3^- > Ca^{++} > K^+$ and for the rural site the order changes to $Cl^- > HCO_3^- > Ca^{++} > Na^+ > K^+$. Chloride is about equal in peak values for both sites. Sodium and K^+ peaks are greater for the urban site although generally K^+ values are higher at the rural site; Ca^{++} and HCO_3^- are greater for the rural site. Pre-storm values are all higher at the rural site except for Cl^-. Thus the rural setting seems to provide a greater supply of these ions to creek waters during lowflow either through more intense weathering process or from anthropogenic sources such as the city landfill site (see Figure 5.6, p. 207). This observation is confirmed in discussion of lowflow relationships in Section 5.3.6 later.

Solute response to the storm event is complex. Generally all solutes display dilution from pre-storm to post-storm values except for rural Ca^{++} values. Recovery from dilution is very slow. After three days values are only just beginning to rise again and the increase is marginally better for the urban site. Although dilution can be used to explain the pre-storm to post-storm lowering, the existence of peak values greater than both the pre-storm and post-storm values suggests that more than simple dilution is controlling solute response. A closer scrutiny of the curves in Figure 5.3 indicates that all solute concentrations (except rural Na^{+} and HCO_3^{-}) increase with rising discharge in the initial storm period, a display of the flushing effect noted by Walling and Foster (1975). However, this effect is soon masked by dilution troughs in all solute curves and correspondingly in pH curves. The causes of these troughs appear to be a complex interplay of the precipitation and runoff peaks in both the rural and urban settings. Influx of dilute rainfall to the channel depresses the ionic concentrations immediately, especially those of HCO_3^{-} almost in direct correspondence with the rainfall peaks simultaneously at Oak Street and Airport Road during the storm. The rain is certainly acidic as evidenced by the sympathetic depression troughs for pH and HCO_3^{-}. The HCO_3^{-} being an amphoteric substance is used up in buffering the incoming rain water. As the storm progresses and rainfall ends, the solute troughs appear to be influenced to a greater degree by dilute portions of the surface runoff corresponding to the hydrograph peaks. These facts also support a flushing effect explanation in that the

runoff supplying peak flow should become more dilute as surficial solute supply becomes exhausted. As well different sources of runoff with variable solute loads may be influencing late-storm solute response. The frequency of solute response can, therefore, be correlated to the frequency of hydro-meteorological events during the storm period.

Rural Na^+ and HCO_3^- values are at first diluted rapidly by rainfall into the channel but show recovery and flushing with hydrograph rise. Bicarbonate values rise beyond pre-storm levels which confirms that sources of runoff in the rural watershed have relatively high HCO_3^- concentrations. Although diluted Na^+ concentrations do not recover to pre-storm levels, there is still a small rise punctuated by peak rainfall dilution troughs as the storm progresses which indicates a delayed flushing effect similar to HCO_3^- above.

Generally, except for rural Cl^-, the curves for the rural solute variance tend to be more subdued than those for the urban setting suggesting a lesser intensity of process in the rural environment. In fact this relationship is also mirrored in the nature of the discharge curves; therefore, the magnitude of hydrological process may well govern the magnitudes of solute response as well as the frequencies of response discussed above. The effects of rainfall also appear to be less dramatic in the rural setting again with the exception of Cl^-. Since rainfall volume is assumed (see Section 3.6.1, p. 82) to be similar for both sub-basins, watershed or channel character must reduce the depression of solute concentrations. A possibility might be that the greater density

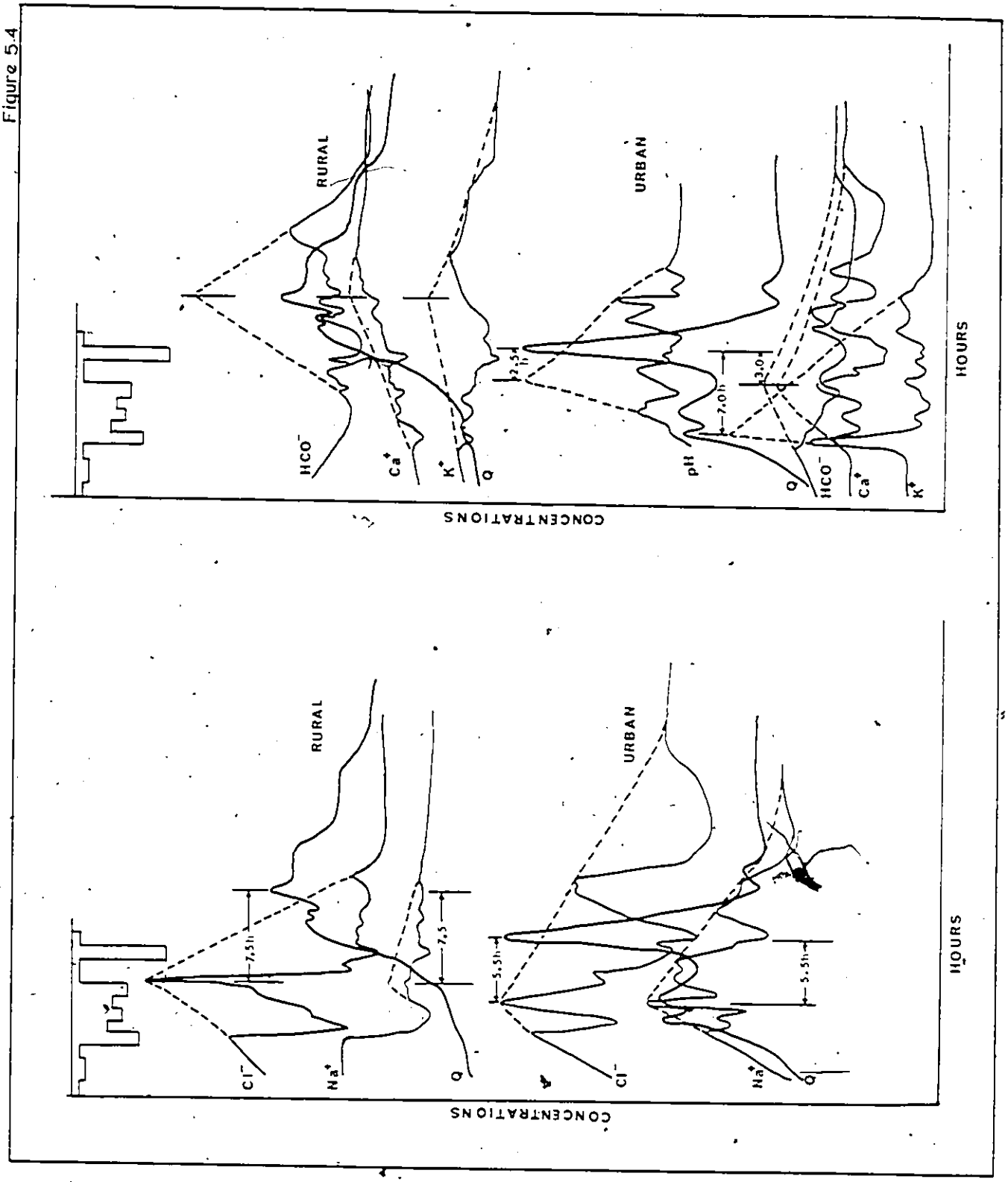
of vegetation close to the channel provides cations in throughfall to prevent large depressions of concentrations.

To further compare the rural and urban responses hypothetical solute peaks have been constructed by extrapolating the rising and recessional curves of the solutes to meet at a peak somewhere during the stormflow. These extrapolated curves represent in effect, the flushing trends in the solutes with much of the dilutional effects of stormflow and rainfall removed. The results are presented in Figure 5.4 below. In all cases the hypothetical solute peaks occur either at or before the hydrograph peak. For Na^+ and Cl^-, urban concentrations peak 5.5 hours prior to the hydrograph peak and for the same two ions, rural peaks occur 7.5 hours prior to hydrograph peak. For HCO_3^-, Ca^{++} and K^+, urban peak values occur 7.0, 3.0 and 3.0 hours respectively in front of peak discharge; whereas, the rural peaks for the same ions all occur at the same time as peak flow. Thus it would seem likely that the peak solute concentrations would materialize more quickly in the urban setting than in the rural, based on these extrapolated curves.

The supply of K^+ (usually produced from forest litter or throughfall during stormflow) appears to be exhausted more quickly in the urban setting than the rural, probably as a result of the lack of vegetative cover and litter in the urban setting. Calcium values fall relatively less after peaking in the rural than in the urban sub-basin, again suggesting a larger, more consistent supply from litter in rural throughflow and throughfall.

Figure 5.4

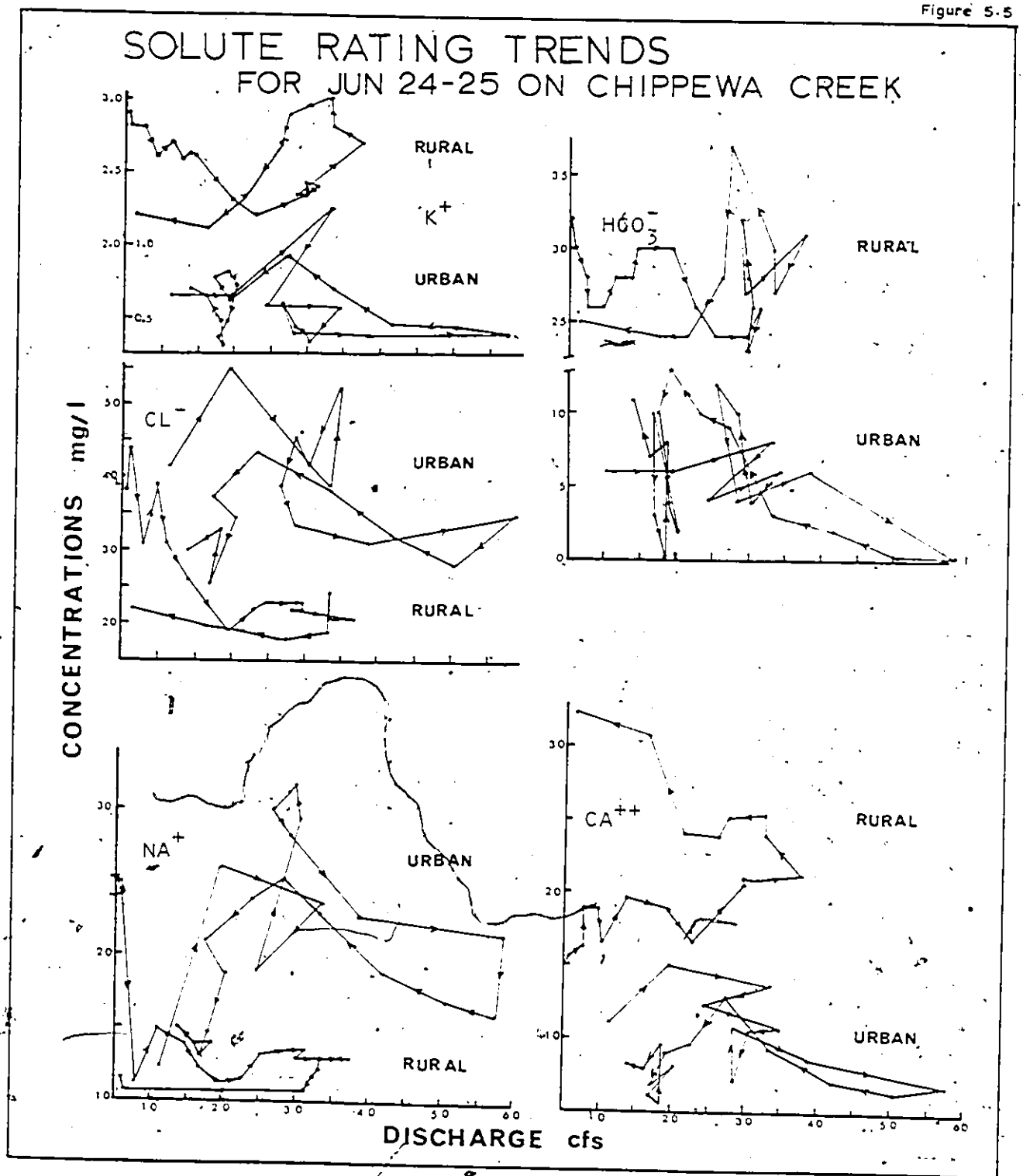
EXTRAPOLATED CHEMOGRAPH LAGS FOR URBAN AND RURAL SITES



Because the relationships between rainfall, discharge, and solute response are very complex, rating trends have been plotted in Figure 5.5 to try to investigate this complexity further. The investigation of overall chemograph lags above, simplified the solute responses by constructing hypothetical solute peaks but much variation occurred within the limits of the storm period's influence in the solute curves of Figure 5.4 due to hysteretic effects as well. In the rating trends this hysteretic variation is analyzed with respect to urban and rural settings.

The rating trends consist of a series of clockwise and counterclockwise loops. On the clockwise loops (positive hysteresis) solute concentrations increase with increasing discharge and in the counterclockwise loops (negative hysteresis) concentrations decrease with increasing discharge (Gregory and Walling, 1973). Thus the rating trends show a very complex, changing solute response during this storm event. Rural relationships appear simpler than the urban ones. Bicarbonate, Ca^{++}, and K^{+} all show generally clockwise trends. The relationship discussed earlier can be identified here again. Calcium exhibits a general buildup on both the rising and falling stages with minor perturbations along the trend due to dilution. Potassium dilutes initially, then rises with increasing discharge to again drop after peak concentration with falling stage. Bicarbonate concentrations fall with initial rise in discharge, then peak to fall again and rise again to a final peak on the rising stage. On the falling stage another major peak occurs, then HCO_3^{-} values drop with decreasing discharge.

Figure 5.5


SOLUTE RATING TRENDS
FOR JUN 24-25 ON CHIPPEWA CREEK
RURAL
K^+
URBAN
HCO_3^-
RURAL
CL^-
URBAN
RURAL
URBAN
NA^+
URBAN
RURAL
CA^{++}
RURAL
URBAN
CONCENTRATIONS mg/l
DISCHARGE cfs

Similarly Na^+ and Cl^- exhibit both positive and negative hysteretic effects. These rural relationships all seem to confirm the flushing hypothesis used earlier. A simple dilution explanation of solute response would not be consistent with the degree of positive hysteresis displayed in Figure 5.5.

The urban trends show even more complexity than the rural with many very tight vertical loops indicating abrupt changes in concentration for small changes in discharge. This situation might reflect the heterogeneity and life span of the various sources of runoff and their concomitant solutes which exist in the urban setting. By contrast the rural setting appears to have a more homogeneous and regulated supply of discharge and solutes. Thus hysteretic effects appear to be more severe in the urban storm data than in the rural data, again underscoring the different solute responses from these two environments.

Thus from the analysis of the storm of June 24-25, 1981, it would seem that there are definite differences between the solute response in the rural and urban environments and that these responses are integrally tied up with changing hydro-meteorological conditions tempered by supply and exhaustion effects. On the average, values of many of the solute parameters during lowflow tend to be equal to or greater than the stormflow values at these two sites (see Figure 5.6, p. 207 or Appendix C). This fact suggests that dilution of highly concentrated baseflow must occur in many of the storms so that the flushing effects in this storm are not likely the general rule.

The general character of solute response then at the rural and urban sites appears to be very complex and whether it exhibits dilution or flushing effects likely depends on the nature of the watershed and antecedent conditions at the time of the storm. In order to determine relationships over a wider range of storms the stormflow data of Appendix C were subjected to statistical scrutiny in a fashion similar to springflow data earlier.

5.3.5.2 Statistical Stormflow Relationships

Early storm solute variance has been assessed above and a great deal of variability was uncovered. Even though some ions displayed a positive relationship to discharge, ultimately all but rural Ca^{++} displayed dilution with recessional flow. To investigate the post-peak variance patterns, the statistical stormflow relationships below have been developed using data selected from only the recessional flows of major storms. This choice eliminates some of the variance introduced by hysteretic effects.

Stormflow stepwise regression relationships are given in Table 5.4 below. The explanation by the hydro-temporal variables is generally low for bivariate relationships but is somewhat better for the multivariate equations. Again, as in the springflow relationships, the rural setting generally has greater R^2 values, signifying less stochastic variation or better explanation by the significant variables. As well the degree of explanation, particularly in the rural equations is generally better than that for springflow data discussed earlier. The quality of explanation is once again a victim of short-term, near-peak

TABLE 5.4

SUMMARY OF STORMFLOW RELATIONSHIPS WITH HYDRO-TEMPORAL VARIABLES

DEPENDENT VARIABLE	RURAL (AIRPORT RD.) EQUATIONS	SIG.	R^2	URBAN (OAK ST.) EQUATIONS	SIG.	R^2
pH	pH = 7.93 - 0.01 API	***	0.59	pH = 7.61 - 0.008 API	***	0.39
TDS	TDS = 85.98 + 0.53 TQP	*	0.33	TDS = 126.68 - 0.65 TS	**	0.35
Cl^-	CL = 43.01 - 11.47 log Q	***	0.53	CL = 32.97 + 429.09 Q^{-1} - 0.12 TS (0.34) (-0.44)	*	0.21
Na^+	NA = 32.41 - 10.56 log Q + 8.26 TQP^{-1} (-0.70) (0.46)	***	0.71	NA = 18.27 - 16.88 TQP^{-1}	**	0.34
K^+	K = 18.49 - 8.13 log API	*	0.17	K = 2.68 - 79.96 QP^{-1}	*	0.19
HCO_3^-	ALK = 84.19 - 29.81 log API - 9.57 log QP (-0.43) (-0.58)	***	0.76	ALK = 3.14 + 11.15 TQP^{-1}	**	0.28
Hd	HD = 178.03 - 59.64 log QP - 0.43 TS (-0.91) (-0.57)	***	0.61	HD = 8.60 + 253.50 Q^{-1}	*	0.11
Ca^{++}	CA = 42.14 - 0.28 API + 23.48 QP^{-1} (-0.60) (0.51)	***	0.71	-	-	-
Mg^{++}	MG = 6.17 - 1.94 log Q - 0.92 log QP (-0.53) (-0.40)	***	0.65			

* significant to .05 ** significant to .01 *** significant to .001

(0.40) Beta weight

fluctuations during hydrologic events, such as those identified above in the storm data of June 24-25, 1981.

All of the hydro-temporal variables are involved in the explanation of solute parameter variance for stormflow conditions, except PT and TD. The absence of TD is easily understood in that variance due to time of day would likely be well masked by hydrological controls during stormflow. The absence of PT from these relationships is also acceptable in view of the storm data discussed earlier. Precipitation is not a strong contributor of solutes and supplies only large quantities of acid radicals, principally H^+ to the streamwaters (see data summary, Table 3.7, p. 104). The effects of precipitation are sporadic, short term, and minimal relative to the effects of discharge from storm runoff. Usually these effects occur prior to peak Q and thus they are generally absent in the data analyzed here. Even though PT relationships are absent, the effects of rainfall are, of course, reflected in the variance of Q and API for the rural setting and in Q for the urban setting as indicated in the factor analysis of the stormflow hydro-temporal variables presented earlier in Section 5.2 (p. 135).

The complex relationships presented in Table 5.4 are not easily dealt with by visual inspection; therefore, as was done in the spring-flow analyses earlier, sample calculations were done to allow examination of the differentials in magnitudes and rates of change of solute parameters over the storm events between the rural and urban environments. The results are given in Table 5.5 below. With the information in Tables 5.4 and 5.5, the following observations and conclusions are made.

TABLE 5.5

COMPARISON OF MAGNITUDES OF RURAL-URBAN RELATIONSHIPS--STORMFLOW

SOLUTE PARAMETER	RURAL (AIRPORT RD.)			URBAN (OAK ST.)			DIFFERENTIAL
	VALUE INDEP. VAR.	VALUE DEP. VAR.	SLOPE	VALUE INDEP. VAR.	VALUE DEP. VAR.	SLOPE	
pH	API = 20.00	7.73		API = 20.00	7.45		
	API = 22.00	7.71	-0.01	API = 22.00	7.43	-0.01	U = R
	API = 55.00	7.38		API = 55.00	7.17		
	API = 60.50	7.33	-0.01	API = 60.50	7.13	-0.01	U = R
TDS	TQP = 65.00	120.43		TS = 60	87.68		
	TQP = 71.50	123.88	+0.62	TS = 66	83.78	-0.65	U = 1.1R
	TQP = 20.00	96.58		TS = 150	29.18		
	TQP = 22.00	97.64	+0.53	TS = 165	19.43	-0.65	U = 1.2R
Cl^-	Q = 15.0	29.52		Q = 15.0 TS = 120	47.18		
	Q = 16.5	29.05	-0.31	Q = 16.5 TS = 132	43.14	-2.69 -0.34	U = 4.9R
	Q = 65.0	22.22		Q = 65.0 TS = 60	32.37		
	Q = 71.5	21.74	-0.07	Q = 71.5 TS = 66	31.05	-0.20 -0.22	U = 3.0R
Na^+	Q = 55.0 TQP = 5.0	15.68		TQP = 5.0	14.89		
	Q = 50.0 TQP = 5.5	15.97	-0.06 -0.58	TQP = 5.5	15.20	+0.62	U = 5.4R
	Q = 16.5 TQP = 60.0	19.69		TQP = 60.0	17.99		
	Q = 15.0 TQP = 66.0	20.12	-0.67 -0.07	TQP = 66.0	18.01	$+0.3 \times 10^{-2}$	R = 124.0U
K^+	API = 20.0	7.91		QP = 40.0	0.68		
	API = 22.0	7.58	-0.17	QP = 44.0	0.86	+0.05	R = 3.4U
	API = 30.0	6.48		QP = 150.0	2.15		
	API = 33.0	6.14	-0.11	QP = 165.0	2.20	$+0.3 \times 10^{-2}$	R = 36.7U
HCO_3^-	QP = 30 API = 30	26.02		TQP = 5.0	5.37		
	QP = 33 API = 33	24.39	-0.54 -0.54	TQP = 5.5	5.17	-0.40	R = 1.4U
	QP = 120 API = 30	20.26		TQP = 50.0	3.36		
	QP = 132 API = 33	18.62	-0.17 -0.67	TQP = 55.0	3.34	-0.4×10^{-2}	R = 105.0U
HD	QP = 20 TS = 110	53.14		Q = 15.0	25.50		
	QP = 22 TS = 121	45.94	-3.60 -0.65	Q = 16.5	23.96	-1.03	R = 2.1U
	QP = 170 TS = 50	23.51		Q = 65.0	12.50		
	QP = 187 TS = 55	18.89	-0.27 -0.92	Q = 71.6	12.14	-0.06	R = 9.9U
Ca^{++}	API = 25.0 QP = 10.0	37.49					
	API = 27.5 QP = 11.0	36.57	-0.37 -0.92				
	API = 55.0 QP = 90.0	27.00					
	API = 60.5 QP = 99.0	25.43	-0.29 -0.1				
Mg^{++}	QP = 170 Q = 40	1.01					
	QP = 187 Q = 44	0.89	-0.7×10^{-4} 0.03				
	QP = 10 Q = 10	3.31					
	QP = 11 Q = 11	3.19	-0.12 0.12				

Within the many storms sampled over the study period the relative magnitudes of the solute parameters appear to have changed from the spring relationships earlier. Although these magnitudes are not exact in relationships of low R^2, there are obvious trends. Total dissolved solids, Na^+ and Cl^- are generally smaller than for springflow; whereas, Ca^+, HCO_3^- and pH tend to be generally larger and more important quantitatively to the solute load. Values of solute parameters tend to be lower for the urban environment except for Cl^- and higher for the rural environment. Intensity of process appears to be greater in the urban setting for TDS, Cl^- and Na^+ (for relationships examined at close to peak flow); whereas, for HCO_3^-, K^+ and Hd, intensities are greater in the rural environment. Rates also vary considerably over the selected ranges of the explanatory variables for individual ions.

(a) Chloride

Chloride is the only ion which exhibits generally greater values in the urban setting. It appears to be discharge controlled and at both the rural and urban sites, it exhibits negative relationships with Q, a dilution relationship. The relationship is more intense at lower discharge values in both environments and for the urban setting dilution rates are greater for large values of TS likely because of diminishing supplies of Cl^- in the watershed. In fact for a given stormflow Q, Cl^- values fall seven-fold over the period from the end of the spring period (early May) to the end of the summer (late September) which supports this view. Thus Cl^- dilution appears to be very sensitive to near-peak stormflow discharges and as TQP gets larger

and Q diminishes, Cl^- dilution levels out likely under the influence of baseflow supply. This conclusion is also consistent with the stormflow behaviour of Cl^- in the storm data of June 24-25, discussed earlier. Also in both high and lowflow conditions urban dilution rates are greater than rural rates by three to five times respectively, emphasizing again the greater intensity of process in the urban setting.

(b) Total Dissolved Solids

TDS shows rather different patterns of variance for urban and rural situations; however, the intensities of the variance appear about equal. TDS values build for increasing TQP in the rural sub-basin but drop for increasing TS in the urban sub-basin. The rural case mirrors strongly the increasing influence of subsurface solute sources in the solute load and the dilution of these solutes by stormflow. Dilution rates are greater for samples closer to peak flow. Recovery is slow as evidenced by relatively small regression coefficients. The rural case shows a general exhaustion of solutes from the spring at a constant rate, indicating that the major components of the solute load are likely Cl^- and as seen above, supplies of this ion diminish considerably over the summer. Thus the supply of Cl^- to stormflow diminishes as summer progresses.

(c) Sodium

Sodium exhibits dilution effects in both the urban and rural relationships. With increasing values of Q and decreasing values of TQP, concentrations of Na^+ decrease in the rural environment. The

intensity of dilution is greater by eleven-fold at lower discharges and greater TQP indicating that dilution must level off in extremely high flows as the chemical character of the creek assumes that of the surface runoff. However, for a given stormflow value of Q, the intensity of change in Na^+ is higher for periods closer to peak flows. These rural relationships between Na^+, Q and TQP appear to be extremely complex. In the urban situation the dilution is still present but the intensity is reversed being greater in magnitude for flows closer to storm peaks by about 207 fold. This would suggest a supply which is rapidly diluted in the initial storm period but rate of dilution slows as the TQP increases. This interpretation is supported by the storm curves analyzed earlier (see Figure 5.3, p. 170). During high Q and low TQP values the urban rate of dilution is about 5.4 times greater than the rural but during lowflows and high TQP values the rural rate of change of Na^+ is 124 times greater than that in the urban.

(d) Potassium

Watershed wetness (API) and previous storm magnitude (QP) form a relationship with K^+ in the rural and urban settings respectively. In rural conditions the wetter the watershed the more dilute is K^+ in streamwaters. The rate of dilution is smaller under wetter conditions suggesting that dilution is likely compensated somewhat by the flushing of K^+ from the litter and biomass of the watershed or may suggest exhaustion of supply. Conversely, in the urban setting K^+ is diluted more dramatically (greater by 16.7 times) after smaller peak flows and thus drier conditions. The reason for this relationship is not readily

apparent except that possibly with larger peaks, waters are coming from more distant parts of the urban sub-basin and carrying greater K^+ concentrations. In both wet and dry conditions, the flux of K^+ is greater in the rural setting.

(e) Alkalinity

Alkalinity (HCO_3^-) also displays a difference in response between the rural and urban sub-basins. In the rural, HCO_3^- is diluted by stormflow and this dilution rate becomes less for larger peak flows by a factor of 3.2 times given the same degree of watershed wetness. This result is consistent with expected results in that HCO_3^- is used to buffer the H^+ content of rain (see Figure 5.3, p. and as the peak flows get greater, a greater supply of HCO_3^- will be brought to the channel from more distant parts of the watershed, thus diminishing the effects of the rain on the HCO_3^- in channel waters. In the urban setting HCO_3^- displays a dilution effect in stormflow with larger values for periods close to storm peaks and smaller values as TQP increases. The rate of decline is greatest just after the peak flows and becomes minimal (100 times less) as TQP gets larger, suggesting quick dilution and a relatively small and limited supply with poor recovery. Thus rural rates of change in HCO_3^- appear to be greater than urban under all conditions.

(f) Hardness, Calcium and Magnesium

Hardness displays dilution for increasing peak flow magnitudes and times closer to spring for rural data and for increasing discharge

in urban data. Both exhibit very high dilution rates under low conditions of flow but these rates tend to level off by 13 to 17 fold during high discharge conditions. Also the rural flux in HD is about twice the urban due to dilution in lowflows but quadruples to 9.9 in high flows. Hardness would appear to be supplied principally from subsurface sources in both the rural and city environments. Stormflow tends to reduce hardness quickly then tapers off as the streamwater concentrations approach those in the runoff and throughflow.

Both Ca^{++} and Mg^{++} concentrations are related to conditions of flow as well in the rural setting and both display a dilution response. Both display a greater magnitude of dilution under wetter conditions.

(g) pH

The pH in both the urban and rural settings relates to watershed wetness (API) in a negative way. With large API values generally, streamwaters become more acidic somewhat more so in the urban than in the rural setting. These relationships reflect the general lowering of pH by acidic precipitation during storm events.

(h) Stormflow Hydro-Temporal Variance: A Summary

Stormflow solute variance has been analyzed by scrutiny of a single storm event and by a statistical analysis of several storm events. In the first case Na^{+}, Cl^{-}, Ca^{++}, K^{+}, HCO_3^{-} and pH have been monitored over a summer storm for storm period variations in an urban and rural setting. In this particular storm Cl^{-} and Na^{+} are quantitatively the major ions in the urban setting; whereas, Cl^{-} and HCO_3^{-} dominate the rural setting. Potassium concentrations are generally

greater in the rural setting although the urban peak concentration is greater than its rural counterpart. Calcium and HCO_3^- display greater rural concentrations as well.

Solute variation is complex. All solutes display a reduction in concentration from pre-storm to post-storm values except rural Ca^{++}. Recovery to pre-storm values is very slow with a slow rise in concentrations beginning about two days after the initial storm effects. However a simple dilution explanation is not adequate to explain the solute variations during the storm event itself. A distinct flushing response is evident but is masked and interrupted by almost instantaneous dilution by rainfall peaks and latter storm dilute runoff. The effect of the rainfall peaks is confirmed by simultaneous depression of pH and ionic concentrations at both the rural and the urban sites. As well the simultaneous depression of HCO_3^- with rainfall peaks corroborates the interpretation of the solute variation in that the HCO_3^- is used to buffer rainfall acidity.

The rural solute response appears to be more subdued than the urban due to the relative magnitudes of peak flows and the intensity of their respective runoff processes. Depression of rural concentrations by rainfall is also somewhat less due to help from a greater supply of flushed solutes, especially HCO_3^-, which tends to reduce the dilution response.

Hypothetical chemograph lags determined by extropolation of the solute curves also underscore the differences between urban and rural responses. In the rural environment solute flushing peaks are

generally coincident with peak discharge except for Na^+ and Cl^- which exhibit solute flushing peaks at 7.5 hours prior to storm peak. At the urban site solute peaks materialize more quickly than the rural ones ranging from three to seven hours prior to peak flow although the Na^+ and Cl^- peaks are slower to form than their rural counterparts peaking at only 5.5 hours prior to peak discharge. These quick peaking responses are likely related to the nature of solute supplies and the times of concentration for runoff to the channel. Also the exhaustion of first flush solute supply is more dramatic in the urban setting.

Solute rating trends for the rural and urban ions tend to mirror the complexity of the flushing and dilution response of the solutes during the storm event. Trends for both sites are a complex series of loops, suggesting both positive and negative hysteretic effects occur throughout the storm period. Urban trends are more complex than rural, exhibiting many tight loops and changes of direction. This complexity is likely related to the variability and life spans of the various sources of solutes in the urban environment as well as to the dilution capabilities of the precipitation peaks. The rural trends display a more orderly pattern suggesting a more homogeneous and regulated supply. Thus it is apparent that solute storm period response differs from ion to ion and from the urban to rural settings. Responses relate to changing hydrometeorological conditions tempered by supply and exhaustion effects as well as antecedent conditions.

The statistical analyses of storm data taken over two years has revealed that solute variance in post-peak stormflow is related

to one or several of API, Q, QP, TQP, and TS. Thus solute variance appears to relate to storm magnitude and wetness of the watershed, the elapsed time from storm peak over which dilution or recovery occurs and the state of the solute supply.

The relative magnitudes of solutes are different from springflow. Sodium and Cl^- appear to be less important; whereas, Ca^{++} and HCO_3^- have become more important. Chloride appears to be the only ion with greater concentrations at the urban than at the rural site.

Solute responses are variable. In the rural watershed all parameters show an increase with drier conditions defined by low values of Q, QP and API and high values of TQP and TS. Likewise in the urban setting all parameters display increased values for drier conditions except K^+ and HCO_3^- which respond in an opposing fashion. Potassium and HCO_3^- appear to undergo dilution from peak values near to stormflow peaks. These two ions would appear to produce strong flush peaks in the urban setting a fact confirmed by the discussion of storm period solute variance earlier. Many of these stormflow solute responses are often sensitive to either high or low magnitudes of storm discharge-related parameters indicating again that rates of dilution or recovery are not linear over a storm but exhibit greater or lesser intensities for given hydrological conditions.

A comparison of urban and rural rates of change or fluxes for the solute parameters shows that again the urban setting displays a greater flux for surficially derived solutes such as Cl^- and to some extent, Na^+. Generally the ions such as K^+, HCO_3^-, Ca^{++}, and Mg^{++} which are associated with "ruralness" (i.e. biomass and subsurface

sources) exhibit greater fluxes in the rural setting.

5.3.6 Lowflow Relationships

During lowflow conditions waters are supplied to the creek from ground and soil water discharge. These waters have infiltrated soil horizons and migrated down gradient to the stream channel. Thus they have contacted various soil and rock horizons and have had enough time to interact with minerals to accumulate reasonably high solute loads by the mechanisms outlined in Chapter II earlier. This should be especially true of soilwater which finds its way to lower soil horizons where Ca^{++} concentrations are relatively quite high (see Table B1, Appendix B). Thus during baseflow, streamwaters tend to have a greater solute load than during stormflow events (see Figure 5.1, p. 136). The longer the period of baseflow the greater the solute load tends to become due to lack of dilution and because ground and soil waters have longer residence times and solutes approach equilibrium values. As a result during extended baseflow periods ionic species which are the result of mineral dissociation can be expected to be in greater concentrations than those derived from other sources.

These principles appear to fit the lowflow data collected for analysis in this thesis. In Figure 5.1 (p. 136), it can be seen that all chemical parameters (except Cl^-) exhibit their highest values during lowflow conditions. In Figure 5.2 (p. 141) it can be seen that most solutes show a gradual increase over extended lowflow periods especially during July and August, 1975 and June 1976. Even during these lowflow periods certain solutes exhibit considerable

variability at both the urban and the rural sites. The explanation of this variance must invoke relationships involving parameters which affect groundwater and soil water behaviour. Such parameters would necessarily include previous storm magnitudes and antecedent precipitation conditions in general. In addition other explanatory variables may come into play such as those related to diurnal variations of biotic and human activity as discussed in Chapter II.

Lowflow stepwise regressions are given in Table 5.6 below. The explanation by the hydro-temporal variables is generally low for bivariate equations in both the rural and urban settings but is much better for the multivariate relationships. Again as in both springflow and stormflow conditions, the rural relationships give better explanation than the urban ones. Urban explanations are likely reduced by the stochastic nature of solute supply and events within the city, such as lawn watering, the operation of sump pumps, street cleaning and numerous other activities. Even so, fewer variables required transformation in order to produce linear regression relationships indicating generally a smaller but more orderly variation in the variables than in springflow and stormflow discussed earlier. Nevertheless, numerous significant relationships have been derived for lowflow solute variance.

The hydro-temporal variables which explain the solute variance in lowflow conditions essentially describe the behaviour of groundwater discharge during the lowflow (QP and API), the occurrence of minor precipitation events (PT), the supply of certain ionic species (TS),

TABLE 5.6

SUMMARY OF LOWFLOW RELATIONSHIPS WITH HYDRO-TEMPORAL VARIABLES

DEPENDENT VARIABLE	RURAL (AIRPORT RD.) EQUATIONS	SIG.	R^2	URBAN (OAK ST.) EQUATIONS	SIG.	R^2
pH	$pH = 7.80 + 0.01\ PT^{-1} + 0.12\ QP^{-1}$ (0.71) (0.47)	***	0.69	$pH = 7.26 + 0.03\ TD$	*	0.23
TDS	$TDS = 184.86 - 0.44\ TS$	**	0.27	-	-	-
Cl^-	$CL = 66.61 + 8.50 \log QP - 22.40 \log TS$ (0.65) (-0.44)	***	0.85	$CL = -6.80 + 26.27 \log QP$	**	0.33
Na^+	-	-	-	$NA = 21.89 + 0.75\ PT$	**	0.37
K^+	-	-	-	$K = 2.74 - 0.07\ PT$	*	0.29
HCO_3^-	$ALK = 40.83 - 0.49\ QP$	***	0.85	$ALK = 5.30 + 106.48\ QP^{-1}$	***	0.47
HD	$HD = 60.52 - 0.64\ API$	***	0.49	$HD = 24.97 - 0.92\ PT$	**	0.37
Ca^{++}	$CA = 57.38 - 0.65\ API$	***	0.53	$CA = 22.60 - 0.82\ PT$	*	0.26
Mg^{++}	-	-	-	$MG = 1.02 + 0.11\ TD$	*	0.16

* significant to .05 ** significant to .01 *** significant to .001

(0.71) Beta weight

and the time of day (TD) (see earlier discussion of factor analysis results in Section 5.3.2, p. 143). The relationships with PT are rather interesting in that the precipitation events which occurred in lowflow periods were of minimal volumes. These rainfall events were not large enough to appreciably affect discharge and yet were large enough to dilute solutes or to wash solutes into the channel from nearby sources. Previously precipitated salts from sewers and ditches would likely raise solute levels; whereas, solutes from baseflow sources would be depressed in similar fashion as discussed in stormflow analyses earlier.

Support for this argument is found in the factor analysis of lowflow variables (Table 5.1, p. 149). In the rural loadings Q, QP and API do not share a high loading with PT on Factor 1 (discharge) which indicates PT does not contribute much to discharge. In the urban loadings Q is divided between Factor 1 and Factor 2 and PT is related to Q in Factor 2. These relationships are reasonable in that minor rainfalls would be absorbed readily in the well-vegetated rural sub-basin but would likely produce some runoff in the city to raise the discharge slightly in the channel.

Sample calculations were done for the relationships in Table 5.6 employing a similar rationale as the springflow and stormflow earlier. The results are presented in Table 5.7 below. Thus by use of the information in Tables 5.6 and 5.7, lowflow relationships are discussed in the following paragraphs.

All concentration values for urban solutes are of lesser magnitude than the rural (see also Figure 5.2, p. 141). However, the urban

TABLE 5.7

COMPARISON OF MAGNITUDES OF RURAL-URBAN RELATIONSHIPS (LOWFLOW)

SOLUTE PARAMETER	RURAL			URBAN			DIFFERENTIAL RATE OF CHANGE URBAN TO RURAL
	VALUE INDEP. VAR.	VALUE DEP. VAR.	SLOPE	VALUE INDEP. VAR.	VALUE DEP. VAR.	SLOPE	
pH	PT = 1.0, QP = 5.0	7.83		TD = 3.0	7.35		
	PT = 1.1, QP = 5.5	7.83		TD = 3.3	7.36	+0.03	U = 0.03R
	PT = 25.0, QP = 15.0	7.81		TD = 11.0	7.59		
	PT = 27.5, QP = 16.5	7.80		TD = 12.1	7.62	+0.03	U = 0.03R
TDS	TS = 80.0	149.66					
	TS = 88.0	146.14	-0.44				
	TS = 200.0	96.86					
	TS = 220.0	88.06	-0.44				
Cl^-	QP = 20.0, TS = 80.0	35.04		QP = 20.0	27.37		
	QP = 22.0, TS = 88.0	34.46	-0.29 -0.07	QP = 22.0	28.46	+0.55	U = 3.1R
	QP = 10.0, TS = 200	23.57		QP = 10.0	19.47		
	QP = 11.0, TS = 220	22.99	-0.58 -0.03	QP = 11.0	20.56	+1.09	U = 3.6R
Na^+				PT = 1.0	22.64		
				PT = 1.1	22.72	+0.80	
				PT = 15.0	33.14		
				PT = 16.5	34.27	+0.80	
K^+				PT = 1.0	2.67		
				PT = 1.1	2.66	-0.10	
				PT = 15.0	1.69		
				PT = 16.5	1.59	-0.10	
HCO_3^-	QP = 20.0	31.03		QP = 20.0	10.62		
	QP = 22.0	30.05	-0.49	QP = 22.0	10.14	-0.24	R = 2.0U
	QP = 5.0	38.38		QP = 5.0	26.60		
	QP = 5.5	38.14	-0.29	QP = 5.5	24.66	-3.90	U = 8.0R
HD	API = 25.0	44.52		PT = 1.0	24.05		
	API = 27.5	42.92	-0.64	PT = 1.1	23.96	-0.86	U = 1.4R
	API = 10.0	54.12		PT = 15.0	11.17		
	API = 11.0	53.48	-0.64	PT = 16.5	9.88	-0.86	U = 1.4R
Ca^{++}	API = 25.0	41.13		PT = 1.0	21.78		
	API = 27.5	39.50	-0.65	PT = 1.1	21.70	40.80	U = 1.2R
	API = 10.0	50.88		PT = 15.0	10.30		
	API = 11.0	50.23	-0.65	PT = 16.5	9.07	-0.80	U = 1.3R
Mg^{++}				TD = 3.0	1.35		
				TD = 3.3	1.38	+0.10	
				TD = 11	2.25		
				TD = 12.1	2.35	+0.10	

rates of change in solutes are still greater than those in the rural data, except for HCO_3^- after low magnitude stormflow episodes. Thus the controls operating on solute variance appear to create more intensive response in the urban environment. As well the degree of difference in the rates of change or slopes over the given ranges in the independent variables are also generally less than for springflow and stormflow data discussed earlier. For example, the lowflow urban Cl^- relationship in Table 5.6 displays a two-fold increase in slope (i.e. from Table 5.7, 1.09 + 0.55 = 2.00) as a result of the relative influences of the selected magnitudes of peak stormflow; whereas, urban Cl^- slopes show 13.5 and 150.5 fold increases over the selected intervals for stormflow and springflow conditions as a result of controlling variables.

(a) Chloride

Generally the rural values of Cl^- are greater, likely in part due to the influence of the landfill site in sub-basin 7. Chloride values in groundwater at 200 m. upslope of the creek channel are about nine times background values (see Table 3.8, p. 106), thus it is inevitable that these excessive Cl^- levels will find their way to the stream and be carried to Airport Road. Likewise the urban environment also produces Cl^- values in excess of background during lowflow conditions. Sources of Cl^- are likely leaking sewers and ground and soil waters flushing infiltrated road salts similar to the situation described by Wulkowicz and Saleem (1974).

Rural Cl^- variance is explained by QP and TS in such a fashion as to suggest dilution by larger QP values and a reduction in supply

as the lowflows occur further from spring. The effect of TS suggests that part of the Cl^- load is contributed by a diminishing supply such as road salts. In fact the concentrations of Cl^- at both rural sites 7 and 8 show nearly equal means for lowflow which confirms this conclusion (see Figure 5.6, p. 207). Dilution rates of Cl^- are two times greater at lower values of QP probably because under higher QP conditions some subsurface stormflow flushing occurs to slow the dilution effect.

Urban Cl^- responds to QP conversely to that in the rural. Chloride displays a flushing response, building in concentration with increase in values of the last peak discharge. Flushing magnitude is two times greater after low QP events when dilution effects are likely weaker. In comparison it appears that the urban rate of concentration is over three times the rate of dilution in the rural setting at both ends of their respective relationships underscoring once again the different effects of the rural and urban environments.

(b) Total Dissolved Solids

Magnitudes for TDS from the rural environment are much above background groundwater values (Table 3.8 , p. 106) also. Total dissolved solids are a function of TS and the negative relationship suggests a decline in supply as lowflows occur further from spring breakup. This relationship strongly reflects the importance of Cl^- in making up the TDS values. The relationship is also linear indicating a gradual and steady decline of TDS in lowflows over the summer.

(c) Sodium and Potassium

Sodium and K^+ relate to PT only for the urban data. Both exhibit concentration values above background so that it is likely that the city supplies excess of these two ions to the baseflow. Sodium relates to PT positively indicating a flushing action. Small values of PT influence Q (as discussed earlier) and salts are washed from sewers and from streets; however, the magnitudes of Q are still below the lowflow cutoff used to define the lowflow sample subset. On the other hand, K^+ exhibits dilution by PT which suggests that these rainfalls are not large enough to flush K^+ from the biomass but are large enough to dilute in-channel K^+ in the dry conditions of the lowflow regime.

(d) Alkalinity

Alkalinity concentrations are greatest in lowflow for both the rural and urban environments indicating a subsurface source for this ion in the watershed. Magnitudes are greater in the rural subbasin where soils tend to be well aerated and infiltration rates higher than for the "impervious" city. Rural HCO_3^- exhibits dilution response in lowflows preceded by stormflow and the dilution rate is linear over the selected magnitudes of QP. Large antecedent stormflows (QP) are associated with subsurface stormflow and a general elevating of the water table which will tend to dilute existing groundwater concentrations reaching the channel or reduce residence times to limit weathering reactions.

In the urban setting dilution is also evident and the rate after high magnitude flows is much less than the rural (about 2.0 times) rate. As well, at the urban site, after low QP the rate of dilution is much greater, about sixteen times greater than for high QP, which makes the rate of dilution in the urban environment about eight times greater than that in the rural one. Thus it appears that in the urban setting low intensity antecedent storms depress HCO_3^- concentrations quickly in subsequent lowflow. Recovery from storms is therefore slow and points out the lack of vegetation, soil moisture and aeration responsible for the production of bicarbonate. This would also reflect a lower intensity weathering environment as well.

On the other hand lower dilution rates after high-intensity storms may reflect the gathering of HCO_3^- from more distant parts of the watershed so that flushing action tends to reduce the effects of dilution.

(e) Hardness and Calcium

Rural hardness (Hd) concentrations are about twice the magnitude of urban concentrations. Urban concentrations approach background groundwater values (see Table 3.8 , p. 106) but rural values are greater, suggesting other sources, likely the landfill site. However, an accelerated rate of weathering may be responsible as evidenced by the deep weathering of rocks in the rural sector reported by Lumbers (1971). As well, the % base saturation (% BS) of the lower horizons in the soils of the rural sub-basin are greater than in the urban sub-basin (see Table 3.2, p. 78) which is strong evidence to support a greater weathering intensity

in the rural environment. Variance in rural Hd is controlled by watershed wetness, API and with increasing API, Hd displays dilution behaviour in a linear fashion. At the urban site, Hd is related to PT and also displays a dilution response which is about 1.4 times greater than in the rural. This differential in response again reflects the greater intensity of hydrologic process within the city environment. The dilution response in urban Hd also suggests a subsurface source for the ions making up hardness. Calcium is controlled almost exactly as Hd over the two sites by the same hydro-temporal variables. Thus Ca^{++} likely makes up the biggest portion of streamwater Hd and as outlined above is released through the weathering of soils and delivered to the channel by soilwater and groundwater.

(f) Magnesium and pH

Magnesium is the only ion, apart from H^+, which relates to time of day (TD) and it forms a positive linear but weak relationship at the urban site. As time after 6:00 a.m. increases, Mg^{++} concentrations increase. This increase could be related either to biotic, anthropogenic or spurious causes. If the variance in Mg^{++} is related to plant nutrient uptake during daylight hours there should be a corresponding uptake in CO_2 as well (Lee and Hoadley, 1967). The reduction in CO_2 should upset the carbonate system equilibrium so that more CO_2 is produced (see Equation 5.6 below).

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \qquad 5.6$$

Thus less HCO_3^- will be present and pH should drop to more acidic values. However urban pH exhibits the same rise with increasing TD which suggests that plant respiration is not a significant control in the streamwaters of the urban environment. The relationship of Mg^{++} to TD may well be a function of human activity. Volumes of sewage increase after 6:00 a.m. considerably as evidenced from statistics reported by the sewage treatment facility (personal communication).

On the other hand the factor analysis results (Table 5.1, p. 149) show that PT and TD are positively related to Factor 2 (discharge factor from minor rainfall). Thus the Mg^{++} relationship to TD may in effect reflect common variance, the influence of PT on TD or vice versa. If this were the case likely pH would respond to TD negatively as seen for the storm of June 24-25 discussed earlier in Section 5.3.5.1 (p. 171) but pH is positively related to TD so the PT and TD relationship may just be a spurious correlation. Thus it would seem that Mg^{++} is really related to TD and is likely due to the addition of wastewaters to the stream channel.

Acidity (pH) at the rural site is related positively to PT and QP which reflects the acidification of the rural environment by larger storms. Values in the rural setting are greater than the urban reflecting a greater supply of bases during lowflow periods than is present in the city. As mentioned above urban pH values rise with the progression of the day and have been shown to be likely a product of human activity.

(g) Lowflow Hydro-Temporal Variance: A Summary

Lowflow concentrations tend to be greater for most ions than values during springflow or stormflow. Chloride and Na^+ are the general exceptions. In terms of magnitudes, all ions exhibit greater concentrations at the rural site due likely to greater weathering rates of soils and the presence of the landfill site in sub-basin 7. Variance of solute concentrations is explained by mostly linear relationships with antecedent stormflow magnitudes (QP), watershed wetness (API), minor precipitation events (PT) and the supply or exhaustion (TS) of certain ionic species (i.e. Cl^-). The first two explanatory variables likely operate through control of groundwater and soilwater elevations, volumes and flows and resultant dilution of weathering products; whereas, the third, PT, operates to dilute some in-channel species. The fourth explanatory variable defines a diminishing supply of Cl^- and to some extent TDS as time from spring becomes greater. The strengths of these relationships are generally better in the rural setting and for multivariate cases. Urban relationships tend to be more stochastic and somewhat weaker.

Overall, the intensities of processes operating to produce variation are weaker than those seen earlier in the springflow and stormflow regimes, especially for Cl^-. Major differences in the directions and magnitudes of solute behaviour occur between the urban and rural environments and amongst the solute parameters. Where solutes are derived principally from surface sources, such as urban Cl^-, positive (flushing) relationships ensue but those that are from subsurface sources, negative (dilution) relationships occur. Urban flushing and dilution rates

are greater than those in the rural for all ions except HCO_3^- under relatively high antecedent QP because small PT values and antecedent storm conditions have less effect in the well-vegetated rural environment.

Rural Cl^-, urban HCO_3^- and rural pH form the only non-linear relationships and also exhibit the greater spread of rate of process. Rural Cl^- has a rate of change at lower values of QP which is two times greater than at higher QP. Urban HCO_3^- displays a sixteen-fold increase under the same conditions. Thus these two ions appear to be very sensitive to small differences in the magnitudes of antecedent storms. After large QP, they appear to level off to more constant values.

Thus it is apparent from the above discussion that there is considerable variation in solute magnitude and response under lowflow conditions. These variations are generally smaller than for spring or storm events and are sensitive to small changes in hydrologic regimen. Again the magnitudes and directions of the responses vary from the urban to the rural environment.

5.4 Spatial Variations: Between-Site Variance

5.4.1 Introduction

Values for the solute parameters have been determined for eight sites on Chippewa Creek. The details of sampling and site selection have been dealt with earlier (see Chapter IV, p. 121 and Chapter III, Section 3.7, p. 113 respectively). Solution variations from site to

site represent spatial or downstream solute variance which reflects the differing characters of the sub-basins draining to each site. Both physical and human elements over the sub-basin may exert spatial control on the production and delivery of the solutes to the channel (see Chapter II). In former sections of this chapter, it has been shown how hydro-temporal controls have influenced the solute variance. To some extent these controls cannot be divorced from the spatial con= trols or vice versa because the character of the sub-basin will also determine the magnitudes of many hydrological events affecting solute responses. However in the sense that these hydrological events are controlled by basin character then they will also show spatial variation in the watershed with a concomitant solute response. Thus differing physical and cultural characteristics of sub-basins should produce differing solute responses.

Downstream solute variation has already been presented in Figure 5.1, p. 136 earlier where the actual means of solute concentrations measured at the sites are presented. These means are cumulative values and for any given site represent the total contribution of all sites above. To compare the contributions made to the solute load by each sub-basin, mean-difference site values were determined by first subtracting sample mean values at each upstream site from those at its adjacent downstream site starting at Site 1, Oak Street, and working upstream, producing a site mean value which is truly the product of the site. This procedure removes autocorrelation from site means and allows the comparison of the effects of each sub-basin on its mean solute load. The results are plotted

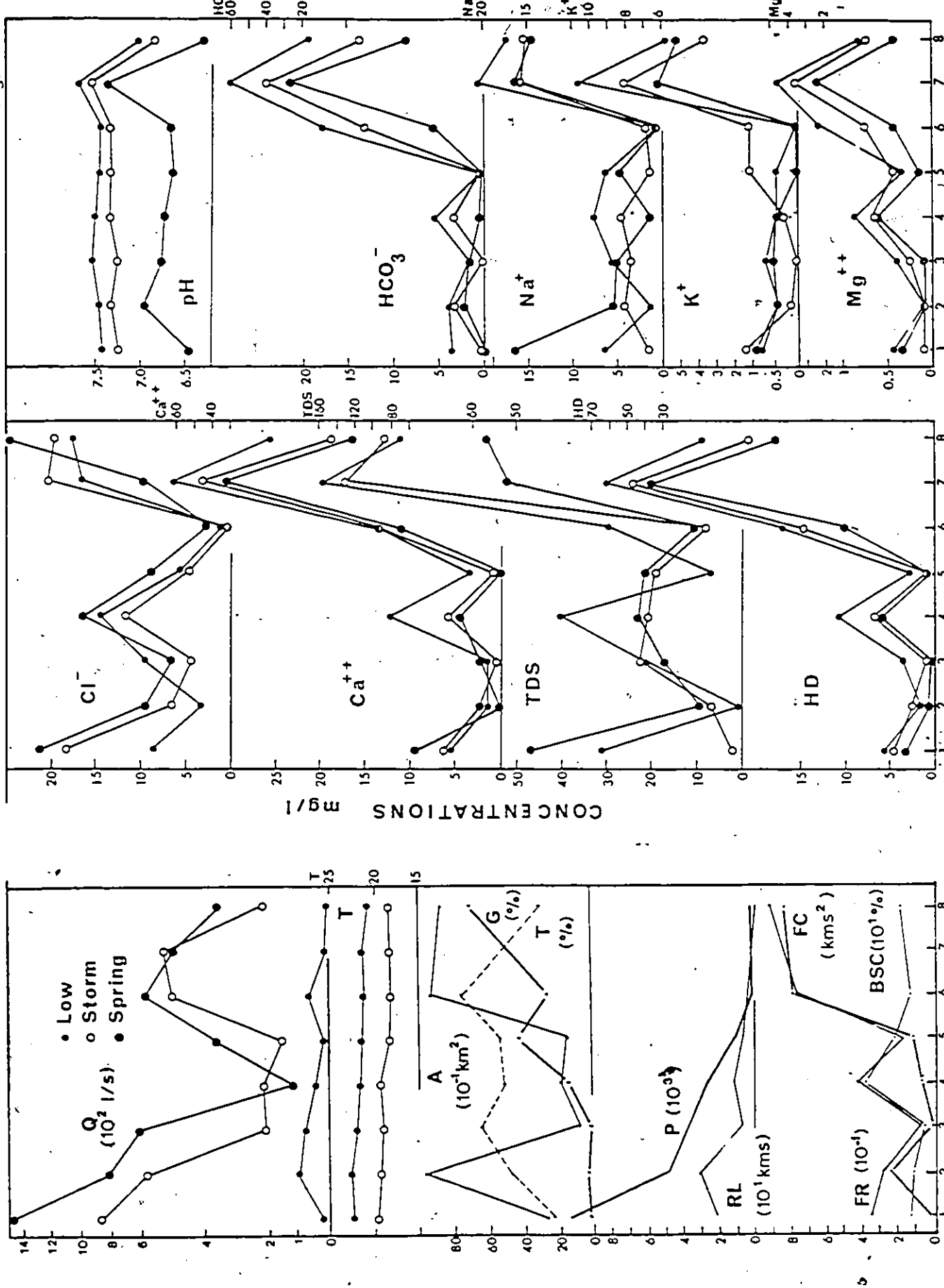
in Figure 5.6 below and are discussed in the following paragraphs.

The relationships in Figure 5.6 illustrate that the solutes respond to spatial controls in a complex pattern and that the effects of spatial controls appear to vary with changing flow regimes. Some consistency of pattern is evident but there are also what appear to be anomalies as well. In the rural setting (Sites 5 to 8) generally, the solutes all exhibit maximum values at Site 7. Solute concentration means are also relatively high at Site 8 and are lowest at Site 5 except for Na^+ and Cl^-. Urban concentrations are generally lower than those for the high rural sites. Within the urban sites, Site 4 generates the highest solute loads except for K^+ and springflow Na^+, Cl^-, Ca^{++} and K^+.

The relative magnitudes of the solute parameters appear in the same orders of quantitative importance as was displayed in the hydrotemporal data analysis earlier except for Cl^- which appears to be rather low for some of the urban sites. All solutes display maxima at Site 7 except spring Cl^- which emphasizes the influence of the landfill site on the creek waters downslope. Springflow and stormflow concentrations generally are more dilute than lowflow concentrations except for Na^+ and Cl^- at downtown sites. Thus most of the solutes appear to be generated either from weathering of soils or leachates from landfill which produce large lowflow concentrations. Sodium and Cl^- again display variance which can be explained for the most part by a surficial source for these ions.

Figure 5.6

SITE VALUES OF WATERSHED AND SOLUTE VARIABLES



A very cursory match of mean discharge (Q) against the solutes reveals that at some sites solutes appear to respond to Q by dilution; whereas, at others there is a positive relationship. Similarly there is no clear and consistent relationship with basin area (BA). Temperature means display little variance downstream as well. However, lowflow temperatures are generally higher than those of streamflow and of course springflow due to the very shallow waters during lowflow and the general lack of channel tree cover.

Sub-basin 6 appears to have an extensive diluting capability. Many of the solutes from Sites 7 and 8 (both contribute water to Site 6) are diluted by Site 6. The degree of dilution varies but is most extreme for Na^+, Cl^-, K^+ and TDS and suggests that sub-basin 6 supplies relatively rather dilute waters with respect to these parameters. Alkalinity, Hd, Ca^{++} and Mg^{++} appear moderately diluted by sub-basin 6 waters and these parameters exhibit lows in sub-basin 5 which is a steep-sloped and shallow-soiled basin. Thus it would seem that these ions may well be principally derived from chemical activity and mineral dissolution in the soils. Also of note is the low Cl^- value for the landfill in springflow which is an enigma. When all other solutes display spring maxima at Site 7, Cl^- exhibits a relatively low value. These facts suggest that the surface waters of spring runoff are relatively dilute in Cl^- but are flushing the other solutes from the landfill site. Why this might be remains a question at this time.

Background surface water values taken from adjacent undisturbed watercourses, presented in Table 5.8 below, illustrate some of the

effects of landuse on Chippewa Creek water quality. Generally the urban streamwater values of Hd, HCO_3^-, K^+ and Ca^{++} seen in Figure 5.6 are lower than surface water background values; whereas, rural values are generally higher with the exception of those at Site 5. Sodium and Cl^- display both urban and rural concentrations higher than background. Thus it would seem that in the former situation soil weathering rates in the city are lower than the rural rates or that discharges in the city tend to dilute these ions and in the latter case that Na^+ and Cl^- are derived mainly from human activity.

Site 7 which collects some of its waters from the landfill, exhibits anomalous values for nearly all chemical parameters. In Table 5.8 creek concentrations are compared to groundwater concentrations taken at 200 m. upslope from the creek channel. Creek values for HCO_3^-, Cl^-, Ca^{++}, K^+ and Na^+ are approximately 5, 5, 11, 10 and 11 times greater than background for local surface waters. Also from Table 5.8, it is obvious that the landfill is supplying considerable solute to the creek. Landfill groundwater values are all very high, much higher than background groundwater values (see Table 3.8 p. 106) and undoubtedly supply Chippewa Creek with nutrients.

Thus it is apparent that solute concentrations exhibit spatially controlled variance in Chippewa Creek. Concentration values are generally higher in the rural setting primarily due to the landfill operation but also likely due to a stronger weathering environment as well. In order to quantify this variance and to determine the factors controlling it, the site means have been subjected to regression analyses with a

TABLE 5.8

COMPARISON OF CREEK AND GROUNDWATER SOLUTES

FOR SITE 7 NEAR THE LANDFILL OPERATION

PARAMETER	CHIPPEWA CREEK *	GROUNDWATER *** (LANDFILL)	BACKGROUND **** (SURFACE WATERS)
Alkalinity (HCO_3^-)	52.29	155	10.25
Chloride (Cl^-)	17.49	36	3.56
Calcium (Ca^+)	52.86	31	4.80
Potassium (K^+)	9.28	5	0.95
Sodium (Na^+)	17.14	60	1.60

* mean values in mg/l

*** values in mg/l measured 200 m. upgradient of creek (Cherry et al., 1981)

**** mean values in mg/l taken from Table 3.11, p. 112 (Myslik et al., 1979)

series of watershed or geo-urban variables. This analysis is developed and discussed in the following sections.

5.4.2 Selection of Geo-Urban Variables

A series of eighteen geo-urban variables were selected in order to try to explain the variance in solutes over the sampling sites. These variables have already been listed and partially discussed earlier in Section 3.7, p.113 of Chapter III but the intent here is to rationalize their choice with respect to their effects on solute variability. Twelve are physical measures describing possible physical controls on spatial variation of solutes and six are measures describing possible urban controls on solute variation. They are all listed in Table 5.9. Their selection is primarily based on the discussion of the theoretical and empirical relationships outlined in Chapter II. The first three variables in Table 5.9 relate to basin geometry. Basin area (BA) is an important variable in that the greater the BA the greater is the potential supply of solutes. In addition BA will also influence the hydrological response of a sub-basin, thereby influencing supply and delivery as well as the concentration of solutes to the channel. Basin slope (BS) will primarily affect the residence times of throughflow and surface storm runoff and therefore the concomitant solute concentrations in stormflow and baseflow or lowflow conditions. Greater basin slope will tend to lessen residence times and concentrations. By the same token the form ratio (FR) will also account for the time taken for runoff and throughflow to reach the channel. The form ratio describes the linearity and narrowness of the basin and a low value

TABLE 5.9

GEO-URBAN VARIABLES

A. GEOMORPHIC-PHYSICAL GROUP

1. BA = basin area (km^2)
2. BS = average basin slope (^{o})
3. FR = basin form ratio
4. FC = forest cover per sub-basin (km^2)
5. G = area of basin covered by gravel (%)
6. T = area of basin covered by till (%)
7. BSA = base saturation of A soil horizon (%)
8. BSAB = base saturation of A + B soil horizons (%)
9. BSC = base saturation of C soil horizon (%)
10. QSP = mean spring discharge per sub-basin (l/s)
11. QST = mean storm discharge per sub-basin (l/s)
12. QLO = mean lowflow discharge per sub-basin (l/s)

B. URBAN GROUP

13. B = number of buildings per sub-basin
14. IA = impervious area per sub-basin (1000's m^2)
15. RL = road length per sub-basin (km)
16. SC = street crossings and road ends per sub-basin
17. SL = sewer length per sub-basin (km)
18. P = population per sub-basin (100's)

indicates a relatively narrow basin from which water will drain quickly with resulting minimal contact time with solute sources.

Forest cover (FC), per cent gravel and per cent till are three variables relating to basin cover. Greater FC will result in the increased supply of certain solutes in throughfall from the forest canopy and in the throughflow and runoff from the forest litter during storm events. As well FC encourages infiltration and subsequent soil weathering and biomass decay resulting in the supply of metallic cations and anions such as HCO_3^- to the soil and groundwaters. Thus FC may control solutes in both the wet conditions of springflow and stormflow as well as in the dry conditions of baseflow. Percent gravel and till are included in the list of explanatory variables because they will likely affect solute supply and delivery. The different textural qualities of these two materials will influence their water-holding capabilities and sorptive capacities, thus having an effect on residence times of aggressive ground and soil waters as well as weathering rates. In terms of chemical composition they are mineralogically similar (Harrison, 1971) and from this point of view would not introduce spatial variance into the solutes in the watershed.

The actual vertical variation in the chemistry of the soils in the sub-basins is represented in the three explanatory variables, base saturation in the A horizon (BSA), the combined base saturation of the A and the B horizons (BSAB) and the base saturation of the C horizon (BSC). The BSA will likely affect streamwater solute concentrations under stormflow conditions when subsurface stormflow passes

through the upper soil horizons and delivers available ions to the channel. Likewise under greater magnitude storm events, subsurface stormflow reaches down to the B horizons, then BSAB variance may reflect a corresponding variance in channel solutes. Under lowflow or baseflow conditions, spatial variance in the % BS of the C horizons may well relate to spatial variance in streamwater quality over the watershed.

Finally mean discharge values for springflow (QSP), stormflow (QST) and lowflow (QLO) are considered. In Section 5.3 earlier, discharge and discharge-related parameters were instrumental in explaining a great deal of within-site variance. There is no doubt that site characteristics also determine the qualitative and quantitative aspects of these discharge parameters so that discharge must be considered here again as a function of site in producing possible between-site variance in solutes.

The degree of urbanization must also be considered as a possible explanation for downstream solute variance. Several parameters have been developed to enter into relationships with the solute means at the sampling sites. General indices of urbanization are number of buildings (B) and population (P) representing landuse and the production of waste, litter, sewage and other sources of solutes. Impervious area (IA) is chosen because of its effective production of generally dilute runoff volumes which tend to reduce solute concentrations in channel waters. Also greater IA values suggest lower infiltration of aggressive rain water into soil horizons, thereby reducing weathering rates in the underlying soils.

Road length (RL) and street crossings over the channel (SC) will likely control the road salt supply and delivery to the channel. Sewer length (SL) may bear some relationship to the solute concentration derived from sewage or septic tank effluent and therefore has also been included. Thus, whereas each of the urban parameters is in itself a measure of urbanization, they each reflect slightly different aspects which may provide variations in solute content of chemical waters.

The above geo-urban variables are to be used in developing regression relationships in an attempt to explain the downstream variation in the solute contributions from the sub-basins displayed in Figure 5.6, p. 207. Again as was done in Section 5.3.2, the variables are analyzed by factor analysis for common variance and internal associations. The results of the factor analysis are given in Table 5.10 below. Only four factors were derived, explaining 94.0 per cent of the variance which suggests a large degree of common variance in the variables.

Factor 1 appears to be a measure of urbanization. The high loadings of the physical variables BS, T, BSA, QSP and QST indicate that Factor 1 is urban. An examination of Table 3.12 p. 118 confirms the low slopes in the very urbanized downtown, the absence of T and the existence of large magnitude mean springflows and stormflows. Likewise the high and positive loadings of all of the urban variables support the interpretation of Factor 1 as an urban factor. Factor 2 is related to the degree of "ruralness" as described by the geo-urban

TABLE 5.10

FACTOR ANALYSIS OF GEO-URBAN VARIABLES

VARIMAX ROTATED FACTOR MATRIX

	FACTOR 1 (URBAN)	FACTOR 2 (RURAL)	FACTOR 3 (URBAN 2)	FACTOR 4 (SOIL)
BA	-.12996	.91744	.23331	-.15761
BS	-.61908	-.70659	.12994	-.07943
FR	-.10595	.78140	-.55436	.14208
FC	-.32628	.85802	-.37937	-.03931
G	-.19154	.24945	-.97478	.17547
T	-.77929	.10724	.55688	-.14752
BSA	.90841	-.04939	.26299	.24058
BSAB	.06286	.09890	.05915	.97526
BSC	-.06842	-.18356	-.18356	.91764
B	.92639	-.06734	.35533	-.06414
IA	.87141	-.00541	.47837	.01534
RL	.79370	.02792	.57365	.05814
SC	.67966	-.53106	.16879	-.23415
SL	.72657	-.11241	.63211	.14865
P	.84562	-.33050	-.00222	-.32931
QSP	.70486	-.00212	.02591	-.66769
QST	.92568	-.11296	-.00223	-.31163
QLO	.17434	-.07076	.92765	-.00270

% variance explained = 94.0

variables. High positive loadings on FC, FR, BA and the lack of significant loadings by the urban variables indicate that this factor is essentially describing the rural setting. Factor 3 is difficult to interpret; however, it may be also related to some degree of urbanization. High and negative loadings from G and FR coupled with high and positive loadings from QLO, SL, RL and IA suggest an urban connotation for this factor. Finally, Factor 4 appears to be associated with soil base exchange in the B and C soil horizons. In terms of contribution to variance, Factor 1 is highest at 48% with Factor 2 at 18% and the remainder split between Factors 3 and 4. Thus it would seem that the majority of the variables can be equated in a positive or negative way to the degree of urbanization or degree of ruralness.

5.4.3 Results

The geo-urban variables selected and discussed in the last section were entered into a series of bivariate relationships with the mean solute concentrations at the sampling sites for springflow, stormflow and lowflow. Values for Site 7 were not entered because of the anomalous effects of the landfill at this site. None of the geo-urban variables used to explain solute variance are sensitive to landfill effects; therefore, inclusion of Site 7 data would only serve to reduce the efficiency of relationships describing downstream solute variance. The results of these regressions are given in Table D2 of Appendix D. Many significant relationships exist and it is obvious from the R^2 values in Table D2 and the factor analysis of the previous section

that many of the independent variables are in fact explaining similar variance in the dependent solute variables. Thus multiple stepwise regressions were done using the significant variables from the bivariate relationships in Table D2. The results of these multivariate analyses are summarized in Table 5.11.

The relationships in Table 5.11 are mostly linear in nature but for some ions, more complex reciprocal, logarithmic and exponential relationships are required to model their variance. The degrees of explanation (R^2) are generally quite good ranging from 0.52 up to 0.96. For some solute parameters the same geo-urban variable explains their variance over all three flow regimes albeit to various degrees; whereas, for others, different controlling variables appear to be operating in the three flow regimes. Thus it would appear that the solutes behave somewhat differently at a site during springflow, stormflow and lowflow.

The physical geo-urban variables form the majority of the relationships. Those related to ruralness as defined by the factor analysis earlier (such as FR and FC), form relationships with those solutes which were identified in discussions of temporal variance earlier as being derived primarily from subsurface sources (i.e. Ca^{++} and HCO_3^-). Other solutes form relationships with the reciprocal of urban variables which in effect suggest that they also are related to ruralness as well. A more intensive inspection of these relationships is conducted in the following sections.

TABLE 5.11

SUMMARY OF SOLUTE PARAMETER RELATIONSHIPS WITH WATERSHED (GEO-URBAN) VARIABLES

SOLUTE PARAMETER	SPRINGFLOW RELATIONSHIPS	SIG.	R^2	STORMFLOW RELATIONSHIPS	SIG.	R^2	LOWFLOW RELATIONSHIPS	SIG.	R^2
pH	$pH = 6.78 - 0.62\ RL^{-1}$	**	0.72	$pH = 7.38 - 0.59\ RL^{-1}$	***	0.89	$pH = 7.54 - 0.57\ RL^{-1}$	***	0.87
TDS	$TDS = 97.65 - 1.18\ RL^{-1} - 1.14\ T$ (-0.59) (-0.99)	***	0.94	$TDS = 2.53 + 0.95\ G$	*	0.52	$TDS = 13.99 + 73.28\ RL^{-1}$	*	0.62
Cl^-	$CL = 34.3 - 0.43\ T$	**	0.84	$CL = 28.26 - 0.39\ T$	**	0.85	$\log CL = 1.16 - 0.07\ BA$	**	0.64
Na^+	$NA = -5.20 + 510.89\ T^{-1}$	**	0.84	$NA = 1.34 + 15.22\ RL^{-1}$	**	0.78	$NA = 5.68 - 0.52\ BA + 16.30\ RL^{-1}$ (-0.50) (0.87)	**	0.90
K^+	$K = -0.18 + 5.86\ RL^{-1}$	**	0.86	$K = -0.12 + 0.05\ G$	**	0.85	$K = -0.19 + 6.70\ RL^{-1}$	***	0.90
HCO_3^-	$ALK = 0.20 + 0.86\ FC$	**	0.86	$ALK = 0.11 + 1.61\ FC$	***	0.96	$ALK = 2.54 + 1.59\ FC$	***	0.93
H+	$HD = -3.12 + 19.68\ FR$	***	0.84	$HD = -3.24 + 23.97\ FR$	***	0.93	$HD = -2.00 + 26.89\ FR$	***	0.87
Ca^{++}	$CA = -1.24 + 17.30\ FR$	**	0.73	$CA = -2.60 + 22.25\ FR$	***	0.95	$CA = -2.00 + 25.83\ FR$	**	0.81
Mg^{++}	$MG = -0.03 + 0.30\ FR + 0.01\ FSC$ (0.47) (0.65)	*	0.65	$MG = 0.87 - 0.36 \log P$	**	0.63	$MG = 0.11 + 2.95\ P^{-1}$	**	0.79

* significant to .05 ** significant to .01 *** significant to .001

(0.92) Beta weight

(a) Total Dissolved Solids

Relationships for TDS over the three flow regimes are varied. Best explanation of TDS variance is given by RL (road length) and T (% till) in the spring in a multivariate equation. In spring, values of TDS increase with increasing RL and decrease with increasing T. The relationship to RL is obvious in that increased RL supplies greater amounts of road salt which forms an important part of TDS load in spring (see earlier discussions, p. 161). However, the relationship to T is more difficult to interpret. Inspection of Figure 5.6 and Table 3.12 (p. 118) suggests that there is a real relationship between TDS and T but that it is not perfect. Large values for T exist for sub-basins in both the urban and rural setting and T is clearly not related exclusively to either the rural or urban setting (see factor analysis result, Table 5.10 earlier). Nevertheless rural values for T are slightly greater and therefore the relationship for TDS in springflow signifies a decline in average TDS with increasing ruralness as represented by rising values of T. Spring trends in TDS represented in Figure 5.6 as well as values in Table 5.3, p. 158, tend to confirm this interpretation.

During stormflow, average TDS concentrations increase with increasing per cent of gravel (G) in the sub-basins. In this case it is obvious that average TDS values increase in the rural setting. It is not likely that this relationship to gravel has any generic significance but is likely related to the ability of the rural environment to generate solutes generally.

Under lowflow conditions mean TDS concentrations are explained by the reciprocal of the number of kilometers of road (RL), As RL increases towards the mouth of the creek (Oak Street) then the mean TDS concentrations decrease and the rate of decrease is considerably greater during lowflow periods. Thus it would seem that in all three flow regimes mean TDS concentrations diminish downstream from the rural to urban sites. The urban sites produce generally less solute load than the rural sites except during the initial spring flush (see Table 5.3 again).

(b) Chloride

Mean, springflow chloride concentrations increase as per cent till (T) decreases. The geo-urban variable, T, has been identified with the rural setting in the Chippewa Watershed; therefore, as T decreases downstream mean Cl^- concentrations increase. The same relationship holds in stormflow as well except that the rate of increase is somewhat less than in spring (comparing the b statistics) and the magnitude, is also less (comparing the intercepts). This difference from springflow to stormflow is likely the result of the diminishing supplies of Cl^- in the urban setting as noted in earlier discussions of temporal variation in Cl^-. During lowflow the mean value of Cl^- at a site is related to the basin area (BA). In fact as BA grows larger mean Cl^- values tend to grow smaller. This relationship is confirmed in Figure 5.6, p. 207 , where Site 2 and Site 6 show drastic reductions in Cl^- concentrations and also concomitant increases in area. This relationship tends to suggest a dilution of Cl^- with increased area

which could well be the case because these two sites drain large areas of limited development (see Figure 3.1, p. 58). Thus the waters provided in lowflow from more distant parts of the watershed would tend to dilute Cl^- supply from the developed portions adjacent to the creek. This conclusion is, in part, supported by the larger baseflows at Sites 2 and 6 in Figure 5.6, p. 207. Thus BA may well mirror a hydrologic control in this case.

(c) Sodium

Sodium also displays a negative relationship with T in springflow conditions suggesting as in Cl^- above that the urban setting generally supplies greater Na^+ concentrations than the rural setting in springflow, a fact confirmed by Table 5.3, p. 158. However, the relationship is not perfect and Site 8 (see Figure 5.6, again) displays a very high Na^+ mean value but low T value. Thus it is doubtful again that T is generically affecting Na^+ and it may well be a spurious correlation.

During stormflow Na^+ means vary with respect to road length (RL). As RL increases, Na^+ decreases so that here Na^+ concentrations are greater at the rural sites where road length is small. This suggests a surficial source of Na^+ available to stormflow in the rural setting. Such a source could be in the litter biomass or from throughflow from upper soil horizons near roads. It is apparent that the urban surficial sources have been exhausted by spring runoff in that urban values tend to be lower except for Site 4 (see Figure 5.6). These stormflow relationships appear to be similar to those developed in Figure 5.4, p. 176 in discussions of temporal variance.

Lowflow Na^+ means relate to both BA and RL negatively. As BA increases, Na^+ concentrations fall suggesting a similar generic relationship as for Cl^- above. With increasing RL, Na^+ concentrations fall as well so that in result mean Na^+ concentrations are largest for rural settings but tend to be reduced where BA is large and dilution of near-channel sources occurs. As well the increase from urban to rural is greater for lowflow than for the stormflow relationship.

(d) Potassium

Springflow K^+ is negatively related to RL so that as RL decreases K^+ increases. This relationship seems reasonable in that greater rural sources for K^+ in springflow are available from forest litter. In fact this relationship mirrors the findings of the springflow temporal variations discussed earlier (see Table 5.2, p. 156). On the other hand, stormflow K^+ variance is described by variance in G which has higher values in rural sub-basins. Thus in stormflow the magnitudes of mean K^+ concentrations at sites is a function of site ruralness as defined by G. Again it is difficult to say if G bears any generic or causal relationship to K^+ concentration variance. Under lowflow conditions, K^+ concentrations again relate negatively to RL indicating that greater mean concentrations occur at rural sites and the magnitude of the b regression statistic indicates that lowflow concentation differences from urban to rural are greater than they were for springflow. Thus supplies of K^+ are rather low in the urban sub-basin especially during lowflow but may be a little larger during the flushing events of springflow and stormflow.

(e) Alkalinity

Alkalinity is positively related to the forest cover (FC) for all flow regimes. Thus as FC increases, mean HCO_3^- concentrations increase. The spread between the urban and rural concentrations is greatest for the stormflow relationship (comparing b statistics) and the least for the springflow, pointing out that during stormflow the rural sub-basins are more effective at producing HCO_3^- than in either springflow or lowflow conditions or conversely urban stormwaters tend to be more acidic than urban spring runoff or urban baseflow. From a perusal of the relationships developed earlier in discussions of temporal variance it would seem that during stormflow, urban runoff is most dilute in HCO_3^- (see Figure 5.3, p. 170) and likely this is the reason for the large spread between urban and rural values shown here.

The relationship of HCO_3^- to FC probably also has causal significance as well. Certainly infiltration and soil CO_2 production are greater in forested areas (as discussed in Chapter II, Section 2.3, p. 15); therefore, more HCO_3^- is produced by the dissociation of H_2CO_3 during mineral weathering or plant decay. Conversely the city has less foliage, compacted soils and more pavement which leads to drier and less aerated soils resulting in a lower production of HCO_3^- especially during lowflow periods.

(f) pH

The pH relationships are all positive with road length (RL) and at first glance these relationships seem to conflict with HCO_3^-

above. However, close scrutiny of Figure 5.6 (p. 207), shows that HCO_3^- generally mirrors pH and FC except at Site 8 where for some reason mean pH values are extremely low for all flow regimes. These extremely low values tend to influence the pH versus RL relationship to create a positive slope which suggests pH operates conversely to HCO_3^-. The relative magnitudes of the spreads between the sites is greatest for springflow and least for lowflow conditions (based on the regression coefficients), a fact which reflects the extreme depression of pH by snowmelt in the spring and rural settings. Both of these phenomena have been discussed in Section 5.3 earlier.

(g) Hardness and Calcium

Both these chemical parameters relate positively to the form ratio (FR) of the sub-basins over all flow regimes. Lowflow relationships for both Hd and Ca^{++} exhibit the largest spread of mean values suggesting a greater difference between the means at rural and urban sites. Form ratios tend to be larger for the rural basins (see Figure 5.6, p. 207) and therefore so are Hd and Ca^{++} mean values. As with HCO_3^- earlier, this relationship here is also likely generic, for it can be argued that larger FR values equate to longer residence of soil and groundwaters in the sub-basins and concomitant higher concentrations of Hd and Ca^{++}.

(h) Magnesium

Magnesium means relate positively to basin form ratio (FR) and base saturation of the C soil horizon (BSC) for springflow. Thus

higher Mg^{++} values occur in sub-basins with greater FR and BSC values. The variance in BSC explains more of the variance in Mg^{++} and inspection of Figure 5.6 again shows that BSC seems to explain the urban variation; whereas, FR contributes to the explanation of the rural variation. The principal source of Mg^{++} in spring meltwaters will probably be forest and street litter and basins with larger FR values will likely be more efficient at removing Mg^{++} from these sources due to longer runoff residence.

Magnesium means are related negatively to population (P) in stormflow and lowflow conditions which suggests that generally large quantities of Mg^{++} are not derived from human sources. However Site 4 is anomalous (see Figure 5.6 again) and does not fit the relationship too well. Generally then, during stormflow and lowflow, Mg^{++} values are greater in the rural sub-basins and are more likely provided by the flushing of the biomass and soil weathering.

5.4.4 Between-Site Variance: A Summary

The solutes studied in this thesis exhibit responses to spatial controls in the watershed and the responses vary due to the different character of the sub-basins as well as due to the different ways in which the sub-basins react to the flow regimes. Generally mean solute values are greater at rural sites except for Cl^{-}, spring Na^{+} and spring and storm TDS which are greater in the urban sub-basins. The relative magnitudes of ionic concentrations do not change a great deal over the three flow regimes and it can be expressed as below.

$$Cl^{-} \quad Ca^{++} \quad Na^{++} \quad HCO_3^{-} \quad K^{+} \quad Mg^{++} \qquad 5.7$$

However the magnitudes of the site means of individual ions do change over the three flow regimes. Generally lowflow values are highest for a given ion except Cl^- and Na^+; whereas, springflow and stormflow values generally reflect more dilute concentrations suggesting that primarily subsurface sources are operating in the Chippewa Watershed.

Urban means tend to be below background for Hd, HCO_3^-, K^+, Ca^{++} and Mg^{++} and above background for Na^+ and Cl^-. Rural means are all higher than background except for those at Site 5 which drains a very rocky, thinly-mantled, steep-sloped basin. These facts relate to lower weathering rates and higher intensities of dilution and flushing (as noted earlier in Section 5.4.3, p. 217) in the urban environment.

Anomalous site means are found at Sites 4, 6 and 7. All chemical parameters except spring Na^+ and K^+ exhibit higher than adjacent urban values at Site 4. Why this is so is difficult to say but discharge values are generally low here and FR and BSC are generally high compared to other urban sub-basins so that the anomalous values at 4 may be a function of more severe weathering or pollution in this sub-basin. Mean values at Site 7 are anomalously high for all parameters except spring Cl^- and are roughly five to eleven times background levels. These anomalous concentrations are attributed to the leachates from the city landfill site entering the channel at this site.

A statistical analysis of the site means using regression analyses identified eight geo-urban site variables which reasonably explained the variance in the mean solute concentrations over the sites. Degrees of explanation (R^2) were high ranging from 0.52 to 0.96. Many of the relationships were strong enough to use as models to predict their

respective solute. Although eight geo-urban variables were required overall to explain the spatial variance in all of the solute parameters over the three flow regimes, the strongest were sub-basin form ratio (FR), forect cover (FC), road length (RL) and per cent till cover (T). Generally the rural variables FC, FR and T formed positive relationships; whereas, the urban variables such as RL tended to form negative relationships. Thus most explanations were due to the degree of "ruralness" of the sub-basins except for spring TDS, Cl^- and spring Na^+ which were related to degree of "urbanness". The explanation by FC and FR is considered to have causal significance in that they control moisture and CO_2 contents of the soils, supply of nutrients in throughfall and litter, and the residence times of water in the basins. Lowflow conditions produce the largest divergence in rural and urban values except for HCO_3^- where the greatest spread occurs during stormflow.

5.5 Chemical Controls

The interactions of the various chemical species studied in Chippewa Creek waters could potentially introduce variance into solute concentrations. Certainly different chemical environments will likely exist in the upland of the watershed in the soils and rocks. Evidence of different soil weathering environments has already been uncovered in the study of the cation exchange capacities of the watershed soils. These differences, due to differential weathering rates in the watershed, will be reflected in the spatial or downstream variations in solute concentrations and this phenomenon has already been discussed in the last section.

The chemical controls which are dealt with here are the possible in-channel controls which are a function of chemical equilibria amongst the dissolved ionic species in the streamwater and/or the exchange of cations with the stream bed material. Saturation and precipitation may result if the various species form pairs which have greater than equilibrium concentrations. This type of chemical activity will exert control on streamwater concentrations. Several theoretical precipitates could occur but some are more likely than others. Garrels and MacKenzie (1967) evaporated spring water from a felsic terrain somewhat similar in composition to the Chippewa Watershed rocks and determined the order of precipitation of solids on concentration of the solution. They found that compounds of Na^+ and K^+ were extremely soluble and did not precipitate even at a concentration factor of 1000. The sulphates and chlorides and hydroxides of these two cations did not form solids to this concentration factor which represented molarities of 0.03 to 0.05 and a pH of 10.00. Thus the precipitation of sodium and potassium salts and compounds is not a highly likely occurrence in the dilute waters of Chippewa Creek where cation and anion concentrations are much below the values cited above. In fact solubilities for KCl and NaCl are 264,000 mg/l and 360,000 mg/l respectively at 25°C and pH 7.0 (Freeze and Cherry, 1979, p. 106), concentrations which are several orders of magnitude above the Chippewa values. Likewise the sulphates of Ca^{++} and Mg^{++} are very soluble and are not likely to produce precipitates in dilute waters. Freeze and Cherry again report high solubilities for these compounds in the order of 2100 to 267,000 mg/l. Conversely

the hydroxides of these cations are highly insoluble and the solubility product ($K_{sp} = [Mg^{++}] \cdot [OH^{-}]^2$) of the marginally soluble $Mg(OH)_2$, is 1×10^{-11} and is not likely present in dilute streamwaters except in very minute amounts at high pH.

Generally the carbonate system is the most important one in producing solute variance in dilute streamwaters through saturation and subsequent precipitation of solids. The species of inorganic carbon present in natural waters is pH dependent and for the range of pH of the water samples used in this research (see Appendix C) the major species is bicarbonate (HCO_3^-) which exists for a pH range from 6.4 to 10.3 (Freeze and Cherry, 1979). This fact is confirmed by the absence of carbonate alkalinity and the presence of only bicarbonate alkalinity in the samples titrated with weak acid in alkalinity determinations (see Appendix A). Thus any possible precipitates will be due to the interactions of the metallic cations and the bicarbonate anion. Generally the bicarbonates are moderately soluble but at concentrations of 120 to 140 mg/l and at pH values over 8.0 (Garrels and MacKenzie, 1967), calcium carbonate may be formed as in Equation 5.8 below from Krauskopf (1967).

$$Ca^{++} + HCO_3^- + OH^- \longrightarrow CaCo_3 + H_2O \qquad 5.8$$

As HCO_3^- concentrations and pH increase the reaction goes to the right, precipitating calcite. In the case of Chippewa Creek, waters seldom achieve pH values greater than 8.0 and never achieve HCO_3^- concentrations of 120 mg/l. As well the presence of NaCl in rather large concentrations would enhance the solubility of $CaCo_3$ even further to reduce.

the likelihood of precipitates forming (Freeze and Cherry, 1979). In addition the solubility of calcite increases by 1.5 times from 30°C to 0°C so that precipitates are even less likely to form in colder waters of early spring or winter.

As mentioned earlier in Section 5.3.5.1 in the discussion of storm period variation, it is apparent that HCO_3^- is in part depressed by the acidity of the rainfall during peak precipitation periods. These depressions are in part the result of buffering by HCO_3^- to consume the excess acidity and in effect this chemical process exerts control on the variance of HCO_3^- concentration. Under acid conditions the HCO_3^- acts as a base (see Equation 2.14, p. 49) to reduce the H^+ concentration and stabilize pH values. Thus some chemical control of H^+ and HCO_3^- concentrations can be expected during early spring or storm events when large volumes of H^+ are introduced quickly into the streamwaters.

Another possible source of solute variance is cation exchange reactions between streamwater and bed materials. As mentioned earlier, Kennedy (1965) has noted significant CEC values for bed sediments in streams. The bed sediment of Chippewa is relatively coarse in texture (see Figure 3.5, p. 68) and could not be expected to have large CEC values. However four bed samples were taken for different discharge conditions over a period of several weeks to determine if CEC of the bed materials varied with respect to streamwater quality. The samples were analyzed using the same techniques as used for the soil analyses described in Appendix B. The results are reported in Table C2 of Appendix C.

As with the soils, Ca^{++} is quantitatively the most important ion adsorbed in the bed materials; whereas, Na^{+} and K^{+} tend to be of minimal values. All CEC cocentration values are greater at Airport Road (the rural site) even though streamwater concentrations are usually smaller. The reason for this difference is unclear but may be related to greater turbulence and consequently better mixing of bed sediment and streamwater at the Airport Road site.

Some common variance appears to be present between the CEC concentrations and the streamwater concentrations and has been examined by regressing the two sets of values. Although correlation coefficients are reasonably high for most relationships, only two proved to be significant and they are listed below.

URBAN: $K_{CEC} = -0.97 + 0.76K_{ST}$ $p = 0.003$ $R^2 = 0.99$ 5.9

RURAL: $K_{CEC} = 6.02 - 1.53K_{ST}$ $p = 0.020$ $R^2 = 0.94$ 5.10

where CEC is the cation exchange capacity concentration
and ST is the streamwater concentration

Thus CEC K^{+} appears to show significant variation with the variance in streamwater K^{+} concentrations and the degree and direction of this variance differs from Airport Road to Oak Street. At Airport Road, bed sediment values decrease with increasing streamwater concentrations suggesting that adsorbed K^{+} is given up during high streamwater concentrations. Why this relationship occurs is again difficult to say and certainly further study is required to make any definitive comments on possible explanatory mechanisms.

At Oak Street the relationship is positive and during high streamflow concentrations, the bed sediment CEC concentrations are higher. This seems reasonable in that excess K^+ would be available to be adsorbed onto the sediment. The rates of adsorption are given by the b statistics of the regressions and in the urban sediment, for every unit increase in streamwater K^+ concentration, a 0.76 increase occurs in the bed sediment. This relationship would suggest that the bed sediment is removing K^+ from the stream but at a constant rate. If this is so then the process will not introduce variability but will tend to produce only a consistently lower magnitude of K^+ concentration. A similar reasoning can be used for the relationship with rural K^+ except that the bed sediments lose K^+ at 1.53 units per unit change in streamwater concentrations.

Thus in view of these relationships, the lack of others and the relative magnitudes in Table C2, it would seem that cation exchange between bed sediment and streamwater is not exerting a great deal of influence on streamwater solute variance in this study. Likewise for the discussion of chemical controls in general, it appears that little control is exerted by chemical equilibria or by biotic respiration (see Section 5.3.6(f), p. 201), except for minor buffering during storm events, on the variation of solute concentrations in Chippewa Creek waters.

5.6 Solute Export

Solute export rates and yeild were calculated for the rural and urban sub-basins in the Chippewa Watershed for a period of approximately

seven months (March 26 to November 9, 1976). Mean solute concentrations at the two sites, Airport Road and Oak Street, were multiplied by the corresponding mean discharges for springflow, stormflow and lowflow to obtain solute discharge rates. Total loads were computed by multiplying discharge rates and the total time over which springflow, stormflow and lowflow occurred (taken from continuous gauge records). Yields were computed by dividing total loads by sub-basin area for the urban and rural sub-basins. The results with the urban/rural differentials are given in Table 5.12.

Magnitudes of urban discharge generally overpower the relative differences of concentration values for the solutes between urban and rural sites. Where rural concentrations are larger, generally the solute discharge rates and resulting loads are nearly equal or greater from the urban setting except for springflow and stormflow K^+, HCO_3^- and Ca^{++}. Discharge rates and loads amongst the ions, of course, display the same relative magnitudes as the concentrations. When yields are calculated, all solutes except HCO_3^- display greater yeilds from the urban sub-basin than from the rural. Thus solute export in general is greater from the urban setting in all flow regimes. The largest differentials are found for Cl^- and Na^+ and surprisingly also for Mg^{++}; the former coming primarily from road salts and the latter coming from some likely pollution source in the urban environment. Only HCO_3^- with such low urban concentrations, has greater yields in the rural sector again underscoring the relative low vegetative cover and infiltration in the city. Differentials overall, range from a low of 1.20 for springflow K^+ to a high of 6.22 for lowflow Cl^- generally in favour of the urban setting.

TABLE 5.12.

SUMMARY OF SOLUTE EXPORT

SOLUTE PARAMETER		RURAL (AIRPORT RD.)				URBAN (OAK ST.)				DIFFERENTIAL	
		$\bar{x}$ (mg/l)	DISCHARGE (l/s)	TOTAL LOADS (tonnes)	YIELD (tonnes/km^2)	$\bar{x}$ (mg/l)	DISCHARGE (l/s)	TOTAL LOADS (tonnes)	YIELD (tonnes/km^2)	TOTAL LOADS (tonnes)	YIELD (tonnes/km^2)
Na^+	1	99.09	18.92	569.00	23.07	96.92	293.06	911.53	61.63	U = 1.60R	U = 2.67R
	2	116.40	101.23	698.96	28.02	92.31	98.34	671.91	45.43	R = 1.03U	U = 1.67R
	3	115.67	11.53	113.57	4.67	94.24	25.43	230.78	15.61	U = 2.03R	U = 3.39R
Cl^-	1	50.89	57.03	177.38	7.19	55.65	168.27	523.39	35.39	U = 2.95R	U = 4.92R
	2	24.86	21.62	147.57	5.98	27.09	50.98	347.97	23.53	U = 2.36R	U = 3.93R
	3	24.46	2.44	24.03	0.97	36.42	9.66	89.20	6.03	U = 3.71R	U = 6.22R
K^+	1	30.85	38.49	119.73	4.86	28.57	86.39	268.71	18.17	U = 2.24R	U = 3.74R
	2	18.19	15.81	107.91	4.38	14.45	37.19	185.59	12.55	U = 1.72R	U = 2.87R
	3	21.46	2.14	21.03	0.86	21.44	5.33	52.51	3.55	U = 2.49R	U = 4.13R
Si^+	1	5.35	9.69	30.15	1.22	2.30	6.95	21.63	1.51	R = 1.39U	U = 1.24R
	2	6.19	5.38	36.75	1.49	1.61	3.03	20.68	1.49	R = 1.78U	U = R
	3	6.16	0.61	6.01	0.24	2.43	0.60	5.95	0.40	R = 1.03U	U = 1.67R
HCO_3^-	1	13.64	35.16	78.27	3.17	2.18	6.59	20.50	1.39	R = 3.82U	R = 2.28U
	2	27.06	23.53	160.61	6.51	5.68	10.69	72.97	4.93	R = 2.20U	R = 1.32U
	3	37.48	3.74	36.84	1.49	15.11	3.76	37.01	2.50	U = 1.01R	U = 1.68R
Ca^{++}	1	24.90	45.97	142.98	5.80	13.77	41.64	129.52	8.76	R = 1.10U	U = 1.51R
	2	33.56	29.01	198.03	8.03	14.73	27.72	189.20	12.79	R = 1.05U	U = 1.59R
	3	41.98	4.18	41.17	1.67	20.99	5.23	51.32	3.47	U = 1.25R	U = 2.08R
Mg^{++}	1	0.80	1.48	4.59	0.19	1.19	3.60	11.19	0.76	U = 2.43R	U = 4.00R
	2	1.50	1.30	8.90	0.36	1.11	2.09	14.26	0.96	U = 1.61R	U = 2.67R
	3	3.06	0.31	3.05	0.12	2.04	0.51	5.02	0.34	U = 1.65R	U = 2.83R
$\bar{Q}$	1	1846.18 l/s				3023.73 l/s					
	2	869.71 l/s				1881.86 l/s					
	3	99.69 l/s				248.65 l/s					

where 1 = Springflow 2 = Stormflow 3 = Lowflow U = Urban R = Rural

Likens et al. (1967) have calculated solute budgets for an undeveloped watershed underlain by gneiss in New Hampshire. Their mean total yields over the year 1963-64 for Ca^{++}, Mg^{++}, Na^{+} and K^{+} are 4.0, 1.3, 2.9 and 0.9 tonnes/km^2 respectively. By comparison the rural Chippewa values are all larger in springflow and stormflow but are consistently smaller in lowflow. Likewise in the urban setting springflow and stormflow values are much greater especially Mg^{++}. Urban lowflow yields for Ca^{++}, K^{+} and Mg^{++} are lower but is greater for Na^{+}. Thus considering that the Chippewa data represents only seven months of export, it is likely lowflow values would equal or exceed those reported by Likens et al. and clearly the springflow and stormflow values are much greater from both rural and urban settings. Compared to an undeveloped forested watershed, the Chippewa Watershed is apparently exporting greater solute volumes especially during spring and storm events--likely a function of the flushing of anthropogenic sources of solutes.

A comparison of spring values to similar solute yields reported for the Randboro Brook Basin by Chyurlia (1976) shows again that the Chippewa yields are high. For the Randboro Basin (spring 1972), a rural partially farmed basin, maximum Ca^{++}, Mg^{++}, Na^{+} and K^{+} yields were 3.23, 0.48, 0.13 and 0.45 tonnes/km^2 respectively. Of these yields only Mg^{++} is greater than the Chippewa values in the rural setting and all are less than Chippewa values in the urban setting. Thus it would seem that generally solute yields are relatively high for the Chippewa Watershed in the rural sector and well above background in the urban sector.

Urban Cl^- values compare favourably with those determined by Wulkowicz and Saleem (1974) for the Salt Creek Basin in Chicago. Maximum chloride yield was computed to be 41.2 tonnes/km^2 over a six-month period which is relatively close to the Chippewa values of 35.39 for the springflow. However the Salt Creek yield was considered to be only 62 per cent of the Cl^- supplied and the rest was removed in groundwater flow. Thus the total yield for the Salt Creek Basin would be 57 tonnes/km^2 which is slightly less than the total of 65.0 tonnes/km^2 for the urban sector of the Chippewa Watershed.

CHAPTER VI

Conclusions

6.1 Introduction

The purpose of the research presented in this thesis is developed explicitly in Chapter I, Section 1.2.1 where it is stated that the purpose is "to investigate and to explain the variability and the nature of selected solute outputs from differing human and physical environments within an established urban setting". To this end both temporal and spatial solute variance have been investigated by the study of samples collected over eight sites both urban and rural during three flow regimes of springflow, stormflow and lowflow. The first conclusion must be that there is definitely both temporal and spatial variance of solutes in Chippewa Creek waters. Moreover this variance is controlled principally by hydrologic conditions and solute supply which are, of course, both functions of the physical and human character of the sub-basins studied. Solute responses are often quite different between the urban and rural sub-basins from the viewpoint of magnitudes, explanatory variables and intensities of process. Differences also occur in solute magnitude and response at the same site over the three flow regimes mentioned above. Thus solute behaviour in Chippewa Creek waters is controlled by the complex interaction of hydrologic events, solute supply and sub-basin character all of which change over either or both time and space. These general conclusions are expanded in the sections below.

6.2 Hydro-Temporal Solute Variation

Hydro-temporal variance can be introduced by hydrometeorological, seasonal, diurnal, chemical and biological factors. In this study chemical and biological factors play insignificant roles in promoting solute variation within the stream channel itself. More important are hydrometeorological, seasonal and diurnal controls of which hydrological overpowers all. The hydro-temporal solute variance has been analyzed for two sites, urban (Oak Street) and rural (Airport Road) over three flow regimes. Statistical relationships formed between the solute parameters and a series of hydrological and temporal variables indicate that, overall, the within-site solute response is a function of one or several of dilution, flushing, supply and exhaustion processes. The extent of these processes vary over the three flow regimes, generating solute responses, which vary from springflow, through stormflow to lowflow and between the rural and urban settings as well.

6.2.1 Springflow

In the spring period, Cl^- and Na^+ concentrations dominate the urban setting and Ca^{++}, Mg^{++}, HCO_3^-, and K^+ concentrations dominate the rural setting. Variability is related to the flushing of solutes supplied from primarily surficial sources (i.e. Cl^-, Na^+, K^+) and dilution of solutes supplied from primarily subsurface sources (i.e. Ca^{++}, Mg^{++}, HCO_3^-). Generally the intensities of flushing and dilution are greatest in early spring under very wet watershed conditions and then they diminish as spring runoff dries up. Exceptions are the intensities of dilution for urban Na^+ and K^+ and the intensity of flushing

for urban HCO_3^- which are all greater for late spring suggesting that these ions are more sensitive to drier conditions. The strengths of these relationships are relatively low overall but are marginally better for the rural sub-basin indicating a more controlled and orderly solute response than in the urban environment. The general lack of good statistical explanation is attributed to first flush effects in early spring and chemograph lags.

Major differences occur in both the magnitudes and the behaviours of ions between the rural and urban sub-basins. In early spring concentration values for Cl^- and TDS are generally larger for the urban environment and the intensities of process are greater by about 8.4 and 1.4 times respectively, especially for those ions exhibiting flushing behaviour. However, Na^+ and K^+ are the exceptions and display greater fluxes in early spring in the rural environment. Ionic concentrations diluted in early spring (HCO_3^-, urban K^+, urban Na^+), all display greater magnitudes of dilution in the rural sub-basin by about 24, 2300 and 900 times the urban rates. Thus based on the analysis of the solute data for the springflow period, it is obvious that there are apparent differences in the magnitudes of solute concentrations and the strengths and directions of their response to hydrologic controls both over the spring season and between the rural and urban environments.

6.2.2 Stormflow

Stormflow solute variance has been analyzed by scrutiny of a single storm event and by a statistical analysis of several storm events.

For the single storm event magnitudes of Cl^- and Na^+ dominate the urban environments and magnitudes of Cl^- and HCO_3^- dominate the rural setting. Concentrations of K^+ and Ca^{++} are generally greater in the rural sub-basin; however, K^+ displays a sharper and greater peak under urban conditions. Rainfall itself is not a significant source of solutes but does contribute considerable acidity. All solutes except rural Ca^{++} display dilution from pre-storm to post-storm values. However the complexity of in-storm solute variance defies a simple dilution explanation and this complexity is analyzed as a distinct flushing response interrupted by almost instantaneous dilution by rainfall peaks and latter storm dilute runoff. Hypothetical chemograph lags of the flushing effects determined by extrapolation of the solute curves, underscore the differences between urban and rural solute responses. Rural solute peaks generally coincide with hydrograph peaks except for Na^+ and Cl^- which peak about 7.5 hours prior to peak flows. On the other hand, urban solute peaks generally occur from 3.0 to 7.0 hours prior to peak flow although the Na^+ and Cl^- peaks occur about 5.5 hours prior to peak flow--somewhat slower than their rural counterparts. These rural-urban differences are thought to be related to the differing natures and locations of the solute supplies and the times of concentration for runoff to the stream channels in the rural and urban environments. Certainly rural dilution responses are generally more subdued in concert with a more subdued hydrological response. In addition the dilution response is often dampened by the greater supply of solutes (HCO_3^-, for example) in the rural environment. Where solutes are flushed and in short supply

(Cl^-, for example) rural response is more dramatic and short-lived. Recovery of solute concentrations is very slow in both urban and rural settings beginning about two days after the storm event in each case.

Hysteretic effects are evident in the single storm data. Solute rating trends display a complex series of loops throughout the storm which indicate the presence of positive (flushing) and negative (dilution) hysteresis. Urban trends are invariably more complex for all ions, exhibiting many tight loops and changes of direction. This complexity is related to the variability and lifespans of the various sources of solutes in the urban environment as well as to the dilution capabilities of the precipitation peaks. Rural trends display a more orderly pattern suggestive of a more homogeneous and regulated solute supply. Thus it is apparent that storm period solute response differs from ion to ion and from the urban to rural settings in sympathy with changing hydro-meteorological conditions tempered by supply and exhaustion effects and antecedent conditions.

Statistical analyses of post-peak stormflow data collected over two years reveals that post-peak solute responses are related to antecedent conditions such as stormflow magnitudes, watershed wetness and state of solute supply as well as the elapsed time from storm peak over which dilution or recovery occurs. In the rural sub-basin all solute parameters exhibit dilution at near peak-flow conditions but rebuild with drier conditions. Likewise urban parameters display the same relationship except for K^+ and HCO_3^- which exhibit strong solute flush peaks with large concentrations near to storm peaks which diminish with

storm recession. Urban solute fluxes are greater for surficially derived solutes such as Cl^- and to some extent Na^+ by 3.0 to 5.4 times those in the rural environment. Conversely the solutes generally associated with ruralness (K^+, HCO_3^-, Ca^{++} and Mg^{++}) exhibit greater fluxes in the rural setting by 3.4 to 124.0 times the urban values. Thus it is apparent that stormflow variance is very complex. It differs from ion to ion and from urban to rural in intensity and direction.

6.2.3 Lowflow

Lowflow concentrations are greater than those for stormflow or springflow except for Cl^- and Na^+. All ions exhibit greater magnitudes in the rural sub-basin likely due to greater soil and rock weathering rates and the presence of a sanitary landfill operation. Solute variance appears to be controlled by antecedent stormflow magnitudes, watershed wetness, minor precipitation events and the supply or exhaustion of ionic species such as Cl^- as defined by time from spring breakup. The first two controls affect water table elevations and subsequent dilution and delivery of solutes to the stream channel. The third affects solute concentrations in the channel, especially in the urban setting and the fourth defines a diminishing supply of Cl^- as time from spring increases. These relationships are generally linear being stronger in the rural and for the two multivariate cases. Urban relationships are weaker due to likely stochastic events which occur in urban environments.

Overall, the intensities of processes operating to produce variation are weaker than those seen in springflow and stormflow, especially for Cl^-. Again those ions with surficial sources (Cl^-) exhibit flushing responses; whereas, those with normally subsurface sources display dilution response. Urban flushing and dilution rates are greater than those in the rural setting by 1.2 to 8.0 times for all comparable ions except HCO_3^- under relatively wet watershed conditions. Bicarbonate flux during these conditions is two times greater in the rural setting. Generally the urban to rural differentials of the rates of processes causing solute variance are much less than for springflow or stormflow, indicating that during lowflow the intensities of these processes are closer to being equal. For example, the maximum urban to rural differentials for Cl^- range from 9.0 for springflow through 4.0 for stormflow to 3.6 for lowflow. Thus it is apparent that lowflow solute responses are different from those during springflow and stormflow and the intensities of these responses vary between urban and rural settings.

6.3 Spatial Solute Variation

Spatial or between-site solute variance is produced by the differing physical and anthropogenic character of the sub-basins supplying water and solute to the Chippewa Creek channel. Thus spatial variation in downstream solute load can be introduced by spatial diversity of such physical aspects as forest cover, geology, soils and geometric properties of the sub-basins. In addition various degrees of urbanization and characteristics of landuse will also introduce spatial

variance to solute concentrations downstream. In this study, differing geology is discounted as a source of variance because the basin is underlain generally by similar rock type. Thus eight sites along the creek have been sampled to determine if downstream solute variability exists in the creek and it is concluded from the analyses of the data that the solutes studied do exhibit spatial variation in concentration along the creek. Furthermore this variance differs over the three flow regimes, springflow, stormflow, and lowflow, because of the differing sub-basin response to these different hydrologic conditions.

Generally mean solute values are greater at rural sites except for Cl^-, spring Na^+ and spring and storm TDS, all of which are greater at the urban sites. The relative magnitudes of ionic concentrations do not change a great deal over the three flow regimes. Chloride is supplied to the creek during all flow regimes in relatively large amounts and since the local rock has little or no chloride, all Cl^- is supplied by road salting or waste disposal with very minor amounts supplied by rainfall. Generally lowflow solute concentration values are highest for a given ion except for Cl^- and Na^+; whereas, springflow and stormflow values generally display more dilute concentrations suggesting that primarily subsurface sources and controls are operating in the Chippewa Watershed. Sodium and Cl^-, derived from surface sources, are highest in springflow but persist for lowflow as well due to infiltration at road sides.

Urban mean concentrations for Hd, HCO_3^-, K^+, Ca^{++} and Mg^{++} are below surface water background values and above background for Na^+

and Cl^-. Rural means are all higher than background surface values except those at Site 5 which because of its steep physiography and lack of cover, produce little solute load.

Anomalous site means are found at Sites 4, 6 and 7. All solute parameters except spring Na^+ and K^+ exhibit greater than adjacent urban values at Site 4, which is thought to be due to either accelerated weathering or soil pollution. Mean values at Site 7, below the landfill operation, are anomalously high for all parameters except spring Cl^- and are roughly five to eleven times background levels of surface waters.

A statistical analysis of the site means using regression analyses identified eight geo-urban variables which reasonably explained the spatial variance in the mean downstream solute concentrations. Strong relationships were found to exist (R^2 values from 0.52 to 0.96) between the watershed variables and the solute means, strong enough in some cases to use as predictive models. The strongest predictors are sub-basin form ratios (FR), forest cover (FC), road length (RL) and percent till cover (T).. Generally the rural descriptors (FR, FC and T) formed positive relationships; whereas, the urban predictors such as RL tended to form negative relationships. Thus most explanations are due to the degree of "ruralness" of the sub-basins especially for ions derived from primarily subsurface sources (i.e. Ca^{++}). On the other hand spring TDS, Cl^- and spring Na^+ were all related to the degree of urbanization. The explanation by FC and FR is thought to have causal significance in that they control moisture and CO_2 contents of the soils,

supply of nutrients in throughfall and leaf litter and the residence times of water in the sub-basins. Lowflow conditions produce the largest divergence in rural and urban values except for HCO_3^- where the greatest spread occurs in stormflow. Thus the spatial diversity of watershed character is definitely responsible for corresponding spatial variation in the solutes of Chippewa Creek.

6.4 Solute Export

Solute export is greater from the city environment for all sites and over all flow regimes except springflow HCO_3^-. In the city springflow loads and yields are generally highest for surficially derived solutes such as Na^+ and Cl^-; whereas, stormflow values are the highest for Ca^{++}, HCO_3^- and Mg^{++}. Basically the same relationship holds true for the rural sub-basin as well except that the yields and their spreads amongst the flow regimes are smaller. Thus the urban environment again displays a higher intensity of process, the export of solutes during springflow, stormflow and lowflow periods. In this case the way in which the urban environment reacts to hydrological events to produce greater mean discharges overpowers the comparison between urban and rural on the basis of solute concentration values.

6.5 Contributions of This Research

This research has successfully investigated the nature of solute response in an urban setting and has uncovered the relative magnitudes and directions of solute variance in response to hydro-temporal and spatial controls. It has compared solute response in a

highly urbanized sub-basin to a less urbanized rural sub-basin and in doing so has been able to show the differences in the intensities of processes controlling solute response between the rural and urban setting. Other studies have defined solute relationships in rural environments, some for springflow conditions (eg. Chyurlia, 1976), some for stormflow conditions (eg. Walling and Foster, 1975). None have investigated the urban environment to determine the nature and magnitudes or even the existence of these relationships. Herein lies the principal contribution of this research - the demonstration of marked differences in the intensities of solute responses between the rural and urban environments over springflow and lowflow regimes and the identification and evaluation of spatial and temporal variables controlling these intensities. As well the research also sheds light on the nature of solute loads generated from a watershed located in the shield terrain of Northern Ontario.

In a more utilitarian light, the research has provided insight into the export of nutrients from landfills, the behaviour and export of road salts from the urban environment as well as the behaviour and magnitudes of solutes within an urban environment in general. Certainly this information can be utilized in planning. In order to prevent degradation or to mitigate streamwater quality, it is necessary to first understand the processes which are supplying and controlling the solutes to the channel. This research has uncovered both physical and human controls which affect the magnitudes and behaviours of solutes in urban streamwaters. The results certainly underscore the need for relatively

undeveloped areas such as sub-basin 6 in the Chippewa Watershed to provide the dilution capability to reduce the effects of landfill leachates in downstream waters.

In addition the thesis data itself has proved valuable to planners and engineers in the development and control of the Chippewa Watershed. M.M. Dillon, an engineering firm in Toronto, has used the hydrological data to calibrate flood models. Planners from Environment and Transport Canada have used the water quality data in planning an airport expansion just inside the northeast portion of the watershed. Finally Northland Engineers of North Bay is presently using the hydrologic and water quality data to design a new five-year watershed plan for the North Bay-Mattawa Conservation Authority.

6.6. Further Work

Further work could be directed towards a number of areas. Basically all work could involve more detailed investigation of the various aspects of solute variance uncovered by this thesis research. A more comprehensive study of the urban sources could lead to better statistical explanation. An expansion of the study into the upland sectors of the watershed to monitor the accumulation of solutes by soil waters and groundwaters and runoff would add more insight into the solute variance in the channel itself. Certainly a long-term study of the reaction of the landfill leachates to the frequency and magnitudes of hydrometeorogical events would be of interest. As well, further more detailed investigation of the movement of road salts through the watershed would be of use and finally, the examination of other urban watersheds would be necessary to test out the universality of the relationship uncovered in this research.

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A P P E N D I X A

CHEMICAL LABORATORY ANALYSES

APPENDIX A

CHEMICAL LABORATORY ANALYSES

A1 Introduction

Samples were analyzed in the laboratory for concentrations of suspended and dissolved loads, of pH, and for various chemical parameters like the concentration of chlorides, hardness, alkalinity, sodium, potassium, magnesium and calcium. The first three chemical parameters were measured by titrating samples of creek water; the next three by use of an atomic absorption photospectrometer and the last by calculation.

Samples were stored for varying lengths of time. Some of the 1974 set were kept over the winter months although rough suspended and dissolved load analyses were done on all when they were first collected. There appeared to be reasonable correspondence between values of immediate analysis and later analyses. Nevertheless, some possible error may have been introduced by chemical activity during long storage, affecting particularly the chemical quality of the samples (Brown et al., 1970). For this reason these samples were rejected for analyses.

Not only could chemical activity have occurred within the samples themselves but it is possible that the concentration of sodium and the hardness could have increased by reaction with the glass container. Just how storage time affects chemical quality is hard to predict. The permissible length of storage between collection and analysis depends

on the individual sample, the analysis to be done and the technique of storage (Brown et al., 1970). A test was undertaken to determine the amount, if any, of change in the above parameters through storage. The results are listed in Table A1.

From Table A1 it can be seen that storage effects are responsible for changes in solute values from 5 to 14 per cent on two samples from Sites 2 and 3 on the creek. Decreases are likely due to precipitation over the storage period, especially in the cases of hardness and alkalinity. Increases could be due to reactions with the glass containers, as for sodium, or due to evaporation which may be responsible for the increases in chlorides and to some extent, those for sodium as well. Overall the storage effects appear to be within the same range of error as that involved in the analytical techniques and this storage-induced error would have equal effect over the sites because of the comparative nature of the study.

Samples taken in 1975 and 1976 were analyzed for the most part within the same week of collection. A few sets collected in the autumn were stored for about a month in brown, opaque, polypropylene bottles.

A1.1 Total Dissolved Solids

Total dissolved solids concentrations were determined from the samples by first filtering out the suspended solids using Whatman #50 filter paper in a funnel and vacuum flask set-up. Two 25 ml portions of the filtrate were then pipetted into two dry, pre-weighed aluminum tart tins and placed into a drying oven for 8 to 10 hours at 70 to 80 degrees Celsius. When dry, they were removed, cooled in a dessicator

TABLE A1

ANALYSIS OF STORAGE EFFECTS

Variable	Site 2		%	Site 3		%
	1976	1979	change	1976	1979	change
Chloride Ion	48*	55	+13	44	50	+14
Alkalinity	58	50	-14	53	58	+ 9
Hardness	62	54	-13	58	52	-10
Sodium Ion	24.73	27.26	+10	23.18	25.31	+ 9
Potassium Ion	7.79	7.29	- 6	7.79	7.39	- 5
Magnesium Ion	2.67	2.45	- 8	2.09	1.90	- 9

* Values are in mg/l.

and weighed again. The weight of the total dissolved solids was calculated by subtracting the pan weight from the total weight of solute and tin, and this value in gms/25 ml was converted to mg/l by multiplying by 1000 and then by 40. When the concentrations differed for the two tins they were averaged.

A2 Chemical Analyses

A2.1 Introduction

Chemical analyses were carried out on the filtered samples to determine the concentrations of constituents mentioned earlier in Section 4.2. Both titrametric and atomic absorption techniques were used. Procedures for titration of samples for chloride ion (Cl^-), hardness (principally Ca^{++} and Mg^{++} ions) and alkalinity (CO_3^-, HCO_3^- and OH^-) were taken from American Public Health Association (1965) and the atomic absorption analysis for sodium (Na^+), potassium (K^+), and magnesium (Mg^{++}) ions, done on a Unicam SP 90 single beam, atomic absorption spectrophotometer, equipped with an acetylene-air burner, were carried out in accordance with instructions accompanying the instrument. The theory and procedure of atomic absorption/emission are discussed in detail by Kahn (1968), and Pinta (1972).

Likens et al. (1967), Galle and Angino (1968), Brown et al. (1970), Church (1972), and others have discussed the various and possible interferences which can reduce the accuracy of ion concentration determination by atomic absorption and/or emission. Of note to this study was the possible interference with Mg^{++} determinations by sulphate (SO_4^{--}),

different acids, phosphates, silicate and aluminum (Galle and Angino, 1968). The problem of interference can be solved by adding strontium chloride to the samples. Addition of a 3 per cent solution of strontium chloride ($SrCl_2.6H_2$) was used in this study for initial analyses to reduce possible interference especially in samples collected close to Third Avenue and Oak Street, where occasional sewage was noted. No appreciable improvement occurred in the magnesium determinations so the buffer was not used in subsequent samples. Likely, concentrations of the interfering substances were dilute enough to cause no problem. In fact, Pinta (1972) has stated that interferences with Mg^{++} are a factor only when Mg^{++} concentrations are below 0.1 mg/l, values not encountered in this study.

The problem of interference by acids is encountered principally in a hydrogen-air flame. The use of the hotter acetylene-air flame as was done for this study has eliminated this problem in the determination of Mg^{++}. Effects from Al^{+++}; P, sulphate and silicate were also eliminated by the use of the premixing air-acetylene system (Kahn, 1968).

Other problems outlined by Brown et al. (1970) were dealt with appropriately. Flame temperature was controlled with careful attention to the specifications for the substance in question to prevent ionization effects in the flame. Filtering of the samples was done prior to testing to reduce the effects or turbidity, and care was taken in handling of all apparatus to prevent contamination from the fingers and hands.

A2.2 Titrations

Chloride concentration was determined by the argentometric methods as described in American Public Health Association (1965). A few drops of potassium chromate solution was added to 100 ml of filtered sample. The sample was then titrated with .01 N silver nitrate solution to a faint pink end point. The number of milliliters of silver nitrate used times 3.55 gave the chloride concentration in mg/l. Reproducibility for chloride analyses is $\pm$ 0.30 mg/l for the largest and smallest sample values respectively.

Total hardness, a measure of the concentrations of the chlorides and sulphates of calcium and magnesium, was determined as follows. To 50 ml of filtered sample, 1.0 ml of buffer (Potassium Biphthalate Buffer, .05 M) was added along with five drops of erichrome black T indicator. This solution was then titrated to a blue end point with sodium versenate (Sodium (di) Ethylenediamene Tetraacetate or EDTA). Each milliliter of EDTA used represents 10 ppm (mg/l) of Ca^{++} and Mg^{++} ions. Thus the Ca^{++} concentration was later determined by subtracting Mg^{++} concentration (by atomic absorption/emission) from the total hardness. The precision of this method is rated at 2.9 per cent on a total hardness of 610mg/l (APHA, 1976). At a precision of 2.9 per cent the deviance for the larger and smaller samples in this study would be $\pm$ 1.7 mg/l and $\pm$ 0.06 mg/l respectively.

Alkalinity, representing the concentrations of carbonates, bicarbonates, hydroxides and occasionally borates, silicates, and phosphates, was determined by titration with a standard solution of strong

acid. Four drops of phenolphthalein indicator were added to a 50 ml filtered sample which turned pink if hydroxide and/or carbonate were present. The solution was then titrated until colourless using .02 N sulphuric acid. If no colour change occurred on the addition of phenolphthalein then the methyl orange indicator was added immediately and the sample titrated to the end point with .02 N H_2SO_4. Lack of reaction to the phenolphthalein indicator suggests most of the alkalinity is due to bicarbonate anions. All of the samples analyzed gave this result. Acid used, times a factor of 20, gave total alkalinity in mgs/l. Precision for this analysis is estimated at about $\pm$ 4% or $\pm$ 2.00 mg/l for larger concentrations in the samples analyzed in this study.

A2.3 Atomic Absorption Determinations

Standard solutions of sodium, magnesium and potassium were according to the instructions for the Unicam SP 90 atomic absorption spectrophotometer and consultations with Dr. D. Ledson who is in charge of chemistry at Canadore College in North Bay. After some experimentation, a reasonable set of standards were derived which could be used to calibrate the spectrophotometer for Chippewa Creek water (see Table A2 below). The standards were run before and after each set of samples and transmittance/absorption values of the standards averaged for each run to compensate for a slight drift in the instrument over the time needed to run samples. Sodium and potassium concentrations were determined by emission and magnesium by absorption modes.

Curves were fitted to the values of the standard concentrations and their corresponding per cent transmittance/per cent absorption values

for each set of samples. Per cent transmittance yields linear curves and per cent absorption gives logarithmic curves. The resulting equations were used to determine concentrations of the three elements in each sample. Regression and curve fitting were done by computer on a Decwriter terminal using a standard regression package from a time-sharing library. The equations and resultant statistics are too numerous to be included here.

Precision of the atomic absorption analyses was estimated at $\pm$ 1% absorption/transmittance. In terms of the standards and samples, the deviance in concentrations is not very large. Table A3 summarizes the effects of precision on concentrations of the elements, Na^{+}, K^{+}, Ca^{++}, and Mg^{++} in the samples of this study. Precision values were determined from the calibration curves of the atomic absorption analyses.

TABLE A2

STANDARDS FOR SODIUM, POTASSIUM & MAGNESIUM

ELEMENT	STANDARDS (mgs/l)
Na	5; 10; 20; 30; 40; 50; 60.
K	5.21; 10.42; 20.84; 31.26; 40.68.
Mg	2; 5; 7; 8.

TABLE A3

PRECISION FOR SODIUM, POTASSIUM AND MAGNESIUM

($\pm$ 1% absorbance/transmittance)

ELEMENT	LOW CONCENTRATIONS	HIGH CONCENTRATIONS	AVERAGE
Na	1.50*	2.00	1.75
K	0.06	0.80	0.43
Ca	0.08	0.98	0.53
Mg	0.04	0.10	0.07

* concentrations in mg/l.

A P P E N D I X B

SOIL PROPERTIES

APPENDIX B

SOIL PROPERTIES

B1 Soil pH

Soil pH was determined in distilled water with a Corning dual, glass electrode pH meter after the methodology described by Peech (in Black, 1965). In a beaker, 20 g. of soil were added to 20 ml of neutral distilled water and stirred periodically over thirty minutes then allowed to settle overnight. The pH of the supernatant liquid was then read using the meter described above. Results are listed in Table B1 below.

B2 Soil Cation Exchange Capacity (CEC)

The CEC of the soils were determined by summing the total exchangeable bases and hydrogen in the soil samples. Total exchangeable bases and hydrogen were determined using a method described by Brown (1943) and also reported in Black (1965).

Exchangeable hydrogen (H^+) was determined by mixing 2.5 g. of soil with 25 ml of 1 N neutral ammonium acetate, shaking vigorously and allowing to stand overnight in a stoppered flask. Then the pH of the solution was determined to 0.01 pH units and the curves in Brown (1943) were used to determine the exchangeable H^+. Likewise total exchangeable bases were determined on a similar 1:10 mixture of 1 N acetic acid and soil. Basically the variation in solution pH from the original pH of the ammonium acetate and the acetic acid is related to the exchangeable H^+ and bases respectively through the titration curves presented in Brown.

Results are given in milliequivalents (meq) per 100 gms. of soil in Table B1.

Concentrations of the cations Ca^{++}, Mg^{++}, Na^{+} and K^{+} were determined from the solutions using acetic acid by means of atomic absorption as described in Appendix A. Standards for the atomic absorption were made up in acetic acid although tests showed no difference between standards made in water or the acid. Results are given in Table B1 below.

TABLE B1

SOIL CHARACTER IN THE CHIPPEWA WATERSHED

SITE/SAMPLE	DEPTH (cm)	SOIL pH	Exchangeable Bases and CEC (meq/100g)						% BASE SATURATION	SOIL COLOUR	HORIZONS	PARENT MATL
			Ca	Na	K	Mg	H	CEC				
1/1	8	5.00	1.69	0.15	0.09	0.70	9.65	12.26	21.0	5 YR 5/1	A	TILL
1/2	28	4.83	0.15	0.16	0.09	0.04	9.95	10.39	4.2	5 YR 5/6	B	
1/3	61	4.92	1.44	0.10	0.06	0.04	7.55	9.19	17.9	10 YR 7/4		
1/4	183	4.76	0.55	0.15	0.12	0.66	6.75	8.23	18.0	10 YR 7/3		
1/5	366	5.17	2.66	0.21	0.10	0.12	5.00	8.09	38.2	10 YR 7/1	C	
2/1	5	5.13	0.12	0.16	0.25	0.07	8.85	9.45	6.4	10 YR 4/2	A	TILL
2/2	13	5.34	2.01	0.09	0.05	0.13	6.75	9.02	25.2	10 YR 4/1		
2/3	28	5.07	0.25	0.07	0.03	0.07	5.78	6.20	6.8	10 YR 5/2	B	
2/4	38	5.11	0.33	0.11	0.07	0.05	9.42	9.98	5.6	10 YR 4/3		
2/5	61	4.81	0.15	0.14	0.05	0.03	6.45	6.82	5.4	10 YR 4/4		
2/6	137	4.90	0.55	0.09	0.04	0.05	3.90	4.63	15.8	10 YR 7/1	C	
2/7	549	4.83	0.61	0.09	0.03	0.02	15+	15.75+	4.8	2.5YR 6/2		
3/1	8	5.15	2.32	1.21	0.18	0.45	10.35	14.51	28.7	10 YR 5/1	A	TILL
3/2	30	5.27	1.56	0.54	0.05	0.07	8.10	10.32	21.5	10 YR 7/1	B	
3/3	61	4.87	0.12	0.49	0.03	0.02	7.60	8.26	8.0	10 YR 6/4	C	
3/4	81	5.22	0.60	0.51	0.03	0.01	7.25	8.40	13.7	10 YR 7/4		
4/1	30	5.25	13.17	0.81	0.18	5.48	14.60	34.24	57.4	10 YR 3/2	A	BOG
4/2	76	7.15	12.87	0.23	0.08	17.27	0.85	31.30	97.3	10 YR 6/1	C	

TABLE B1

SOIL CHARACTER IN THE CHIPPEWA WATERSHED

SITE/SAMPLE	DEPTH (cm)	SOIL pH	Exchangeable Bases and CEC (meq/100g)						% BASE SATURATION	SOIL COLOUR	HORIZONS	PARENT MATL
			Ca	Na	K	Mg	H	CEC				
5/1	5	5.73	3.47	0.08	0.11	0.24	9.40	13.30	22.7	10 YR 7/2	A	TILL
5/2	25	4.78	0.12	0.07	0.06	0.02	13.75	14.02	1.9	10 YR 4/2	B	
5/3	38	5.54	0.15	0.07	0.04	0.02	9.40	9.68	6.0	10 YR 5/3		
5/4	64	5.81	1.50	0.10	0.06	0.04	8.32	10.92	17.0	10 YR 7/2		
5/5	91	5.64	3.44	0.09	0.10	0.09	8.32	12.04	30.9	10 YR 7/1	C	
6/1	10	4.61	0.60	0.09	0.05	0.12	5.45	6.31	13.6	10 YR 7/4	A	GRAVEL
6/2	23	5.08	1.65	0.05	0.03	0.02	3.90	5.65	30.9	10 YR 6/3	B	
6/3	71	4.70	0.90	0.09	0.05	0.02	4.30	5.36	19.8	10 YR 7/3	C	
7/1	5	5.09	0.49	0.11	0.25	0.12	9.15	10.10	10.0	10 YR 6/4	A	GRAVEL
7/2	33	4.67	0.12	0.16	0.65	0.03	11.75	12.71	7.6	10 YR 7/3	B	
7/3	92	4.66	0.12	0.17	0.11	0.03	10.00	10.43	4.1	10 YR 6/2		
7/4	173	5.09	0.13	0.12	0.09	0.03	8.30	8.67	4.3	10 YR 6/6		
7/5	213	5.25	1.26	0.11	0.12	0.20	6.25	7.94	21.3	10 YR 6/3	C	
7/6	610	5.25	1.49	0.13	0.06	0.06	5.25	6.99	24.9	10 YR 6/1		
8/1	5	5.05	0.15	0.65	0.03	0.01	15.30	16.14	5.2	10 YR 5/2	A	TILL
8/2	13	4.81	0.28	0.37	0.06	0.02	15.20	15.93	4.6	10 YR 4/2	B	
8/3	30	4.91	0.15	0.43	0.04	0.02	16.30	16.94	3.8	10 YR 5/6		
8/4	81	5.11	0.24	0.60	0.03	0.00	8.15	9.02	9.7	10 YR 5/4		
8/5	107	5.28	0.75	0.51	0.03	0.02	7.62	8.93	14.7	10 YR 6/3	C	
8/6	640+	6.12	3.08	0.74	0.11	0.37	7.62	11.92	36.1	10 YR 6/2		

TABLE B1

SOIL CHARACTER IN THE CHIPPEWA WATERSHED

SITE/SAMPLE	DEPTH (cm)	SOIL pH	Exchangeable Bases and CEC (meq/100g)						% BASE SATURATION	SOIL COLOUR	HORIZONS	PARENT MATL
			Ca	Na	K	Mg	H	CEC				
9/1	5	4.75	0.10	0.09	0.11	0.02	6.45	6.77	4.7	10 YR 4/3	A	TILL
9/2	23	5.80	0.13	0.05	0.06	0.01	4.75	5.00	5.0	10 YR 5/4	B	
9/3	56	4.24	0.27	0.05	0.04	0.01	4.55	4.92	7.5	10 YR 6/4		
9/4	84	4.88	0.15	0.06	0.03	0.01	4.30	4.55	5.5	10 YR 7/3		
9/5	244±	5.41	0.39	0.07	0.04	0.02	3.40	3.92	13.3	10 YR 6/3	C	
10/1	5	4.95	0.15	0.68	0.11	0.05	11.70	12.69	7.8	10 YR 5/4	A	TILL
10/2	20	4.94	0.18	0.59	0.09	0.06	10.82	11.74	7.8	10 YR 5/4	B	
10/3	43	4.80	0.20	0.58	0.03	0.01	9.00	9.82	8.4	10 YR 6/4		
10/4	81	4.88	0.42	0.59	0.04	0.01	7.50	8.56	12.4	10 YR 6/3	C	
11/1	5	5.22	0.96	0.08	0.15	0.23	11.15	12.57	11.3	10 YR 3/1	A	SAND
11/2	25	4.66	0.06	0.07	0.03	0.03	12.93	13.12	1.5	10 YR 6/3	B	
11/3	107	4.71	0.09	0.12	0.03	0.04	13.90	14.18	2.0	10 YR 5/3		
11/4	132	4.91	0.09	0.09	0.04	0.03	13.55	13.80	1.8	10 YR 4/4	C	
11/5	203	5.35	0.94	0.05	0.03	0.03	8.25	9.30	11.3	10 YR 6/4		

A P P E N D I X C

SUMMARY OF SOLUTE PARAMETER DATA

TABLE C1

SUMMARY OF SOLUTE AND STREAMFLOW DATA

STREAM VARIABLE	SITE NO.	SPRINGFLOW mean	s.d.	max.	min.	n.	STORMFLOW mean	s.d.	max.	min.	n.	LOWFLOW mean	s.d.	max.	min.	n.
TDS	1	196.00	107.30	378	72	12	168.71	59.62	312	66	32	209.91	51.32	430.00	136.00	35
	2	149.33	86.74	326	62	12	166.60	58.64	326	42	33	178.31	52.36	280.00	96.00	35
	3	139.50	93.74	334	58	12	159.59	66.28	410	32	33	177.64	41.51	258.00	114.67	35
	4	122.17	77.74	300	56	12	137.39	54.59	308	10	32	155.92	42.53	220.00	80.00	35
	5	99.08	53.17	210	64	13	116.40	42.43	264	50	33	115.67	32.42	160.00	52.00	35
	6	77.09	40.58	146	30	11	96.66	48.96	268	10	33	108.86	36.85	250.00	47.33	33
	7	61.43	21.78	84	20	7	131.72	68.98	302	30	32	158.24	63.73	280.00	46.00	34
	8	66.55	34.68	146	28	11	89.31	35.32	170	20	32	78.91	25.54	122.67	22.00	32
Cl	1	86.54	61.18	269.80	34.70	16	51.95	19.15	99.40	21.06	34	60.88	18.55	124.20	37.87	35
	2	63.67	53.85	237.00	29.11	15	47.55	14.67	84.70	17.87	33	52.13	14.87	85.20	28.76	35
	3	53.98	45.55	200.90	25.50	15	41.08	15.63	88.04	14.08	33	48.75	16.23	88.75	26.51	35
	4	47.27	38.73	154.00	21.30	15	36.68	12.76	62.19	12.31	34	39.03	12.51	70.29	22.96	35
	5	30.89	19.91	77.30	3.00	16	24.86	6.50	39.05	10.65	35	24.46	6.00	35.14	14.79	35
	6	22.12	11.62	47.92	4.26	14	19.94	4.61	28.40	8.52	34	18.51	5.00	33.37	9.59	33
	7	9.91	2.37	12.78	6.39	10	20.94	20.81	84.50	3.20	34	16.40	7.69	39.76	4.60	35
	8	24.81	12.64	48.28	11.30	14	19.79	5.08	30.10	9.11	34	17.63	4.69	28.04	7.10	33
Alk	1	15.81	6.21	28.00	6.00	16	32.74	11.74	56.00	14.00	34	52.59	15.27	89.0	26.00	35
	2	18.13	10.41	32.00	4.00	15	32.63	14.31	88.00	14.00	34	48.81	14.47	85.3	30.33	35
	3	16.00	9.33	32.00	4.00	15	29.27	10.97	53.33	10.00	35	44.87	11.78	73.0	20.60	34
	4	14.27	7.21	32.00	4.00	15	30.40	13.59	56.00	14.00	34	43.29	11.24	62.0	24.00	35
	5	13.63	8.46	34.00	2.00	16	27.06	10.29	44.33	8.00	35	37.48	9.02	62.0	20.00	35
	6	14.43	9.32	38.00	4.00	14	26.53	10.42	51.60	8.00	35	37.00	10.54	68.0	20.00	33
	7	28.20	17.60	62.00	6.00	10	40.93	22.65	96.00	12.00	34	61.53	23.21	99.0	14.00	35
	8	8.71	5.36	26.00	4.00	14	13.47	5.56	28.00	4.00	35	19.09	5.61	40.0	10.00	33

* All concentrations are in mg/l

TABLE C1

SUMMARY OF SOLUTE AND STREAMFLOW DATA

STREAM VARIABLE	SITE NO.	SPRINGFLOW mean	s.d.	max.	min.	n.	STORMFLOW mean	s.d.	max.	min.	n.	LOWFLOW mean	s.d.	max.	min.	n.
Hardness	1	36.13	9.52	50	14	15	50.22	13.75	98	32.00	33	66.17	8.10	82	40.00	35
	2	33.00	9.28	48	14	12	45.27	9.03	60	30.00	32	60.57	13.45	94	12.00	34
	3	32.33	6.02	48	24	12	42.89	12.48	82	20.00	33	58.91	11.74	82	22.00	35
	4	32.67	8.84	50	24	12	41.95	11.16	68	24.00	34	55.31	11.86	84	30.00	35
	5	26.67	9.62	42	10	12	35.10	7.39	50	24.67	34	44.37	8.37	58	26.00	35
	6	26.83	10.14	42	8	12	34.36	9.32	60	18.00	35	42.01	7.57	58	26.67	33
	7	36.75	10.58	50	24	8	47.47	20.95	98	20.00	34	64.01	20.49	92	28.00	32
	8	17.85	4.04	28	12	13	20.44	4.59	32	14.00	35	25.37	8.13	58	16.00	33
Ca	1	38.67	4.89	47.23	26.00	12	48.09	14.23	93.92	30.79	26	62.93	3.31	76.35	28.35	24
	2	29.10	8.15	40.62	13.04	10	41.79	8.56	59.77	29.26	25	57.08	11.19	87.65	36.36	25
	3	31.56	5.24	48.19	23.46	11	39.57	13.03	78.52	16.37	24	55.56	9.61	69.28	39.28	25
	4	29.56	6.58	41.62	23.65	11	39.19	10.45	68.28	23.81	27	54.09	8.93	79.55	32.24	27
	5	24.90	8.57	39.11	17.12	11	33.36	6.97	47.25	21.91	25	41.98	8.60	56.05	21.45	26
	6	26.56	7.46	38.81	19.56	10	32.53	8.71	58.0	17.88	26	38.70	8.58	55.36	23.71	26
	7	32.36	8.62	45.41	22.57	7	45.73	18.26	90.42	19.66	27	60.62	16.13	93.65	21.57	25
	8	16.03	2.56	19.94	11.07	10	19.51	5.01	31.63	12.84	27	25.67	9.00	56.29	14.88	23
Na	1	49.42	23.22	85.09	19.18	12	32.63	9.62	54.70	14.32	25	42.90	9.21	64.99	28.35	24
	2	32.77	12.50	54.54	17.65	11	30.67	10.14	65.34	13.09	27	36.32	8.11	55.61	24.50	26
	3	27.20	11.05	48.19	14.92	12	26.40	7.91	47.62	11.72	26	34.95	9.83	56.15	18.82	25
	4	22.17	9.85	45.77	8.93	11	22.94	5.95	34.91	16.09	26	29.35	8.82	53.17	16.26	26
	5	20.85	9.79	43.67	12.39	12	18.18	4.80	30.37	8.74	26	21.46	7.24	48.64	19.15	26
	6	15.94	9.36	39.72	6.45	11	16.96	8.42	44.36	7.01	25	18.29	6.51	32.89	5.37	25
	7	10.56	5.21	17.46	2.63	7	15.55	7.95	36.44	6.48	27	20.97	9.05	47.11	9.59	25
	8	14.94	10.89	44.06	5.36	12	15.36	4.94	31.04	9.07	26	17.42	8.05	36.66	10.12	24

TABLE C1

SUMMARY OF SOLUTE AND STREAMFLOW DATA

STREAM VARIABLE	SITE NO.	SPRINGFLOW					STORMFLOW					LOWFLOW				
		mean	s.d.	max.	min.	n.	mean	s.d.	max.	min.	n.	mean	s.d.	max.	min.	n.
K	1	7.55	1.52	10.37	5.37	12	7.80	3.89	8.98	5.02	26.	8.59	1.88	15.12	5.48	24
	2	6.68	2.40	10.73	1.88	11	6.33	1.32	8.66	4.44	27	7.77	1.33	11.25	6.03	26
	3	6.23	1.23	8.34	3.48	12	6.17	1.79	9.59	4.30	26	7.29	1.24	9.74	4.33	25
	4	5.72	1.49	8.67	3.48	11	6.46	2.80	16.48	3.17	26	6.61	1.16	9.06	4.44	26
	5	5.25	1.47	7.81	3.07	12	6.19	3.21	16.48	2.48	26	6.16	1.30	10.06	3.80	26
	6	5.28	1.64	8.83	2.80	11	5.01	1.52	8.20	2.63	26	5.67	1.18	8.98	3.50	25
	7	6.38	1.01	8.18	5.18	7	8.17	4.02	22.05	4.29	27	10.87	4.20	26.49	6.39	25
	8	5.16	2.27	9.80	1.88	12	3.93	1.54	12.93	1.56	26	5.87	3.42	16.48	2.56	24
Mg	1	1.99	1.02	3.370	0.350	12	2.61	1.47	4.55	0.001	24	5.10	1.51	7.86	0.850	25
	2	1.64	0.95	2.800	0.100	11	2.76	1.37	5.13	0.001	27	4.69	1.36	7.64	2.630	26
	3	1.55	0.71	2.260	0.240	11	2.85	1.14	4.55	0.170	26	4.70	1.37	7.86	2.090	24
	4	1.56	0.85	2.620	0.100	11	2.60	1.30	4.55	0.110	26	4.30	1.51	6.55	0.040	26
	5	0.95	0.66	1.850	0.001	12	1.94	1.41	5.06	0.075	26	3.41	1.12	6.21	1.930	25
	6	0.80	0.53	1.840	0.170	11	1.50	1.14	3.96	0.001	26	3.06	1.35	5.41	0.090	25
	7	2.50	1.49	4.590	0.600	7	3.71	2.03	6.80	0.340	27	4.78	0.65	7.86	1.690	25
	8	0.38	0.40	1.030	0.001	11	0.73	0.66	1.78	0.001	22	0.80	0.79	3.12	0.010	24

TABLE C1

SUMMARY OF SOLUTE AND STREAMFLOW DATA

STREAM VARIABLE	SITE NO.	SPRINGFLOW mean	s.d.	max.	min.	n.	STORMFLOW mean	s.d.	max.	min.	n.	LOWFLOW mean	s.d.	max.	min.	n.
Temp °C	1	0	0	0	0	7	14.94	4.05	22.20	6.11	25	17.36	3.54	21.67	7.22	26
	2	0	0	0	0	8	14.52	3.92	21.11	6.11	28	17.80	3.08	22.20	7.22	25
	3	0	0	0	0	6	14.18	4.10	22.20	5.56	27	17.08	3.65	21.67	6.67	27
	4	0	0	0	0	6	14.22	3.99	21.11	5.00	27	16.93	3.64	21.67	6.67	27
	5	0	0	0	0	8	13.64	4.15	22.22	5.00	28	16.77	3.57	21.67	6.67	27
	6	0	0	0	0	6	13.43	4.07	21.11	5.00	28	16.26	3.28	21.11	7.22	27
	7	0	0	0	0	3	13.42	3.69	18.89	3.89	27	16.34	3.24	20.56	6.67	26
	8	0	0	0	0	7	13.84	3.97	21.11	6.11	28	16.09	3.11	20.56	7.78	26
Q (cfs)	1	171.96	144.68	494.82	25.25	15	97.16	173.78	494.82	21.98	35	12.30	3.41	18.96	7.04	33
	2	121.13	91.62	324.93	24.38	15	65.97	96.22	482.13	14.89	34	11.37	3.31	20.18	5.03	34
	3	91.65	65.71	210.73	14.69	15	45.49	70.52	351.35	5.28	35	8.00	2.19	11.71	4.25	34
	4	69.20	44.14	153.51	12.36	15	38.32	57.60	313.50	8.61	34	5.36	2.46	9.32	1.10	39
	5	65.19	38.48	128.80	11.65	16	30.71	42.12	202.10	6.48	35	3.52	2.11	7.71	0.42	35
	6	52.22	27.33	86.38	10.97	13	25.37	32.24	146.34	4.83	32	2.59	1.86	6.40	0.40	35
	7	17.70	12.14	45.52	2.29	10	18.26	51.55	67.73	1.36	34	0.62	0.59	2.07	0.08	34
	8	12.66	6.78	29.51	4.24	13	7.40	7.20	38.46	1.19	35	0.44	3.46	2.61	0.01	30
pH	1	6.49	1.57	7.2	5.3	16	7.28	0.20	7.6	6.73	34	7.42	0.15	7.7	7.10	35
	2	6.97	0.56	7.7	5.2	15	7.32	0.21	7.7	6.80	34	7.48	0.16	7.8	7.20	35
	3	6.78	0.90	7.3	4.4	15	7.29	0.30	7.6	6.00	35	7.54	0.18	8.0	7.20	35
	4	6.73	1.00	7.4	4.1	15	7.35	0.23	7.8	6.80	34	7.51	0.15	7.8	7.20	35
	5	6.62	1.00	7.4	3.9	16	7.34	0.23	7.8	6.90	34	7.48	0.16	7.9	7.20	35
	6	6.70	0.90	7.4	3.8	14	7.34	0.23	7.8	6.90	35	7.46	0.15	8.0	7.20	33
	7	7.38	0.18	7.6	7.1	9	7.55	0.29	8.1	6.96	36	7.70	0.26	8.6	7.26	35
	8	6.24	0.63	6.9	4.5	14	6.85	0.35	7.6	6.40	35	7.03	0.26	7.7	6.30	33

TABLE C2

SUMMARY OF CEC DATA FOR BED MATERIALS

PARAMETERS		URBAN (OAK ST.)				RURAL (AIRPORT)			
ION		1	2	3	4	1	2	3	4
NA	CEC BED MATL*	1.80	1.85	1.85	1.82	2.00	2.10	1.90	2.40
	CONC. STREAM* SOLUTE	52.00	51.50	34.50	42.50	12.80	24.50	13.10	27.10
	DISCHARGE+	0.13	0.70	1.51	0.13	0.05	0.16	0.81	0.02
K	CEC BED MATL	1.90	1.75	1.34	2.20	2.00	1.55	2.54	1.10
	CONC. STREAM SOLUTE	3.82	3.55	3.01	4.11	2.62	2.82	2.34	3.28
	DISCHARGE	0.13	0.70	1.51	0.13	0.05	0.16	0.81	0.02
CA	CEC. BED MATL	32.64	33.99	38.01	27.95	42.71	48.08	48.08	38.01
	CONC. STREAM SOLUTE	43.38	30.00	28.08	48.08	26.74	15.60	22.31	30.63
	DISCHARGE	0.13	0.70	1.51	0.13	0.05	0.16	0.81	0.02

Note: * all chemical values in mg/l

+ discharge values in cu. m./sec.

A P P E N D I X D

SUMMARY OF REGRESSION ANALYSES

TABLE D1

SUMMARY OF REGRESSIONS USING HYDRO-TEMPORAL CHARACTERISTICS

DEPENDENT VARIABLES		RURAL (AIRPORT RD.) EQUATIONS	SIG	R^2	URBAN (OAK ST.) EQUATIONS	SIG	R^2
pH	SPRING	$pH = 5.94 + 0.43\ TS$	*	.1919	$pH = 7.32 - 4.78\ TS^{-1}$	*	.1492
	STORM	$pH = 7.66 - 0.26 \log Q$	***	.2037	$pH = 7.49 - 13.55\ Ts$	*	.1606
		$pH = 7.81 - 0.28 \log QP$	**	.4469	$pH = 8.51 - 0.78 \log API$	***	.4291
		$pH = 7.09 + 0.003\ TS$	**	.3413	$pH = 7.61 - 0.79\ API$	***	.3892
		$pH = 7.93 - 0.14\ API$	***	.5915			
	LOW	$pH = 7.51 + 0.13 \log QP$	*	.1762	$pH = 7.26 + 0.03\ TD$	*	.2315
		$pH = 7.53 + 0.01\ PT$	**	.4253			
		$\log pH = 0.88 + 0.01 \log Q$	*	.1822			
TOTAL DISSOLVED SOLIDS (TDS)	SPRING	$TDS = 203.36 - 104.18 \log TS$	***	.6558	$TDS = 19.36 + 663.33\ TS^{-1}$	**	.5377
		$TDS = -88.74 + 1768.09\ TD^{-1}$	**	.4237			
	STORM	$TDS = 85.98 + 0.53\ TQP$	*	.3299	$TDS = 126.68 - 0.65\ TS$	**	.3452
	LOW	$TDS = 184.86 - 0.44\ TS$	**	.2663			
CHLORIDE (CL)	SPRING	$CL = 51.28 - 0.27\ Q$	**	.3203	$CL = 11.50 + 401.66\ TS^{-1}$	***	.6312
		$CL = 21.54 + 47.98\ TS^{-1}$	***	.5581			
	STORM	$CL = 34.60 - 7.15 \log Q$	***	.5862	$CL = 15.72 + 552.05\ Q^{-1}$	**	.2080
		$CL = 36.01 - 0.22\ API$	*	.2178	$CL = 34.71 - 26.90\ TQP^{-1}$	**	.3343
		$CL = 30.68 - 0.20\ PT$	**	.2684	$CL = 46.88 - 0.15\ TS$	**	.2714
	LOW	$CL = 18.72 + 1.45\ Q$	***	.4939	$CL = -6.80 + 26.27 \log QP$	**	.3260
		$CL = 16.51 + 10.96 \log QP$	***	.6952			
		$CL = 100.85 - 35.30 \log TS$	***	.5034			
		$CL = 0.38 + 35.07 \log TD$	**	.4098			
SODIUM (NA)	SPRING	$NA = 35.51 - 1307 \log TS$	*	.2796	$NA = 13.15 + 1035.45\ Q^{-1}$	*	.2201
	STORM	$NA = 23.89 - 4.15 \log Q$	*	.1069	$NA = 8.45 + 304.10\ Q^{-1}$	*	.1316
		$NA = 18.68 + 8.41\ TQP^{-1}$	*	.1893	$NA = 18.27 - 16.88\ TQP^{-1}$	**	.3387
	LOW				$NA = 28.21 - 0.55\ QP$	**	.4127
					$NA = 21.36 + 0.78\ PT$	**	.3550

TABLE D1

SUMMARY OF REGRESSIONS USING HYDRO-TEMPORAL CHARACTERISTICS

DEPENDENT VARIABLES		RURAL (AIRPORT RD.) EQUATIONS	SIG	R^2	URBAN (OAK ST.) EQUATIONS	SIG	R^2
POTASSIUM (K)	SPRING	$K = 7.12 - 1.71 \log TS$	*	.1820	$K = 1.00 + 79.16 Q^{-1}$	*	.3066
	STORM	$K = 18.49 - 8.13 \log API$	*	.1678	$K = 3.13 - 114.33 Q^{-1}$	*	.1327
		$K = 6.68 - 1.22 \log PT$	*	.1346	$K = 2.68 - 79.96 QP^{-1}$	*	.1927
	LOW				$K = 3.47 - 0.15 TD$	*	.1698
					$K = 2.74 - 0.07 PT$	*	.2852
ALKALINITY (ALK)	SPRING	$ALK = 5.98 + 0.48 TS$	**	.3950	$ALK = -0.48 + 0.02 Q$	*	.1936
	STORM	$ALK = 42.84 - 12.67 \log Q$	**	.2557	$ALK = 3.14 + 11.15 TQP^{-1}$	**	.2809
		$ALK = 43.19 - 13.23 \log QP$	***	.6281			
		$ALK = 9.67 + 0.14 TS$	***	.5007			
		$\log ALK = 2.97 - 1.05 \log API$	***	.5717			
		$ALK = 96.73 - 46.77 \log API$	***	.4316			
		$ALK = 27.96 - 0.27 PT$	*	.1591			
	LOW	$ALK = 40.32 - 12.37 \log Q$	**	.4749	$ALK = 5.01 + 308.04 QP^{-1}$	**	.4350
		$ALK = 40.83 - 0.49 QP$	***	.8499			
		$ALK = 30.90 + 0.03 TQP$	*	.1723			
		$ALK = -49.65 - 2042.52 TS^{-1}$	**	.4052			
		$ALK = 65.23 - 44.97 \log TD$	**	.4731			
		$ALK = 42.97 - 0.43 API$	**	.3614			
HARDNESS (HD)	SPRING	$HD = 19.08 + 289.57 Q^{-1}$	*	.4036			
	STORM	$HD = 47.59 - 9.72 \log Q$	***	.2769	$HD = 8.60 + 253.50 Q^{-1}$	*	.1081
		$HD = 48.97 - 8.75 \log QP$	**	.4791			
		$HD = -15.92 + 27.14 \log TS$	***	.4755			
		$HD = 52.50 - 0.42 API$	***	.4915			
		$HD = 39.98 - 0.22 PT$	*	.1740			
	LOW	$HD = 41.65 + 11.23 Q^{-1}$	*	.2838	$HD = 24.97 - 0.92 PT$	**	.3723
		$HD = 60.52 - 0.64 API$	***	.5039			
		$HD = 48.68 + 4.88 \log PT$	*	.1731			

TABLE D1

SUMMARY OF REGRESSIONS USING HYDRO-TEMPORAL CHARACTERISTICS

DEPENDENT VARIABLES		RURAL (AIRPORT RD.) EQUATIONS	SIG	R^2	URBAN (OAK ST.) EQUATIONS	SIG	R^2
CALCIUM (CA)	SPRING	$CA = 18.36 + 280.51\ Q^{-1}$	*	.3896			
	STORM	$CA = 47.11 - 9.96 \log Q$	***	.3846			
		$CA = 31.36 + 24.82\ QP^{-1}$	*	.3975			
		$CA = 45.92 - 871.93\ TS^{-1}$	**	.4141			
		$CA = 24.58 + 1.39\ TD$	*	.1852			
		$CA = 47.98 - 0.36\ API$	***	.4485			
		$CA = 37.26 - 0.19\ PT$	*	.1552			
	LOW	$CA = 37.71 + 12.27\ Q^{-1}$	*	.3291	$CA = 22.60 - 0.82\ PT$	*	.2619
		$CA = 57.38 - 0.66\ API$	***	.5301			
		$CA = 45.21 + 4.90 \log PT$	*	.1736			
MAGNESIUM (MG)	SPRING				$MG = 1.45 - .002\ Q$	*	.3811
					$MG = -1.14 + 1.58 \log TQP$	*	.4520
	STORM	$MG = 3.74 - 1.39 \log Q$	*	.1997			
		$MG = 4.56 - 1.55 \log QP$		.4000			
		$MG = 0.18 + 0.02\ TS$		.4254			
		$MG = 9.99 - 5.14 \log API$		.2167			
	LOW				$MG = 2.85 - 0.24\ TD$	*	.1603

* significant at .05 level

** significant at .01 level

*** significant at .001 level

TABLE D2

SUMMARY OF REGRESSIONS USING WATERSHED (GEO-URBAN) VARIABLES

DEPENDENT VARIABLES	SPRINGFLOW			STORMFLOW			LOWFLOW		
	EQUATIONS	SIG.	R^2	EQUATIONS	SIG.	R^2	EQUATIONS	SIG.	R^2
TOTAL DISSOLVED SOLIDS (TDS)	TDS = 11.72 + 0.65 G	*	.4744	TDS = 2.53 + 0.95 G	**	.5248	TDS = 3.05 + 63.28 FR	*	.5014
	TDS = 73.09 - 0.93 T	*	.5704				TDS = 13.99 + 73.28 BL^{-1}	*	.6249
	TDS = 16.37 + 53.26 BL^{-1}	*	.4338				log TDS = 1.76 - 0.23 SL	*	.4674
	log TDS = 3.58 - 1.35 log P	*	.5807				TDS = 1.62 + 857.32 QLO^{-1}	*	.5485
pH	pH = 6.86 - 0.008 G	**	.7003	pH = 7.40 - 0.006 G	*	.5130	pH = 7.60 - 0.42 FR	*	.4620
	pH = 6.78 - 0.62 BL^{-1}	**	.7532	pH = 7.38 - 0.59 BL^{-1}	***	.8906	pH = 7.57 - 0.006 G	**	.6787
							pH = 7.54 - 0.57 BL^{-1}	***	.8708
							pH = 7.64 - 6.86 QLO^{-1}	**	.8389
CHLORIDE (CL)	CL = 34.13 - 0.43 T	**	.8445	log CL = 1.23 - 0.10 BA	*	.4504	log CL = 1.16 + 0.07 BA	**	.6394
				CL = 28.26 - 0.38 T	**	.8502			
				log CL = -0.24 + 1.68 log SC	*	.4736			
				log CL = -1.25 + 0.90 log QTI	*	.6161			
ALKALINITY (ALK)	ALK = -1.17 + 9.14 FR	*	.6955	ALK = -2.88 + 18.13 FR	***	.8830	ALK = 2. 5 + 1.59 FC	***	.9322
	ALK = 0.20 + 0.86 FC	**	.8635	ALK = 0.11 + 1.61 FC	***	.9551			
	ALK = 0.68 + 0.65 SL^{-1}	**	.8408	log ALK = -1.00 + 2.00 log BA	*	.5887			
	ALK = 0.72 + 11.58 P^{-1}	*	.6361	ALK = 0.82 + 23.30 P^{-1}	**	.8398			
HARDNESS (HD)	HD = -3.12 + 19.68 FR	***	.8692	HD = -2.81 + 23.54 FR	***	.9562	HD = -1.99 + 26.89 FR	***	.8750
	HD = 0.91 + 1.48 FC	*	.6165	HD = 1.87 + 1.84 FC	**	.7531	HD = 2.42 + 2.05 FC	**	.6480
	HD = 0.25 + 0.20 G	*	.4707	log HD = 1.34 - 0.20 AC	*	.4648	HD = 3.88 + 25.51 BL^{-1}	**	.6482
	log HD = 1.41 - 0.34 BS	*	.4732	HD = 2.63 + 20.99 BL^{-1}	*	.6059	HD = 3.36 + 29.55 P^{-1}	*	.5539
	HD = 2.09 + 1.02 BL^{-1}	*	.6981	HD = 2.64 + 1.46 SL^{-1}	**	.8141	HD = 4.21 + 1.68 SL^{-1}	**	.7541
	HD = 5.61 - 7.04 log SL	*	.5848	HD = 2.73 + 25.97 P^{-1}	*	.6170	HD = -0.02 + 286.20 QLO^{-1}	*	.5079

TABLE D2

SUMMARY OF REGRESSIONS USING WATERSHED (GEO-URBAN) VARIABLES

DEPENDENT VARIABLES	SPRINGFLOW EQUATIONS	SIG.	R^2	STORMFLOW EQUATIONS	SIG.	R^2	LOWFLOW EQUATIONS	SIG.	R^2
CALCIUM (CA)	$CA = 1.24 + 17.30\ FR$	**	.7311	$CA = -2.60 + 22.25\ FR$	***	.9491	$CA = -2.01 + 25.83\ FR$	**	.8094
	$CA = 2.90 + 1.03\ SL^{-1}$	*	.5570	$CA = 1.86 + 1.70\ FC$	**	.7113	$CA = 3.53 + 1.86\ FC$	*	.5073
				$CA = 1.37 - 0.23\ BS$	*	.4506	$CA = 2.04 + 0.28\ G$	*	.5079
				$CA = 2.45 + 19.80\ RL^{-1}$	*	.5979	$CA = 3.35 + 25.83\ RL^{-1}$	**	.6852
				$CA = 2.62 + 1.36\ SL^{-1}$	**	.7762	$CA = 4.29 + 1.50\ SL^{-1}$	*	.5802
				$CA = 2.75 + 23.89\ P^{-1}$	*	.5697	$CA = -0.98 + 301.43\ QLO^{-1}$	*	.5994
SODIUM (NA)	$NA = -5.20 + 510.89\ T^{-1}$	**	.8400	$NA = 1.34 + 15.22\ RL^{-1}$	**	.7763	$\log NA = 1.09 + 0.07\ BA$	*	.5498
	$\log NA = -0.62 + 0.59\ \log QST$	*	.6350				$NA = 2.26 + 0.17\ G$	*	.4885
							$NA = 2.15 + 15.59\ RL^{-1}$	*	.6224
							$NA = 0.34 + 187.82\ QLO^{-1}$	*	.5912
POTASSIUM (K)	$K = -0.34 + 0.57\ G$	*	.5040	$K = -0.10 + 0.66\ G$	***	.9510	$K = -0.41 + 0.07\ G$	*	.5552
	$K = -0.18 + 5.86\ RL^{-1}$	**	.8640	$K = 0.39 + 0.87\ RL^{-1}$	**	.7081	$K = -0.19 + 6.70\ RL^{-1}$	***	.8952
							$K = -1.21 + 75.07\ QLO^{-1}$	**	.7111
MAGNESIUM (MG)	$MG = 0.07 + 0.01\ BSC$	*	.4527	$MG = 0.64 - 0.092\ B$	*	.5611	$MG = 0.28 + 4.58\ B^{-1}$	*	.5736
	$\log MG = -0.30 + 0.64\ \log FR$	*	.4709	$MG = 0.93 - 0.43\ \log IA$	*	.5745	$MG = 0.18 + 4.22\ IA^{-1}$	**	.7093
				$MG = 0.45 - 0.31\ \log SL$	*	.5696	$MG = 0.04 + 1.97\ SC^{-1}$	*	.6657
				$MG = 0.69 - 0.02\ RL$	*	.4898	$MG = 0.39 + 0.11\ SL^{-1}$	*	.4661
				$MG = 0.87 - 0.36\ \log F$	**	.6978	$MG = 0.30 + 2.59\ F^{-1}$	**	.6685
				$MG = 0.66 - 0.007\ QST$	*	.5940			

* significant at .05 level

** significant at .01 level

*** significant at .001 level