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Summer stormflow generation in a small Precambrian Shield basin

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SUMMER STORMFLOW GENERATION IN A SMALL PRECAMBRIAN SHIELD BASIN

BY

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ABSTRACT

The environmental isotope oxygen-18 ($\delta^{18}O$) and natural water chemistry were used to identify both the percent individual source component and mechanisms responsible for generating summer surface storm runoff in a small Precambrian Shield catchment. In addition, variations in radon gas (Rn-222) concentration in both surface and groundwaters were monitored in order to gain additional information not obtainable through use of the above stated tracers.

Results indicate that the percent component contribution and the mechanism(s) responsible for stormflow generation within the study basin are largely dependant upon antecedent basin conditions and physical storm characteristics. Generally speaking, shortly after initiation of precipitation under any given antecedent condition a piston flow type mechanism operates delivering pre-event water (primarily phreatic zone water) to the stream channel. Rapid throughflow of water occurs during intense precipitation events as well as during wet antecedent conditions. The composition of throughflow varies. During dry antecedent conditions throughflow is largely composed of event water. Under wet antecedent conditions throughflow is generally a mixture of event and pre-event waters. In this case pre-event water is primarily vadose zone water.

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1
INTRODUCTION

1.0 The Problem

The components and mechanisms responsible for generating surface storm runoff have been of interest to earth scientists for many years. Information of this nature is of value in predicting the timing and magnitude of storm runoff, in estimating stream and lake water quality and in the prediction of the effects of watershed modification to the quantity and quality of storm runoff.

Despite extensive research efforts over the past several decades, exact sources of storm runoff (ie., overland flow, direct rainfall, groundwater and subsurface interflow) often remain questionable. Contributions from different sources will vary according to a number of parameters. Antecedent soil moisture, climate, hydrologic conditions, physical storm characteristics, soil characteristics, time, topography, and vegetative cover are the major parameters affecting individual source contributions to surface storm runoff (Kennedy et. al., 1986). In addition to questions regarding the components responsible for generating storm runoff, the paths and processes by which these waters from different sources reach stream channels also remain controversial.

With the aid of isotopic information several recent studies have successfully identified the components of stormflow and their respective percent contribution to total

storm runoff in a given basin. The exact mechanism(s) by which these components reach a stream channel, however, is speculative. In order to comprehend fully the mechanisms and components responsible for generating surface storm runoff, infield measurements of various physical and hydraulic processes and parameters are required.

The purpose of this chapter is to give an overview of the recent literature related to investigations of stormflow generation. Common approaches to studying stormflow generation are dealt with initially, followed by discussion of commonly cited and the most widely accepted mechanisms for stormflow generation. Mass balance equations used for storm hydrograph component separation and a brief but concise review of previous related studies follow the cited mechanisms. In conclusion to the first chapter the objectives of this study are stated.

1.1 Review of Literature

1.1.1 Introduction

According to Sklash and Farvolden (1979), studies of storm runoff generation can be classified under three different approaches which include aspects of time, ultimate delivery mechanism aspects and historical approaches. Emphasis in this study is placed on aspects of time and ultimate delivery mechanisms.

Studies which consider only what portion of the runoff

water existed in the basin prior to the runoff event and what portion was added by the runoff-inducing event are concerned with aspects of time. Investigations concerned with ultimate delivery mechanisms generally examine the movement and pathways runoff inducing water travels over the last several tens of meters to a stream. The third approach to studying storm runoff generation is concerned only with the history of the water from its arrival in the basin to its ultimate delivery to the stream. This aspect of study is termed historical.

1.1.2 Time Aspects

Conclusions of time aspect studies are based mainly on the examination of temporal variations of selected tracers in a stream (Sklash and Farvolden, 1979). In essence,

> "a tracer is any substance whose atomic or molecular, physical, chemical or biological properties provide for the identification, observation, and study of its behaviour (its dispersion or concentration, flow, kinetics and dynamics) during a certain more or less complicated process which occurs either instantaneously or in a given time lapse" (Molecular Trends in Tracer Hydrology, 1987).

Time aspect studies are often only concerned with two components of stormflow; event ("new") and pre-event ("old") water contributions. Pre-event water contributions can include phreatic water (saturated zone water or groundwater), vadose water (unsaturated zone water or water above the water table) and surface storage; while event

water could be either rain or snow or both.

1.1.3 Ultimate Delivery Mechanism Aspects

Studies of the ultimate delivery mechanisms are generally slope related and are concerned with processes occurring elsewhere in the basin than within the stream itself. Currently the most widely accepted and commonly reported theories for storm (and snowmelt) runoff studies stem from the ultimate delivery mechanism approach to the subject. In humid vegetated areas mechanisms related to the variable-source area concept (see Hewlett and Hibbert, 1967) are generally considered operative and feasible to account for both the rapid response of the stream to runoff-inducing events and the observed increase in discharge. Figure 1 lists the various mechanisms considered operative in humid forested catchments according to the variable source area concept. The papers listed for each mechanism are the major studies providing field evidence for each process (Pearce et.al., 1986). Each of the listed mechanisms is summarized below with the addition of the traditional Horton overland flow concept and direct channel precipitation.

1.1.3.1 Horton Overland Flow

First proposed by Horton in 1933, this mechanism of stormflow generation is a result of the direct surface runoff of event water. Horton overland flow occurs when

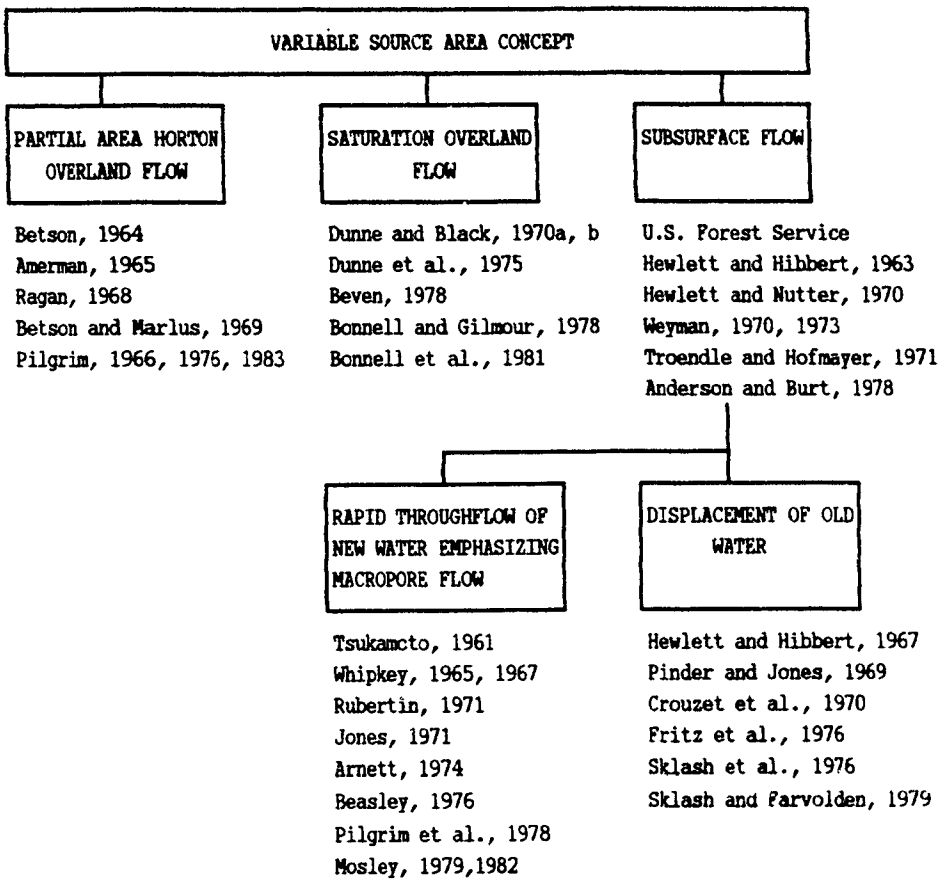

Figure 1: Summary of storm runoff mechanisms applicable to the variable source area concept and studies providing field evidence for mechanisms. (After Pearce et al., 1986).

rainfall rate or intensity exceeds infiltration rate plus surface depression storage. The resulting excess rain travels downslope overland in sheets to small rivulets and then to streams (Sklash et al, 1976). Horton overland flow is uncommon in a forested watershed, the result of heterogeneity in soil types, variations in rainfall patterns in both time and space and rainfall interception by standing vegetation and litter on the forest floor. Horton overland flow is generally confined to such locations as roads, parking lots and areas of saturated concrete frost where infiltration is inhibited.

1.1.3.2 Partial Area Horton Overland Flow Concept

First proposed by Betson (1964) this mechanism of runoff production stipulates that Horton overland flow occurs from limited areas of a catchment during moderate storms. Such a mechanism is a result of the non-uniformity of soil characteristics within a basin. This theory suggests that overland flow is a result of the soil becoming saturated from above by the infiltrating water. "Excess" water or water remaining after surface detention requirements have been satisfied runs off rapidly to the stream channel as overland flow. Partial areas of flow may be located anywhere within a basin and are normally characterized by a shallow "A" soil horizon (Sklash, 1978). Partial area overland flow implies that new or event water

dominates storm runoff.

1.1.3.3 Variable Source Area-Saturated Overland Flow

Surface runoff is generated primarily by the contribution of water flowing overland to the stream channel, according to the variable source area-overland flow theory (Dunne and Black, 1970a, 1970b, Dunne et al., 1975). Unlike the partial area Horton overland flow mechanism (section 1.1.3.2) where the soil is saturated from above, overland flow according to this concept occurs in areas which have become saturated from below by a rising water table. Saturated overland flow areas are generally located near the stream and may expand or contract in response to climatic factors and basin characteristics. The rising water table is a result of both infiltrated rainwater in the saturated areas and subsurface contributions from infiltrated areas upslope of the saturated area. Although this mechanism implies that both groundwater and surface water contribute to storm runoff, event water is the dominant contributor to storm runoff (Pearce et al., 1986).

1.1.3.4 Variable Source Area-Subsurface Flow

The variable source area-subsurface flow concept suggests that a large percentage of water producing stormflow runoff has reached the stream channel by means of underground or subsurface flow routes. As a consequence,

water contributing to stormflow may be the result of rapid throughflow of (primarily) event water or through the displacement of (primarily) pre-event water.

In the first scenario, rapid throughflow of event water can occur through or along preferred pathways in soils. Preferred pathways may be;

1) subsurface channels (commonly called pipes, pores or macropores, see Beven and Germann, 1982) formed by soil fauna burrowing or plant root decay;

2) cracks and fissures formed by the desiccation of clay soils or by chemical and physical weathering processes; or

3) the result of a given soil structure and composition. For example, in coarse textured highly permeable soils or along saturated soil horizons water may flow at velocities as quickly as overland flow (Beven and Germann, 1982).

Although many studies (see Figure 1) have identified pipe flow as a mechanism contributing to the generation of surface storm runoff, the means by which pre-event water is introduced into pipes is questionable. More commonly pipe flow delivers recently introduced event water. One important fact regarding pipe flow is that pipes may conduct large quantities of water under both saturated or unsaturated flow conditions (Beven and Germann, 1982).

If displacement of stored water occurs, stormflow will be dominated by pre-event water. Many recent studies using naturally occurring tracers such as oxygen-18 (^{18}O) and

major ions suggest that pre-event water dominates storm runoff in humid forested watersheds (Pinder and Jones, 1969; Dincer et al., 1970; Nakamura, 1971; Martinec et al., 1974; Fritz et al., 1976; Sklash et al., 1976, 1978, 1986; Bottomley et al., 1984/85, 1986; and Pearce et al., 1986).

The exact mechanism(s) governing the displacement of pre-event water is still questionable. At the present time there are two concepts proposed to explain this rapid response of groundwater during a storm. The first concept, as explained by Hewlett and Hibbert (1967) is termed "translatory flow". This concept describes a mechanism by which new water entering the saturated zone on a hillslope causes a displacement of old water at the base of the slope. This is achieved only when the soil is within the field capacity range or wetter. Such a mechanism is due to a rapid wavelike transmission of the pressure changes at the boundary of the saturated zone. This is the result of infiltrating water causing a thickening of water films surrounding soil particles immediately above the zone of saturation and creating a pulse in water flux as the saturated zone is approached.

The second concept has been termed the capillary fringe effect. According to Sklash (1978), Sklash and Farvolden (1979) and Sklash et al. (1986), a disproportionately large rise in the water table is caused by conversion of the tension-saturated capillary fringe into phreatic water by

infiltrating rain. This groundwater ridging effect occurs in areas where the capillary fringe is at or near ground surface (ie. near streams and seeps). These groundwater ridges provide early impetus for groundwater (primarily phreatic zone water) discharge while later high groundwater discharges are sustained by a basin-wide water table rise (Sklash, 1978). The capillary fringe effect is more commonly referred to as "piston-flow" (Seip and Seip, 1985).

1.1.3.5 Channel Interception of Precipitation

Although channel interception of precipitation is an operative mechanism to some extent during all storm events, the amount of water contributed to stream channels during runoff can vary greatly. The relative importance of direct precipitation onto stream channels as a source contribution to storm runoff is dependant upon such parameters as channel area, percent canopy coverage over a given channel and the intensity and duration of a particular precipitation event.

1.1.3.6 Historical Aspects

Historical aspects of runoff describe the history of the runoff during the interval between its arrival in the basin (temporal) and its arrival at the stream (ultimate delivery mechanism). Studies of this nature commonly attempt to identify changes in chemistry and isotopic content of runoff water while en route to the stream. Because contact

time relationships between the rainfall and earth materials on the hillslopes, in the vadose zone and stream channels are not generally known, the use of chemical tracers in historical approaches to stormflow generation are generally considered non-reliable.

1.2 Mass Balance Equations Used For the Separation of Storm Hydrograph Components

The use of mass balance equations for the separation of storm hydrographs into their component parts became popular in the 1960's (Kunkle, 1965; Pinder and Jones, 1969; and Newbury et al., 1969). The basis for this procedure requires the simultaneous solution of two mass balance equations; one for describing the flux of water in a stream (equation 1) and the other involving the flux of some species or tracer(s) in the water (equation 2) (Sklash, 1978). These two equations are;

$$Q_g + Q_d = Q_t \qquad (1)$$

$$C_gQ_g + C_dQ_d = C_tQ_t \qquad (2)$$

where; Q_g, Q_d and Q_t refer to groundwater, direct and total stream discharge respectively in $m^3 \cdot second^{-1}$ (m^3/sec) or $L \cdot second^{-1}$ (L/sec) and C_g, C_d and C_t refer to the concentration (parts per million (ppm) or milligrams per litre (mg/L) of a given parameter such as chloride or electrical conductivity in groundwater, direct runoff and total stream runoff respectively. Rearranging for

groundwater discharge we obtain the following equation;

$$Q_g = (C_t Q_t - C_a Q_a)/C_g \quad (3)$$

Tracers used in hydrological studies can be either conservative or non-conservative.

> "The concentration of conservative tracers alter only in response to physical processes such as diffusion, dispersion, condensation, evaporation, mixing or radioactive decay. The concentration of non-conservative tracers are primarily dependent on chemical reactions, but can also be influenced by physical processes" (Fritz et al., 1976).

If the above equations are used in percent component computations, groundwater must have a distinctively different species concentration than the direct runoff component(s). During runoff episodes this distinction should preferably remain constant both over time and space. Any discrepancies must be acknowledged and their variations accounted for in the equations in order to get valid and reliable results.

1.3 Previous Studies

1.3.1 Isotopes ($\delta^{18}O$), Water Chemistry and Mass Balance Equations

Several studies have investigated groundwater response during high runoff episodes in humid forested catchments. Studies that have made use of natural or artificial tracers, hydrometric and/or hydrochemical data or a combination of the above are numerous (Dincer et al., 1970; Martinec, 1975; Fritz et al., 1976; Sklash et al., 1976; Sklash and

Farvolden, 1979; Rodhe, 1981; Bottomley et al., 1984/85; Pearce et al., 1986; Kennedy et al., 1986; Blowes and Gillham, 1987; Lee and Hollyday, 1987; Dewalle et. al., 1988).

In the late 1960's it was common to use mass balance equations to differentiate stormflow into its component parts on the basis of water quality. Total dissolved solids concentration was used by LaSala (1967) and Archer et al. (1967) to estimate the quality of streamflow on the basis of quantity and quality of both groundwater discharge and direct runoff. Shortly thereafter Pinder and Jones (1968) investigated chemistry variations in total runoff in three small drainage basins in Nova Scotia to determine the groundwater component of discharge during periods of high flow. Through the use of bicarbonate, calcium, magnesium, sulfate ions and mass balance equations, Pinder and Jones concluded that the groundwater component during high stream discharge contributed between 32 and 42 percent of total flow. Direct runoff of event water contributed the remaining percentage to stormflow.

In the 1970's hydrological studies by Dincer et al. (1970), Martinec et al. (1974), Mook et. al. (1974) and Fritz et al. (1974) were among the first to utilize isotopes of oxygen and hydrogen as natural tracers. Studies by Fritz et al. (1976) in two small watersheds, one on a limestone escarpment and another situated on the Canadian Shield

concluded that more than 50% of total storm runoff had originated from within the basin and was flushed out during and shortly after the storm event.

Since then several studies making use of such isotopes, water chemistry and hydrometric observations have been published. Although results vary, the majority of isotopic studies performed within humid, forested catchments conclude that groundwater contributions to total stream runoff during high flow periods is substantial. Results of studies located within the Canadian Shield (Sklash and Farvolden, 1979; Bottomley et al., 1984/85; Bottomley et al., 1986) indicate that the groundwater component represents a significant percentage of high flow stream stages, some 40-80% of the total volume of runoff.

1.3.2 Radon-222 Gas

The importance of using radon-222 gas (^{222}Rn) as a conservative, radioactive tracer/indicator of groundwaters has only recently been recognized. Although studies as early as 1909 by Schlundt and Moore determined ^{222}Rn concentrations in spring waters at Yellowstone National Park, little emphasis was actually placed on the use of ^{222}Rn as a tracer in hydrological studies.

There are several applications involving the use of radon gas. Among the most popular uses are studies of atmosphere-water gas exchange rates in oceans and lakes

(Broecker, 1965; Broecker et al., 1967, 1974; Elsinger and Moore, 1980, 1983), population dose studies (Sasser and Watson, 1978; Hess et al., 1983 ; Cross et al., 1985), earthquake prediction and research (Ulomov and Mavashev, 1967; Sultankhodzhayev et. al., 1976; Sykes and Raleigh, 1975), and geological investigations (Skvarla, 1964; Dyck, 1969; Bowie, Ball and Ostle, 1971; Stevens, Rouse and DeVoto, 1971) each of which require the analysis of large numbers of samples.

To date few studies have been published emphasizing the use of ^{222}Rn gas in hydrological studies. Perhaps the first paper to shed light on the possibilities of ^{222}Rn in hydrological studies is that of Rogers (1958). In his study Rogers recognized the potential applications related to ground and stream water problems.

A paper by Jacoby et al. (1979) discussed ^{222}Rn applications to ground and surface water inter-relationships. This investigation was essentially a pilot study to help demonstrate the value of using a natural occurring tracer to identify locations where groundwater enters the surface water regime of rivers in significant quantities. Results stressed the importance and ease of using ^{222}Rn as a tool to identify specific locations of groundwater input into river systems, a conclusion earlier suggested by Rogers.

A more recent paper by Lee and Hollyday (1987) also

used ^{222}Rn as a natural tracer. This study took place on small streams in the Ordovician limestone areas of mid Tennessee. Again results indicated the usefulness and ease of determining location and magnitude of ground water seepage to surface streams.

In all three of the related papers mentioned above, ^{222}Rn is proved to be a useful tool for terrestrial hydrological studies. Note, however, that in each of the studies described above, ^{222}Rn was sampled during low flow stages, in different geologically traversed streams and obtained data were used without the aid of additional tracers for comparison. In this study ^{222}Rn data were compared with $\delta^{18}O$ and water chemistry data. In addition measurements of ^{222}Rn activity were obtained during both high and low streamflow stages.

1.4 Study Objectives

The primary objectives of this study are;

1) to evaluate the relative contributions of event and pre-event water in the surface storm runoff during summer precipitation events in a small forested basin;

2) to attempt to identify the mechanisms operative and responsible for generating surface storm runoff in the study basin using primarily water chemistry and environmental isotopes. Hydrometric observations have been used where possible; and

3) to test the usefulness of ^{222}Rn as a conservative tracer in storm runoff studies on the Precambrian shield.

CHAPTER 2
STUDY SITE DESCRIPTION AND METHODOLOGY

2.0 Introduction

The purpose of this chapter is to introduce the area of study and discuss the methodologies involved in this investigation. Study area location and history are discussed initially, followed by brief sections on geology, climate and vegetation. The study site is described next, followed by methodological sections on environmental isotope techniques, study site instrumentation, water sample collection and analysis.

2.1 Study Site Description

2.1.1 Location and History

The study site is in the Turkey Lakes Watershed (TLW) situated on the Precambrian Shield approximately 50 km north of Sault Ste. Marie, Ontario at 47°3' north latitude and 84°25' west longitude (Figure 2a). Located in an area of moderate acid deposition the average annual pH of incident precipitation lies between 4.3 and 4.5. Covering an area of 10.5 km^2, TLW contains a chain of five lakes ranging in area from 5.8 to 52.0 hectares (ha) (Jeffries et al., 1988). Drainage via the five lakes starts at the headwater Batchewana Lakes at an elevation of 497 metres above mean sea level (m.a.s.l.) and proceeds through Wishart, Little Turkey and Big Turkey Lake to the Batchewana River at an

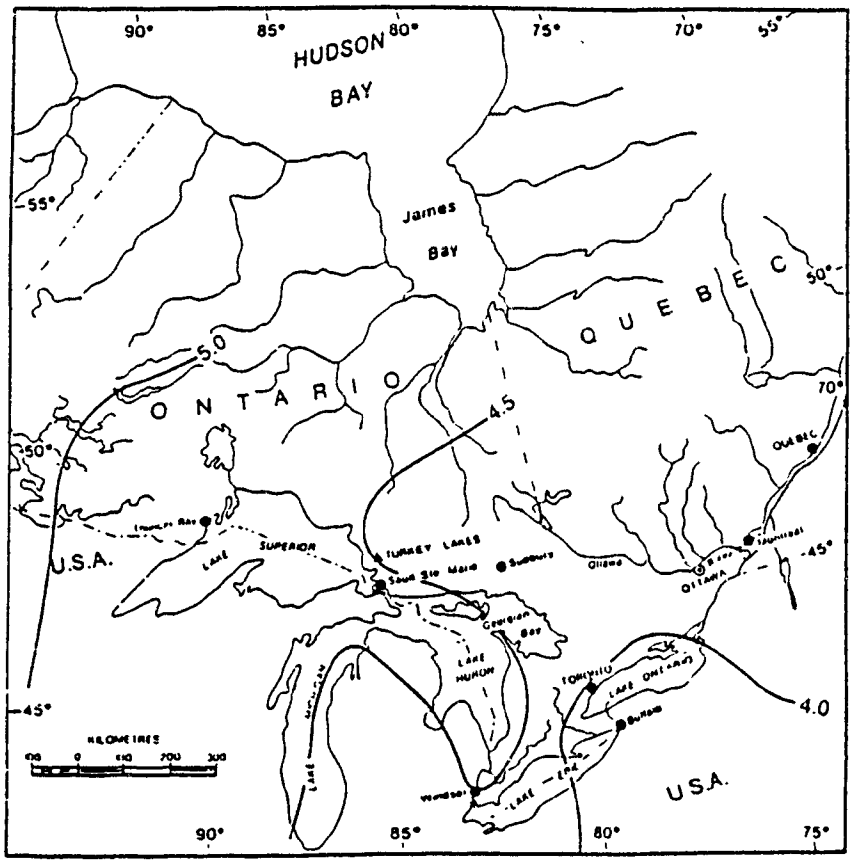

Figure 2a. Location of the Turkey Lakes watershed. Also shown are weighted mean precipitation pH contours from Wisniewski and Keitz (1983). Source: Bottomley et. al., 1986.

elevation of approximately 244 m. The Turkey Lake Watershed study was established as a multi- government agency project in 1980 to monitor the impact of acidic deposition on a relatively undisturbed terrestrial and aquatic Canadian Shield ecosystem. Studies within the watershed have involved intensive chemical, hydrological and biological investigations on the five lakes and 20 sub-basins. The location of the site used for this study at TLW is shown in Figure 2b as basin 35. Primary reasons for choosing this particular site include: 1) ease of accessibility; 2) the presence of a V-notch weir and discharge stage recorder; 3) remoteness from anthropogenic activity and industrial emissions; and 4) it remains in a relatively unaltered and natural state.

2.1.2 Geology

The TLW is primarily underlain by Precambrian silicate greenstone with minor granitic outcrops to the northeast (Semkin and Jeffries, 1983). Major bedrock faults tending approximately northwest-southeast and southwest-northeast have exerted control over basin drainage patterns (Jeffries et al., 1988). Absolute relief in the watershed is approximately 400 metres, the highest elevation being Batchewana Mountain at approximately 644 m.a.s.l. and the lowest at the basin outlet approximately 244 m.a.s.l.

Last glaciated during the Wisconsinan Ice Age, the TLW

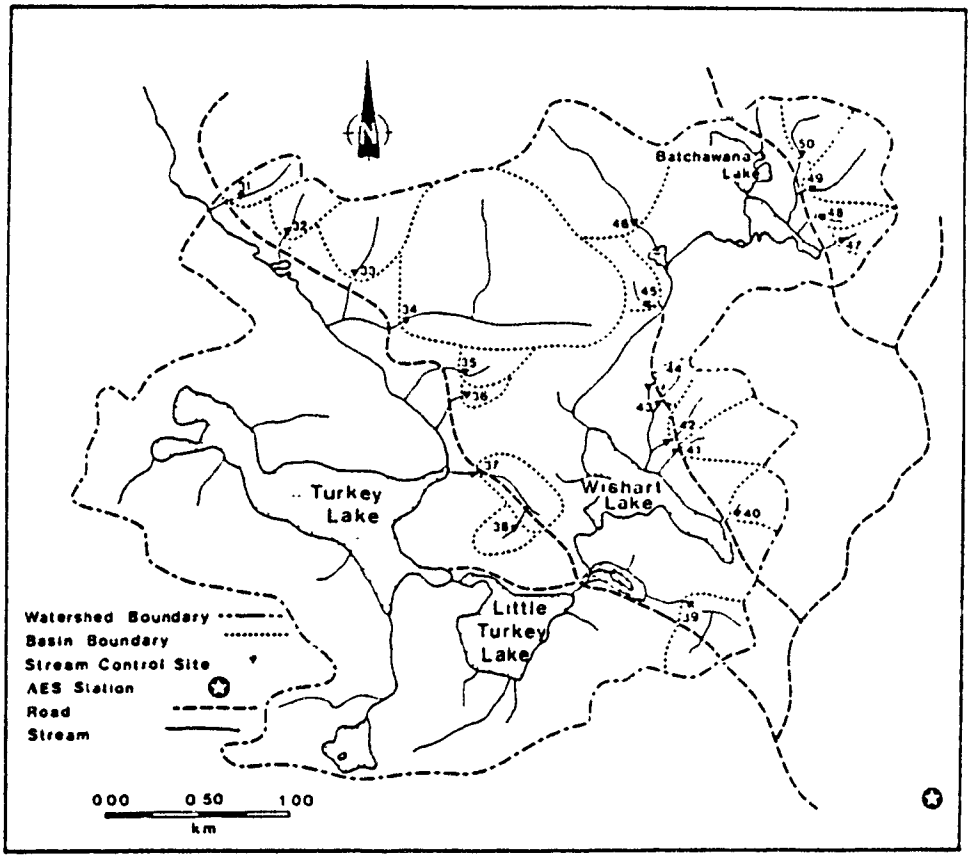

Figure 2b. Location of sub-basins within the Turkey Lakes watershed. Source: Nicolson, 1988.

remains characterized by a ground moraine of silty to sandy till with large amounts of boulders, cobbles and gravel. Overburden is deepest in large valleys and in bedrock depressions having measured depths up to 70 m (Elliot, 1985). The till can be divided into two types; an upper boulder ablation till generally less than 1 m thick overlies a more compact sandy basal till (Wickware and Cowell, 1985). Permeability of the overburden decreases with depth. The shallow ablation till has higher permeabilities ($1x10^{-3}$ cm/sec) and generally low (near zero) carbonate content, while the basal till has lower permeabilities ($1x10^{-5}$ cm/sec) and higher carbonate content (0.5-1.5%) (Craig and Johnston, 1988). According to Kusmirski and Cowell (1983), the mineralogy of the till is more felsic than the underlying bedrock showing that the material was likely primarily delivered from the large granitic intrusions that occur just north of the basin. Well developed Orthic Humo-ferric podzols are the dominant soils in the watershed (Wickware and Cowell, 1985).

2.1.3 Climate and Vegetation

The TLW is characterized by a moist continental climate as defined by Strahler (1979). Mean annual daily temperature at Sault Ste. Marie is 3.3°C with a July mean daily temperature of 17.8 and a mean daily January temperature of -10.2°C. In 1981 and 1982 measured annual precipitation in

the watershed was 1189 and 1285mm respectively.

Situated within the Great Lakes- St. Lawrence Forest Region, TLW is heavily forested. Vegetation is mostly old growth (120-180 yr.) forest predominantly composed of sugar maple (Acer saccharum Marsh) and yellow birch (Betula alleghaniensis). Typically on upland forested sites maple accounts for approximately 90%, other hardwoods 9% and conifers 1% of the total phytomass. On lowland sites the proportion of conifers to hardwoods is higher (Jeffries et al., 1988).

Physical anthropogenic influences within the watershed are minimal. Construction of forest access roads and a light selective harvest of large pine and veneer-quality yellow birch took place in the mid-1950's (Nicholson, 1988). Apart from that and the presence of a single hunter's cabin inhabited perhaps two weeks per year, the basin is undisturbed and uninhabited (Jeffries et al, 1988).

2.1.4 Basin 35

Figures 3a and 3b display basin relief and study site instrumentation respectively. Covering an area of 8.71 ha, relief in Basin-35 is near 120 metres. Upslope of the V-notch weir, which is situated at 378 m.a.s.l., the visible surface stream channel is approximately 50 m in length. Relief of this stream is approximately 12-15 metres.

Canopy coverage within this basin is virtually 100%

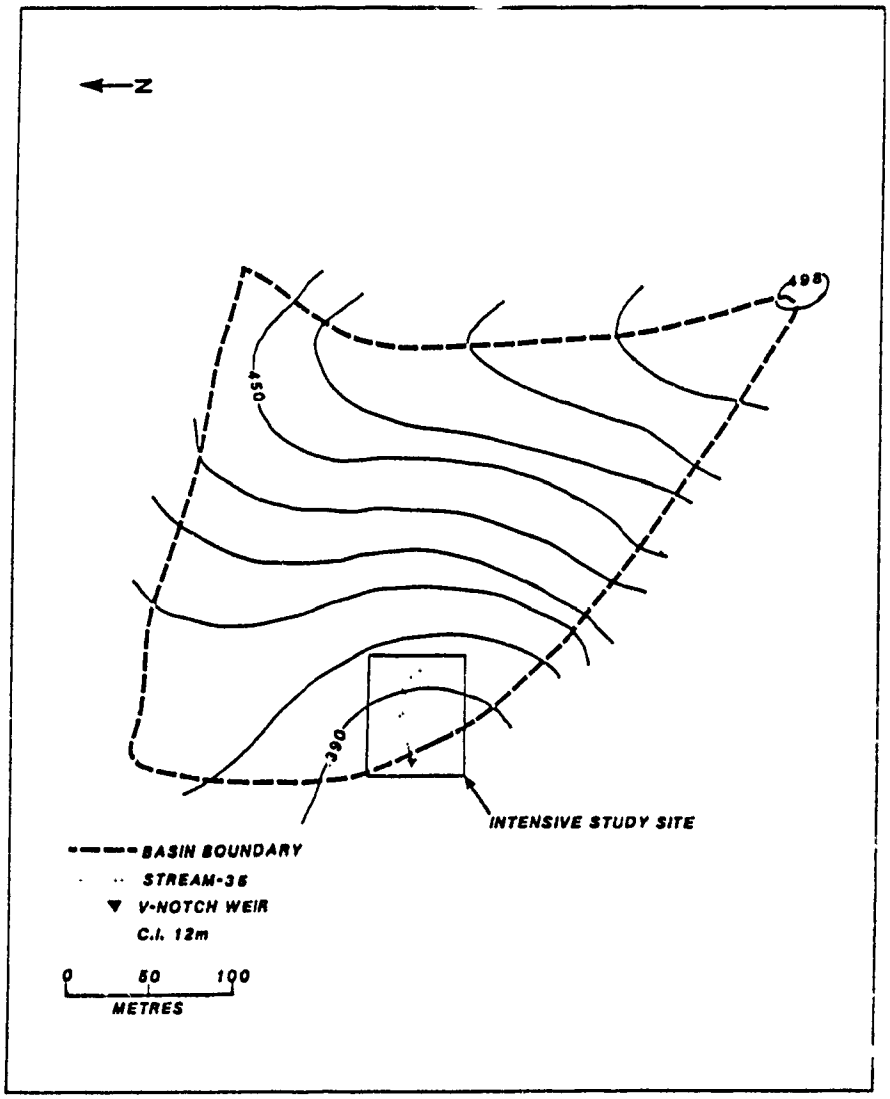

Figure 3a. Contour map of Basin-35. Instrumentation of the intensive study site is shown in figure 3b.

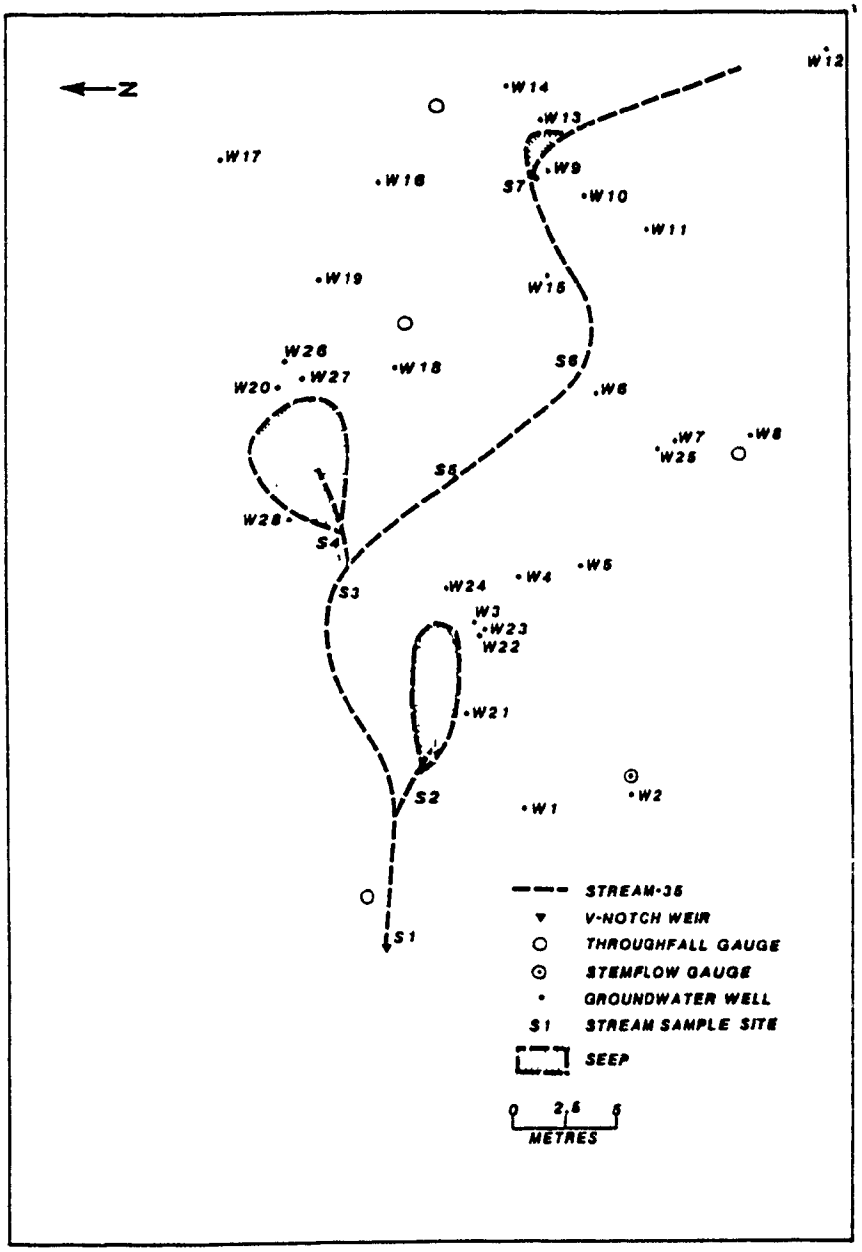

Figure 3b. Location of stream sample sites, groundwater wells and precipitation gauges within the intensive study site.

with very minor openings above the stream channel and seeps. To provide shelter from precipitation for electrical and gas-powered field equipment, a small canopy was erected approximately 3 m to the south-west of the weir.

2.2 Methodology

2.2.1 Water Chemistry

Because of their non-conservative nature, water chemistry data has only been used to augment environmental isotope results and conclusions in chapters 3 and 4. One exception, however, is the chloride ion. Studies using tritiated water have shown that chloride behaves very much like water (Eriksson, 1985). Also, it is generally thought that in nature, chloride does not accumulate in sizeable quantities in either living or dead biomass. Thus chloride has generally been considered the most conservative of the ionic species. As a result, where possible (i.e. when baseflow Cl^- concentrations are significantly different than event throughfall Cl^- concentrations) Cl^- has been used as a conservative tracer. Under such circumstances results are presented with caution and included within the text merely as supplimentary or additional data augmenting the environmental isotope data.

2.2.2 The Environmental Isotope Technique

Stable, naturally occurring isotopes of oxygen are

constituent parts of natural water molecules. As a result $\delta^{18}O$ is an excellent conservative tracer of water origin and movements. Several runoff studies have used $\delta^{18}O$ and other stable isotopes to quantify old and new water contributions to storm runoff episodes. Their use is based on the premise (and requirement) that event and pre-event water have distinct and different isotopic signatures. δOxygen-18 contents are commonly expressed as the relative difference in parts per thousand (called per mil, $^{o}/_{oo}$) between the $^{18}O/^{16}O$ ratio of a sample and the ratio in a standard. The reference international standard is SMOW (standard mean ocean water) (Craig, 1961b) where;

$$\delta^{18}O = [(Rsample - Rsmow)/Rsmow]*1000^{o}/_{oo} \quad (4)$$

and R represents the $^{18}O/^{16}O$ ratio in the water.

Using this method for hydrograph separation, the old and new water contributions at any specified time can be calculated by solving the two component mass balance equations for the water and isotopic fluxes in the stream. In this case, the mass balance equations can be expressed as;

$$Q_o = (C_s - C_n/C_o - C_n)\, Q_s \quad (5)$$

$$\text{and } Q_n = Q_s - Q_o \quad (6)$$

where Q_s, Q_o and Q_n refer to total stream, old and new water discharge and C_s, C_o and C_n express tracer concentrations in the stream, old and new water respectively. The natural chemical tracer of chloride can also be used in the above

equations.

The use of mass balance equations has limitations. When isotopic data are used in the above equations certain criteria must be met;

(1) the isotope content ($\delta^{18}O$) of the event component must be significantly different than that of the pre-event component;

(2) the phreatic and vadose zone waters are characterized by a single isotopic content or vadose water contributions to the stream are negligible;

(3) the event component maintains a constant isotopic content or variations in the isotopic content are documented and accounted for, and;

(4) surface storage contributions to the stream are minimal. These criteria must also be met if Cl^- is used in the above equations.

A second environmental isotope used in this study yet less frequently in hydrological studies is radon-222 gas (^{222}Rn). It is a chemically inert radioactive gas and an intermediate decay product of the uranium series created by the decay of radium-226 (^{226}Ra) (Figure 4). Concentrations of ^{222}Rn in groundwater are primarily related to; 1) the concentrations of ^{226}Ra present in the aquifer (which generally increased with depth), and 2) the proximity to and contact time groundwater has with the radon generating source.

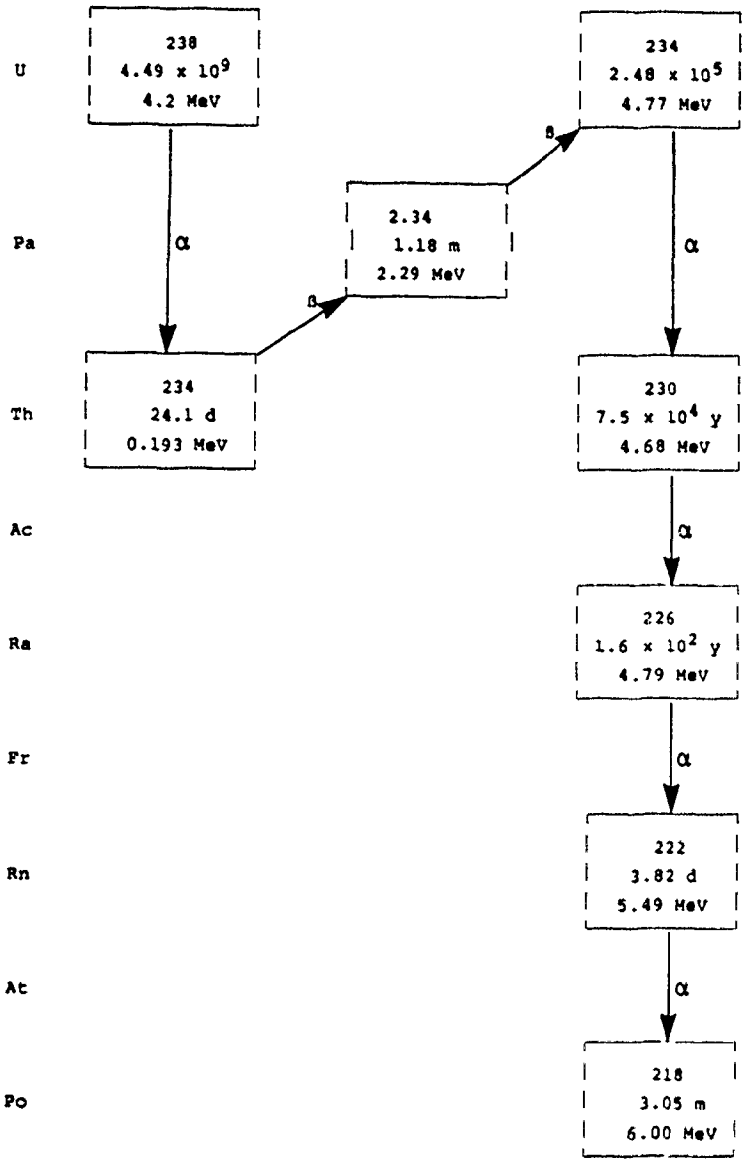

Figure 4. Decay for U^{238} to Po^{218}. Within each block are atomic weight, half life and energy of the decay. (Source: Brutsaert et. al., 1981).

The concentration of ^{222}Rn (half-life 3.82 days) in groundwater increases until the rate of loss by radioactive decay of ^{222}Rn atoms in solution balances the rate of supply by radioactive decay of ^{226}Ra in the source material (Jacoby et. al., 1979). Radon-222 concentrations in water are generally high in most granite and in high grade metamorphic rocks, a result of high concentrations of ^{226}Ra. In contrast less metamorphosed rocks have somewhat lower ^{222}Rn concentrations (Curi, 1910). Typical activities range from 100 disintegrations per minute per litre (dpm/L) in waters situated in clastic sedimentary rocks to greater than 10000 dpm/L in waters situated within igneous and metamorphic rocks (Lee and Hollyday, 1987).

The location and magnitude of groundwater seepage can be determined by measuring the activity of ^{222}Rn in streams (Lee and Hollyday, 1987). Because ^{222}Rn is readily soluble in water yet diffuses rapidly into the atmosphere upon aeration, activities of ^{222}Rn in groundwater may be 2 to 4 orders of magnitude greater than the surface water to which it contributes. As a result, knowledge of the ^{222}Rn concentrations in groundwater, seeps and streams at various site-specific locations makes ^{222}Rn a potentially suitable geochemical candidate for hydrological considerations if proper collection procedures are followed, eliminating aeration of the water sample. As with other isotopic data, ^{222}Rn values obtained can be used in mass balance equations

to determine relationships between ground and surface waters.

Note that because ^{222}Rn is readily diffusable upon aeration and there is no atmospheric source of ^{222}Rn, concentrations in the atmosphere can be considered nil. Analysis of precipitation samples has confirmed this statement.

Based on the above and because the relative amount of ^{226}Ra bearing rock in Basin-35 is unknown yet assumed to increase with depth, measured ^{222}Rn concentrations in groundwater directly reflect water residence time and source (i.e. vadose zone or phreatic zone water). Thus ^{222}Rn concentrations in groundwater increase with depth and, to a limited degree (meaning for a short period of time until equilibrium is reached), with residence time within the basin.

2.3 Instrumentation

A total of 28 groundwater wells (hereafter referred to as W1, W2, W3, ..., W28) were installed throughout the study area to monitor groundwater (see Figure 3b). Installation of the wells proved a difficult and frustrating experience, a result of the bouldery ablation till. Of the three methods used to install wells (gas powered rotary auger, percussion and sonic vibration coring and manual hand auguring), manual auguring proved most effective. Well depths ranged from 40-

110 cm. Well location was determined primarily by infield surface topographic observations based on the assumption that groundwater flow paths followed surface topography.

Each well was made of polyvinylchloride (PVC) pipe, capped at the base and slotted (approximately 2 cm apart) over 30cm from a point 5cm above the base. The slotted length of the pipe was wrapped with a vinyl mesh and nylon screen to prevent sedimentation at the bottom of the well. Changes in the position of the water level within each well were monitored by one of two techniques; 1) a calibrated rod attached to a ping pong ball floated on top of the water within each well depicting the water height from the base of the well and 2) through the use of a weighted water level tape.

Incident precipitation volume was measured using a standard Atmospheric Environment Service (AES) rain gauge situated approximately 4 km from basin 35. Reasons for the location of the open precipitation rain gauge are two-fold; 1) Because the TLW is heavily forested, few sites within the watershed represent true open areas in which falling precipitation would be unaffected by proximity to standing vegetation, and 2) close proximity to the field laboratory ensured continuous monitoring and recording of precipitation volume and intensity. Approximate rain gauge and field laboratory location is depicted in figure 2a as the AES station. According to Semkin and Jeffries (1986)

precipitation quantity measurements may be up to 15% in error, a result of orographic effects within TLW. Bulk precipitation samples used for chemical analyses were collected in open 24 cm inside diameter (i.d.) pails covered with a cleaned cotton screen to prevent organic and particulate matter from contaminating samples. These samples were collected at the AES station.

Samples of throughfall precipitation, or that portion of gross rainfall which directly reaches the forest litter through spaces in the vegetative cover and as drip from leaves, twigs and stems (Helvey and Patrick, 1965) were collected from four locations. These gauges consisted of pails of similar dimension and construction as that mentioned above. A third type of rain gauge used in this study collected stemflow. Stemflow is defined as that portion of the gross rainfall which directly reaches the litter or mineral soil by running down the stems or trunks of trees (Helvey and Patrick, 1965). This rain gauge was composed of a coiled 2.5 cm i.d. slit Tygon tube wrapped tightly to the tree bark at the base of a sugar maple. Gaps between the tree and tubing were filled with non-toxic silicon sealant. Water traveling down the stem of the tree was diverted into the coil and eventually into a precipitation collector. Galvanized nails were used to secure the coil to the tree in order to minimize contamination of the stemflow sample with ferric oxide from

regular steel nails. Whenever possible precipitation collectors were rinsed with distilled water prior to rain events in order to remove any debris or particulate (including dry deposition particulate) matter deposited during interstorm periods.

2.3.1 Stream Discharge

Continuous stream discharge was recorded by a Steven's Automated Water Level Recorder situated adjacent to the 90° V-notch weir (Figure 3b). Stage values recorded were substituted into the equation

$$Q = 1.38h^{2.5} \quad (7)$$

where; Q = total discharge in $m^3 \cdot sec^{-1}$ and h = the water stage head in metres as recorded by the Steven's recorder (Gregory and Walling, 1973). Discharge values were later converted to litres per second ($L \cdot sec^{-1}$) for ease of interpretation.

2.4 Water Sample Collection

The collection of all water samples for analysis took place through May-September 1988. Stream water samples, collected either manually or with a peristaltic pump were obtained at regular sites on the stream. In total seven stream sampling sites (hereafter referred to as S1, S2, S3, S4, S5, S6 and S7, see Figure 3b) were initially chosen. However, due to extended drought during the sampling period

only four sites (S1, S2, S3 and S4) remained wet. S1, S2 and S4 were continually sampled throughout the summer. During August, when antecedent conditions were wet, a small number of samples were collected from S7.

At the time of sampling, groundwater wells were pumped dry and allowed to recharge prior to sampling. Samples were collected using a peristaltic pump. Again due to extended summer drought all wells except W3, W22 and W27 went dry for most of June, July and early August. Heavy rains during the first two weeks of August and continued frequent precipitation events throughout August resulted in standing water in most of the groundwater wells from this time until the completion of field work.

Samples used for chemical analysis, electrical conductivity (EC) and pH measurements were collected in 500 ml polyethylene bottles. Prior to sampling each bottle had been acid washed (HNO_3) and rinsed with distilled deionized water (Environment Canada, 1983). Isotope samples were collected and stored in sterile 22 ml glass scintillation vials. Radon-222 samples were collected in evacuated and sealed 250 ml graduated cylinders to minimize gas loss by diffusion to the atmosphere.

Sampling intensity varied greatly throughout the summer. During periods of low flow, samples were collected on average, every second or third day. Prior to expected rain events, samples were collected from the stream and

wells when possible. During precipitation events water samples were collected from the wells, stream and precipitation gauges at varying intervals. The time interval between collecting samples was a function of several factors; storm intensity, storm duration and quantity, basin response and antecedent conditions. Due to the large number of parameters investigated and logistical constraints, it was not possible to collect continuous data for all of the parameters investigated.

2.5 Water Analysis

All chemistry samples were filtered through prewashed .45µm glass fiber filters to remove particulate matter. Bottles containing samples for chemical analysis were refrigerated at 6°C at the TLW field laboratory within twenty minutes of collection. Conductivity was measured for each sample within 24 hours of collection. Measurements of pH were taken irregularly. Electrical conductivity (EC) was measured using a portable Cole/Parmer Digital conductivity meter model 1481-50. Sample temperature measurements were taken concurrently with EC measurements using a Cole/Parmer Digital Thermometer. Conductivity values were later corrected to 25°C. The pH of samples was measured using an Orion meter and electrode.

At the Great Lakes Forestry Centre (GLFC) laboratory in Sault Ste. Marie, chemistry samples submitted were analyzed

within two weeks in accordance with methods outlined by the Department of the Environment (1979). A Technicon Auto Analyzer II-C^{+} was used to analyze sulphate (SO_4^{2-}) by methyl-thymol blue, and chloride (Cl^-) by mercuric thiocyanate. Coloured samples (usually those of throughfall and stemflow) were analyzed for SO_4^{2-} and Cl^- using a Dionex ion chromatograph. A Varian 1275 spectrophotometer was used to analyze calcium (Ca^{2+}) and magnesium (Mg^{2+}) by atomic absorption spectrophotometry and potassium (K^+) and sodium (Na^+) by flame emission spectrophotometry. Maximum analytical error ranges between 3-5 %. Samples collected for $\delta^{18}O$ analysis were stored and later analyzed at the Isotope laboratory of the Earth Sciences Department of the University of Waterloo using a varion mass spectrometer. Analytical error is better than $0.2^{o}/_{oo}$ at a 95% confidence level (Pearce et al., 1986).

Unlike sampling for water chemistry and $\delta^{18}O$, sample collection of ^{222}Rn was more complicated. Radon gas is readily soluble in water yet quickly escapes to the atmosphere upon aeration. As a result, on site techniques for the sampling of water for ^{222}Rn need to minimize aeration of the water and avoid transfer of samples through the open air. Analysis must then take place as soon as possible so that the radon does not diffuse through the sample container.

In this particular study, direct de-emanation and

alpha-scintillation counting was used to determine ^{222}Rn activity in water samples. Surface water samples were collected by drawing water directly into an evacuated 250 ml graduated cylinder via a tygon tube. To sample ^{222}Rn activity in groundwater, wells were emptied and allowed to recharge. Unaerated water samples were again collected in evacuated 250 ml graduated cylinders. In order to ensure adequate suction to obtain sufficient volume for analysis, unaerated water samples were delivered through a flexible tygon tube via the peristaltic pump prior to being attached to the graduated cylinder. Between 75 and 175 ml of water were obtained for each sample. Factors regulating the volume of sample collected were; graduated cylinder capacity, maximum vacuum potential obtainable in each cylinder and rate and volume of recharge in groundwater wells.

Samples were degassed within one hour of collection. The graduated cylinder is attached to an alpha-scintillation counting cell on an airtight de-emanation board and the entire system is evacuated. The scintillation cells are coated internally with silver activated zinc sulfide powder (ZnS). A carrier gas, in this case air is then bubbled through the water. Dissolved radon gas is collected at the top of the water column and diverted through a tube containing desiccant directly into the alpha-scintillation counting cell. Once the evacuated system has reached equilibrium the scintillation cell is disconnected from the

graduated cylinder and the time of sample de-gassing (day, hour, minute and second) and water sample volume is recorded. The alpha-scintillation counting cell is then placed into a dual counting portable radon counter which simply measures, with the use of a photomultiplier tube, alpha radiation induced phosphorescing inside the counting cell. With the alpha-scintillation cell placed in the light-proof counting chamber the cell is allowed approximately 20-30 minutes for the ^{222}Rn daughters ^{219}Rn and ^{220}Rn to ingrow; they decay with half lives of 4 and 56 seconds respectively. The sample is then counted approximately 45 minutes. Radon-222 is immediately flushed out of the cell after the data has been recorded. The counting efficiency of each alpha-scintillation cell and counting instrument varies. Counting efficiencies of each scintillation cell are determined using ^{226}Ra standards of 481 dpm/L. Average error of reported ^{222}Rn activity is approximately 10%.

CHAPTER 3
RESULTS

3.0 Introduction

To complete the objectives of this study field work was performed continually from May 12 to September 4, 1988. Full instrumentation of the study site was completed by the last week of May. Between June 1 and September 4 a total of eleven rain events (hereafter referred to as Event 1, Event 2, Event 3, ..., Event 11 or E1, E2, E3, ..., E11) of varying magnitude and duration were observed and monitored. Of the eleven precipitation events investigated, four (E1, E2, E4 and E7) had minimal precipitation quantity (<5 mm) and physical and chemical responses in the basin were insignificant. As a result, this chapter presents results from the seven intensively monitored storm events. Table 1 summarizes the parameters analyzed (at S1) for each of the seven precipitation events monitored. Due to the large number of samples collected from various sample sites, results emphasize data and trends noted specifically at S1 unless otherwise mentioned. The complete data set for each of these seven storm events is listed in Appendix 1. Baseflow and precipitation chemistry results are presented prior to storm event results.

3.1 Baseflow Periods: June-August 1988

During sustained low flow stages samples of both stream and groundwater were collected. Table 2 shows the average

Table 1: Results Table Showing Parameters Measured at S1 for Each Precipitation Event Monitored

Date	Event#	$[SO_4^{2-}]$	$[SiO_2]$	$[Cl^-]$	$[Ca^{2+}]$	$[Mg^{2+}]$	$[Na^+]$	$[K^+]$	pH	EC	$[^{222}Rn]$	$\delta^{18}O$
June 24	E3	*	*	*	*	*	*	*	*	*	*	*
July 11-12	E5	*	*	*	*	*	*	*	*	*		
July 13-14	E6	*	*	*	*	*	*	*	*	*		
Aug. 12	E8	*	*	*	*	*	*	*	*	*	*	*
Aug. 13-16	E9	*	*	*	*	*	*	*	*	*	*	*
Aug. 27-28	E10	*	*	*	*	*	*	*		*	*	*
Sept. 3-4	E11	*	*	*	*	*	*	*	*	*	*	

Table 2: Average Baseflow Ion (ppm) and ^{222}Rn (dpm/L) Concentration, pH and EC ($\mu S/cm$) for a Variety of Sample Sites

Sample Site	N	Parameter $[SO_4^{2-}]$	$[SiO_2]$	$[Cl^-]$	$[Ca^{2+}]$	$[Mg^{2+}]$	$[Na^+]$	$[K^+]$	pH	EC	$[^{222}Rn]^*$
S1	8	7.92	7.17	0.58	7.13	0.58	0.91	0.35	6.36	44.3	105.4
STDEV		0.19	0.42	0.17	0.41	0.02	0.13	0.05	0.06	4.37	16.4
S2	7	7.79	6.89	0.36	7.57	0.59	0.80	0.21	6.40	43.9	279.5
STDEV		0.09	0.04	0.04	0.26	0.02	0.05	0.03	0.02	4.35	28.1
S3	7	7.23	5.89	0.28	5.85	0.55	0.69	0.21	6.38	36.7	NA
STDEV		0.16	0.06	0.02	0.23	0.02	0.03	0.02	0.02	3.33	NA
S4	8	7.23	5.88	0.33	5.89	0.54	0.74	0.24	6.32	35.7	414.6
STDEV		0.17	0.12	0.08	0.25	0.02	0.08	0.05	0.07	4.33	81.5
W3	8	7.79	7.06	0.40	7.36	0.62	0.90	0.28	6.13	43.9	610.1
STDEV		0.15	0.07	0.12	0.41	0.03	0.21	0.06	0.09	4.65	122.2
W22	7	7.73	7.16	0.57	7.55	0.63	1.02	0.27	6.19	46.2	NA
STDEV		0.08	0.09	0.37	0.31	0.01	0.30	0.06	0.06	4.59	NA
W27	3	7.33	6.93	0.90	6.18	0.69	1.83	0.76	6.49	43.8	NA
STDEV		0.28	0.34	0.40	0.27	0.02	0.37	0.39	0.12	4.95	NA
W28	5	7.17	7.11	0.69	7.63	0.78	0.90	1.27	6.37	52.5	NA
STDEV		0.86	0.09	0.08	0.43	0.06	0.09	0.24	0.09	5.59	NA

N = Number of Observations

NA = Not Available

* Averages obtained during week of Aug. 18-25 when entire stream was flowing

baseflow ion and radon-222 (^{222}Rn) concentrations, pH and electrical conductivity (EC) values for a variety of sample sites (see Figure 3b for sample site location). Note the high standard deviation of the mean at S1 compared to other stream sample sites.

3.2 Precipitation

Table 3 displays the average ion concentrations, pH and EC for open, throughfall, and stemflow precipitation as measured for individual storm events. Throughfall rather than incident precipitation is emphasized in this study for the following reasons;

1) Because this basin is entirely forested, throughfall represents the majority of precipitation reaching the forest floor and stream channel. Between 1981 and 1985, a study conducted by Foster and Nicolson (1988) in Basin-31 of the Turkey Lakes Watershed (TLW; see Figure 2b), approximately 1.5 km NW of Basin-35 determined that annual interception by the predominantly maple covered canopy averaged 9% and ranged from 6 to 12%. Because Basin-31 is very similar to Basin-35 with regards to vegetation type and canopy coverage it is reasonable to assume similar percentages of interception;

2) throughfall generated during the growing season in mature hardwood forests and sampled at this study site is greatly enriched in dissolved ions, especially K^+, Mg^{2+} and Ca^{2+}

Table 3: Average Open, Throughfall and Stemflow Precipitation Chemistry

Date	Event#	$[SO_4^{2-}]$	$[SiO_2]$	$[Cl^-]$	$[Ca^{2+}]$	$[Mg^{2+}]$	$[Na^+]$	$[K^+]$	pH	EC	$\delta^{18}O$
June	E3[a]	4.23	0.05	1.06	0.77	0.16	0.73	0.28	4.23	49.0	NA
24	E3[b]	4.73	0.41	0.53	1.84	0.57	0.14	4.80	5.14	38.5	-6.31
	E3[c]	3.66	0.65	0.76	2.40	0.56	0.32	6.31	5.53	50.1	NA
July	E5[a]	0.37	0.04	0.04	0.29	0.05	0.34	0.11	4.83	6.66	NA
11-12	E5[b]	0.61	0.20	0.18	0.43	0.10	0.14	2.57	5.11	11.1	NA
	E5[c]	18.2	1.09	1.96	9.21	1.22	0.37	33.3	5.88	70.2	NA
July	E6[a]	4.96	0.06	1.02	0.69	0.12	0.68	0.25	3.96	49.8	NA
13-14	E6[b]	6.66	0.27	0.48	1.32	0.31	0.09	3.24	4.31	44.4	NA
	E6[c]	4.18	0.95	2.24	3.26	0.49	0.54	10.3	NA	NA	NA
Aug.	E8[a]	1.44	ND	0.31	0.27	0.04	0.18	0.10	4.44	15.1	NA
12	E8[b]	3.15	0.07	0.20	0.48	0.09	0.07	1.87	5.17	13.7	-5.69
	E8[c]	8.39	0.78	0.36	1.85	0.23	0.18	13.2	6.10	38.5	NA
Aug.	E9[a]	3.49	0.10	0.06	0.40	0.07	0.31	0.26	3.84	76.9	NA
13-16	E9[b]	3.43	0.63	0.26	0.85	0.10	0.08	0.77	4.65	12.5	-4.77
	E9[c]	10.7	1.80	0.39	7.37	0.75	0.47	21.8	6.40	46.7	NA
Aug.	E10[a]	0.65	ND	0.34	0.15	0.02	0.20	0.07	NA	7.2	NA
27-28	E10[b]	1.35	0.06	0.28	0.61	0.07	0.05	0.92	NA	7.7	-13.65
	E10[c]	4.30	0.46	0.38	1.88	0.24	0.08	10.6	NA	39.7	NA
Sept.	E11[a]	7.07	ND	0.20	0.46	0.09	0.07	0.17	3.89	50.9	NA
3-4	E11[b]	11.5	0.23	0.23	2.80	0.44	0.14	4.03	4.71	43.7	NA
	E11[c]	11.5	0.27	0.41	2.91	0.42	0.14	4.93	5.00	43.5	NA

ND = Not Detectable
NA = Not Available
EC = Electrical Conductivity (μS/cm)
[a] Open precipitation
[b] Throughfall precipitation
[c] Stemflow precipitation
$\delta^{18}O$ (‰)

and;

3) recent studies have shown that throughfall $\delta^{18}O$ may be different than that in incident rainfall. In a study by Pearce et. al. (1986) a 0.11°/$_{oo}$ enrichment in $\delta^{18}O$ was noted between incident and throughfall isotopic composition under a dense pine stand. Although this enrichment is close to analytical error, it suggests that larger variances are possible under the optimum conditions.

3.3 Precipitation Events

3.3.1 Rain Event 3; June 24, 1988

3.3.1.1 Introduction

On June 24 between 05:30 and 18:00 hours, 8.6 mm of rain fell on Basin-35 with an intensity near 1.5 mm/hour (Figures 5 and 6 where T0= 05:30 hours). Prior to this storm Basin-35 was subject to hot (28-34°C) and dry conditions for nearly two weeks.

3.3.1.2 Isotopes: Oxygen-18

Figure 5 displays variations in stream $\delta^{18}O$ during E3 storm runoff. A bulk throughfall sample collected after this event had a $\delta^{18}O$ value of -6.31°/$_{oo}$ while baseflow collected before precipitation initiation had an isotopically lighter value of -13.49 °/$_{oo}$. Assuming that vadose and phreatic water have the same ratio of $^{18}O/^{16}O$, separation of the runoff components by two-component mass balance equations

using isotopic methods according to Sklash and Farvolden (1979) is possible. This has been done in chapter four.

3.3.1.3 Radon-222

Fluctuations in ^{222}Rn activity in water samples collected fr m a number of sample sites during E3 are shown in Figure 5. At S1 measured ^{222}Rn activity in stream water fluctuated between 92 and 144 dpm/L throughout sampling of the event with the largest increase (approximately 56%) noted between T0 and T1. At S2, measured ^{222}Rn activity in stream water fluctuated between 250 and 298 dpm/L until near peak discharge. Samples collected approximately one hour after peak discharge (T6.5) measured increases in activity to 654 dpm/L. By T9, ^{222}Rn activity measured in S2 water samples remained slightly higher than pre-storm baseflow activity with a value of 355 dpm/L. In groundwater sampled from W3, approximately 2 hours after rain initiation (T2), measured ^{222}Rn activity increased from 298 to 718 dpm/L. Although ^{222}Rn activity in groundwater sampled from W3 decreased shortly after T3.5 activity remained approximately 80% greater than the measured pre-event groundwater activity in W3 through the duration of E3 sampling. Although data for W27 is not shown in Figure 5, limited data obtained from this well, located between 5 and 10 m upslope of the seep in proximity to S4 displays results similar to those obtained at S2. Activities increased from 197 to 390 dpm/L near peak

discharge and fluctuated little through the remaining duration of E3 sampling (T5.5-T13).

3.3.1.4 Chemistry

Figure 6 shows fluctuations in stream water chemistry during E3 storm runoff. Event water chemistry is shown in Table 3. Apart from Cl^-, K^+ and Na^+, minor ion concentration variations (<6%) were noted during E3 storm runoff.

Between T0 and T2, Cl^- concentrations decreased from .58 to .34 ppm. During the same time period concentrations of K^+ and Na^+ in stream water showed notable dilutions by 26 and 23% respectively. Variations in Cl^- concentration were less than 18% thereafter (T2-T13) while K^+ and Na^+ concentrations fluctuated between 12 and 31%. Values of EC reflect the trends of major ions deviating only slightly (at most by 8%) from its pre-storm baseflow value of 45.1 µS/cm.

3.3.2 Rain Event 5; July 11, 1988

3.3.2.1 Introduction

On July 11 between the hours of 12:00 and 16:30 (T0-T4.5, see Figure 7) approximately 27 mm of rain was deposited on Basin-35 with varying intensity. On July 10th at 03:00 hours, approximately 33 hours prior to the onset of this event, some 9 mm of rain had fallen on the same basin in 4 hours. Response was minimal with discharge varying at most approximately 30%. Hot and sunny weather with

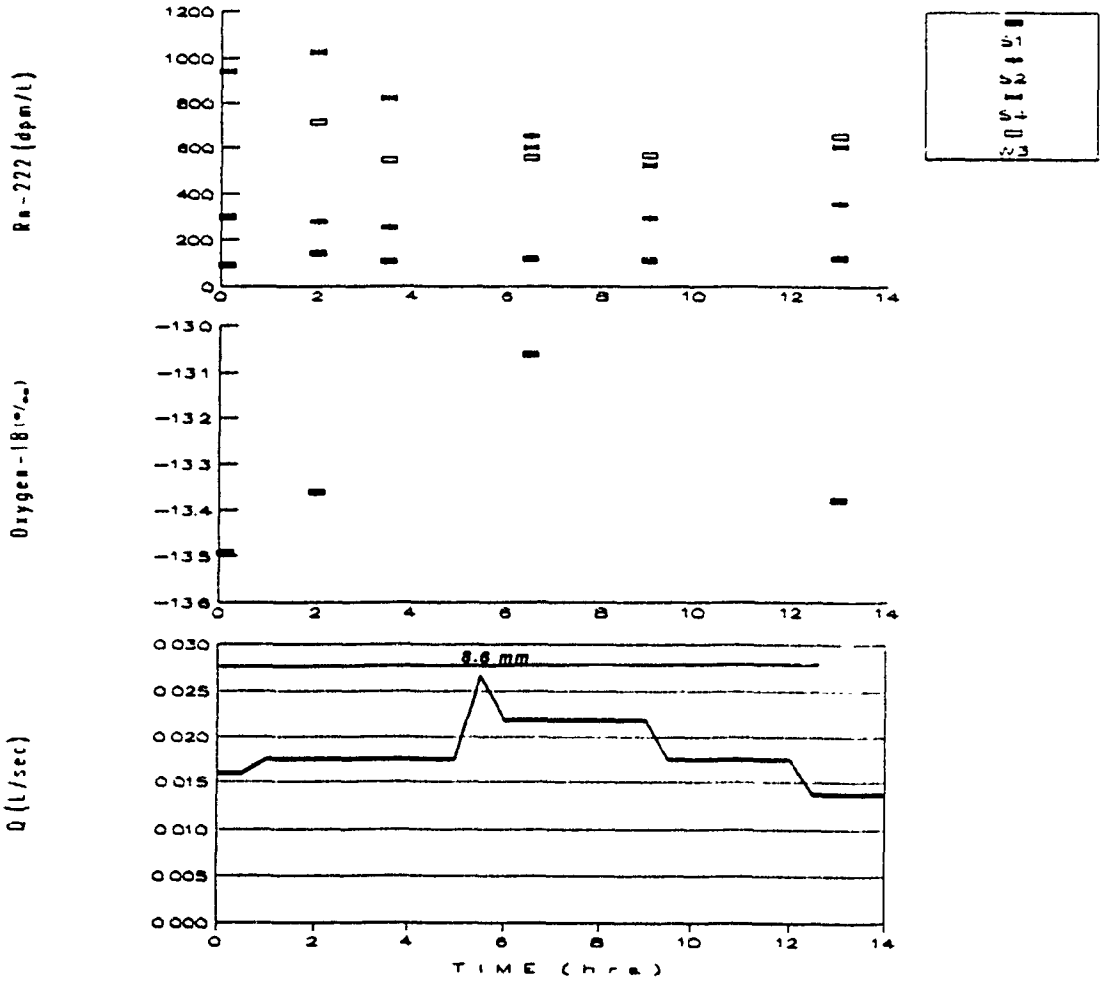

Figure 5. Temporal trends in stream ^{18}O at S1 and measured ^{222}Rn activity at S1, S2, S4 and in W3 with discharge (Q) during E3 storm runoff. Time "zero" corresponds to the commencement of rain at 05:30 hr, June 24. The solid black line above the hydrograph indicates precipitation duration and quantity.

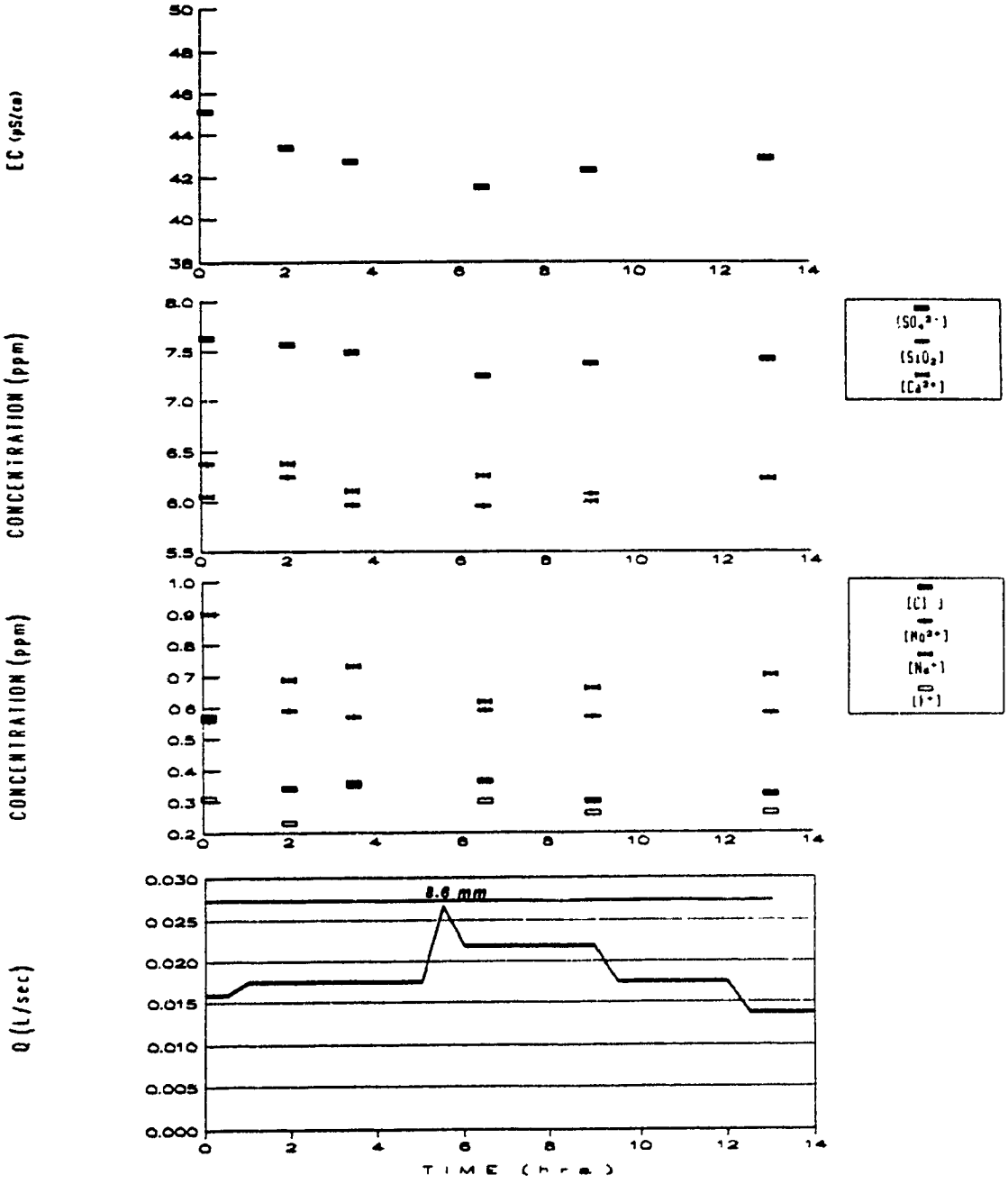

Figure 6. Temporal trends in stream water chemistry and EC with discharge (Q) at S1 during E3 storm runoff. Time "zero" corresponds to the commencement of rain at 05:30 hr, June 24. The solid black line above the hydrograph indicates precipitation duration and quantity.

temperatures in the mid to upper 30°C range were the prevalent meteorological conditions in TLW for 14 days before July 10. Water samples collected at peak flow and during the descending limb of the hydrograph for the July 10 precipitation showed minor variations in chemistry.

Event 5 precipitation came in two stages. The first stage occurred between T0 and T2.17 resulting in approximately 14 mm of rain. During the second stage (T3-T4.5) approximately 13 mm of rain fell. As a result, the storm hydrograph displays two distinct peaks. Figure 7 displays the variations in water chemistry and EC with discharge at S1.

3.3.2.2 Chemistry

Although $\delta^{18}O$ and ^{222}Rn data is not available for this event, water chemistry data are interesting. All ion con-concentrations in pre-storm baseflow were significantly higher than their respective event water concentrations except K^+ (see Figure 7 and Table 3). During the initial peak in discharge all ion concentrations except Cl^-, K^+ and Na^+ decreased between 10 and 30%. Concentrations of K^+ and Na^+ peaked with runoff increasing 133 and 63% respectively over baseflow concentrations. Chloride concentrations remained constant. Conductivity followed the trend set by major ions decreasing from 43.5 to 36.6 µS/cm.

After the initial peak but prior to the secondary peak

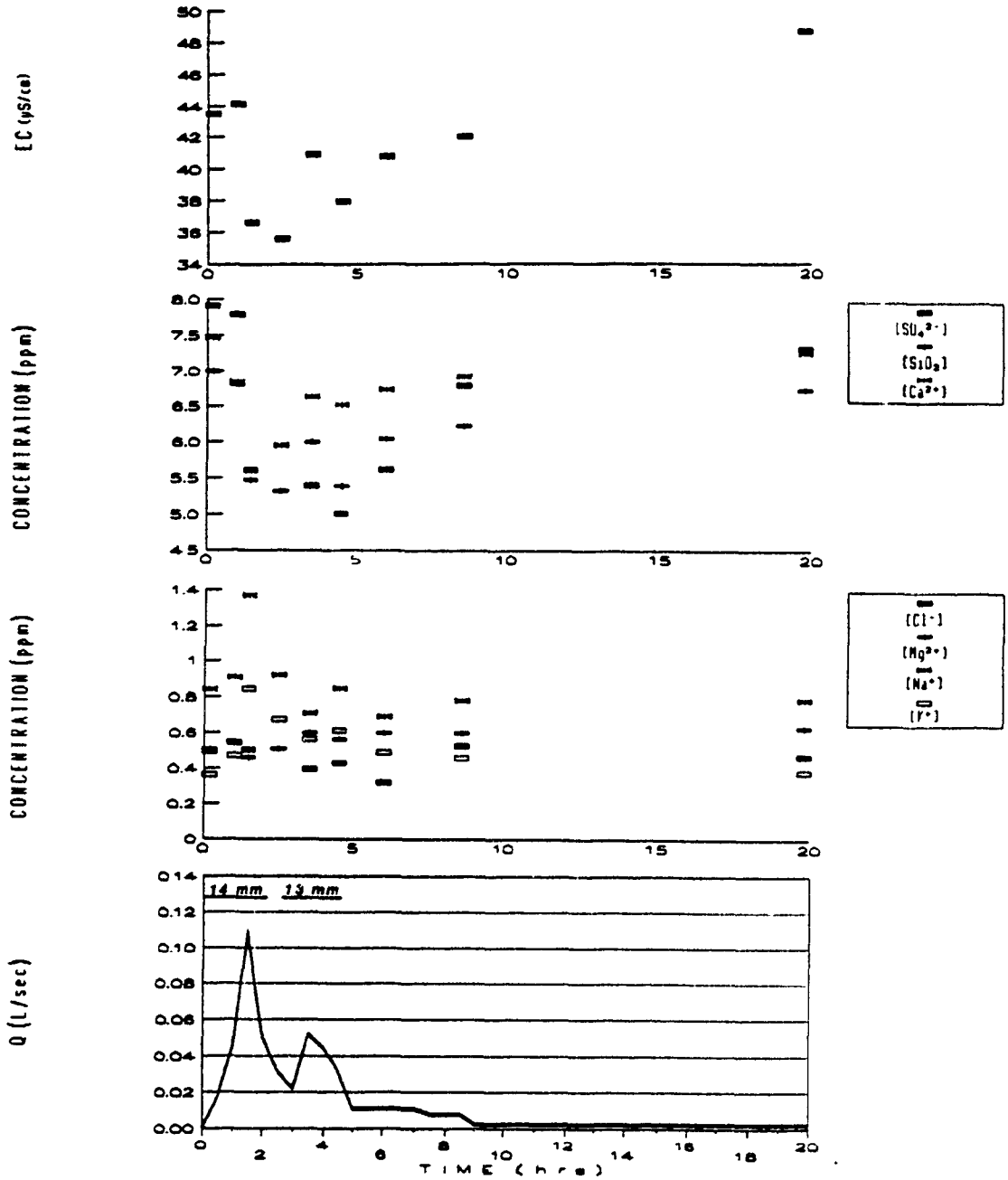

Figure 7. Temporal trends in stream water chemistry and EC with discharge (Q) at S1 during E5 storm runoff. Time "zero" corresponds to the commencement of rain at 12:00 noon, July 11. The solid black line above the hydrograph indicates precipitation duration and quantity.

in runoff most ion concentration trends reversed. Potassium and Na^+ concentrations decreased to 67 and 52% of the concentration attained during the initial discharge peak while concentrations of most other ions remained constant or increased only slightly. Chloride concentration at this time is not known due to error in lab procedures. Conductivity increased from 36.6 to 40.9 µS/cm. Samples collected approximately one hour after the second peak in discharge show similar trends in chemistry as those sampled during the first discharge peak. All ion concentrations decreased to near or below initial depressed concentrations reached during the first peak in discharge except Cl^-, K^+ and Na^+. Concentrations of these three ions increased to between 60 and 80% of the concentrations obtained during initial peak in discharge. Conductivity followed the trend of most other ions decreasing to 37.9 µS/cm. Electrical conductivity increased thereafter as did all ion concentrations except K^+ which decreased to near the pre-event baseflow concentration.

3.3.3 Rain Event 6; July 13, 1988

3.3.3.1 Introduction

Forty-eight hours after the onset of precipitation Event 5 a rainstorm measuring 12.7 mm occurred. This event (E6) had a duration of 5 hours between 12:00-17:00 hours (T0-T5; see Figure 8). As in event 5 there were two periods

of moderate to heavy rain resulting in a double peaked hydrograph. Between T0 and T3.5 hours approximately 3 mm of rain fell on the basin producing the first and smaller of the two runoff peaks. Between T3.5 and T5 hours moderate to heavy rains dropped an additional 9 mm of water on the basin resulting in the formation of a second, more pronounced peak on the hydrograph. Figure 8 displays results for this event in a similar fashion as those presented for E5.

3.3.2.2 Chemistry

Electrical conductivity and all ions measured (except Ca^{2+} and Cl^-) in pre-storm baseflow had concentrations representative of average baseflow (±9%, see Table 2). Chloride and Ca^{2+} concentrations were 27% and 17% respectively below and above mean baseflow concentration. All pre-event stream water ion concentrations were significantly higher than event water ion concentrations except K^+ which was only 10% of event water concentrations.

Observation of runoff data show that during the first and smaller of the two runoff peaks minor variations in stream water chemistry occurred for all ions except K^+ and Ca^{2+} which increased by approximately 29% and 15% respectively. Electrical conductivity remained constant.

During the second more pronounced discharge peak Na^+ and Cl^- concentrations increased initially by 19 and 22% over baseflow values while K^+ concentrations increased 36%.

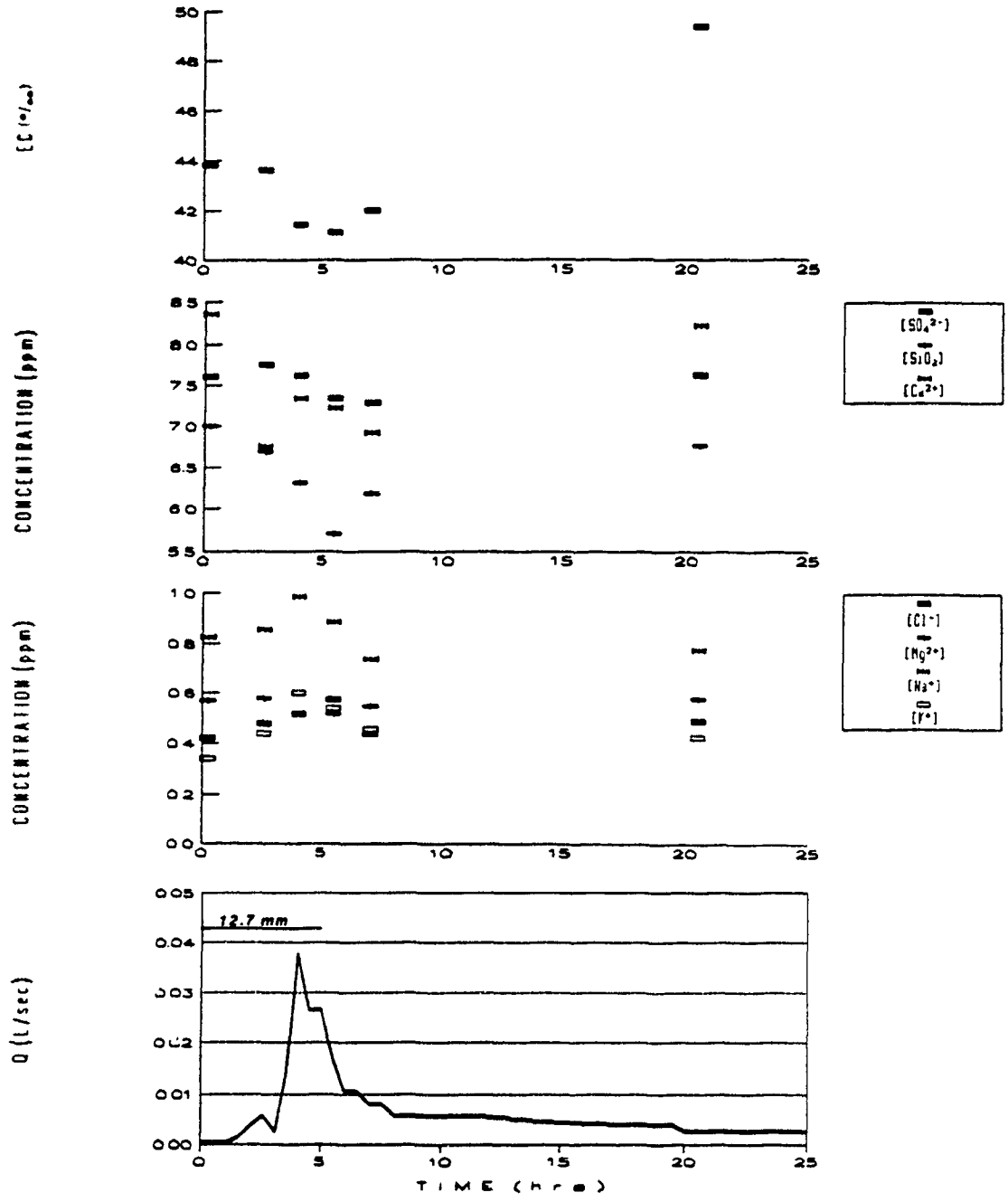

Figure 8. Temporal trends in stream water chemistry and EC with discharge (Q) at S1 during E6 storm runoff. Time "zero" corresponds to the commencement of rain at 12:00 noon, July 13. The solid black line above the hydrograph indicates precipitation duration and quantity.

Silica, Ca^{2+} and Mg^{2+} concentrations decreased between 9 and 14% while SO_4^{2-} varied little. All ion concentrations decreased when measured at T5.5 except Cl^- which increased and Mg^{2+} which remained constant. Samples collected at T20.5 on July 14 had ion concentrations approaching those of pre-storm baseflow.

3.3.4 Rain Event 8; August 12, 1988

3.3.4.1 Introduction

For 13 days between July 18-30, hot and dry weather persisted in TLW with daily temperatures between 25 and 35°C. On July 20 no streamflow was observed in Basin-35. Although water remained ponded behind the weir and there was visible saturated area in the seep in proximity to S4, evapotranspiration effects were significant as noted by diurnal fluctuations recorded on the Steven's (automatic stage recorder) chart paper. Between August 1 and August 6, a series of severe thunderstorms dropped a total of 96.2 mm of precipitation on the TLW. Although sampling took place during several of these storm events, lightening strikes in close proximity to the study site frustrated all attempts to sample frequently.

On August 12 Basin-35 had no visible flow. Between T0 and T1.42 hours (see Figures 9 and 10) a severe thunderstorm passed over the TLW. Approximately 25 mm of precipitation fell on Basin-35. Response was instantaneous. Discharge

increased from 0 to 4.5 L/sec within 15 minutes. Sampling continued until T8 on August 13. At 02:50 hours a second severe thunderstorm entered the region. An additional 27.2 mm of rain fell on Basin-35 by 05:00 hours. Due to mechanical problems with the peristaltic pump and a portable generator used to provide electricity for lighting, this secondary storm was not sampled.

3.3.4.2 Isotopes: Oxygen-18

Significant differences in $\delta^{18}O$ between event and pre-event water make separation of the components of runoff possible. Event water had $\delta^{18}O$ values of -5.73 and -5.64°/$_{oo}$ while pre-event baseflow water samples had an average $\delta^{18}O$ value of -12.27°/$_{oo}$. Figure 9 displays stream $\delta^{18}O$ response during E8 storm runoff. At T1, stream $\delta^{18}O$ was -7.34°/$_{oo}$. This indicates that peak storm runoff was dominated by event water contributions.

3.3.4.3 Radon-222

During E8 ^{222}Rn activities were measured frequently at S1, S2, S4 and in W3. Temporal variations in ^{222}Rn activity at the monitored sites with discharge are displayed in Figure 9. Approximately 40 minutes after peak runoff (T1.2) measured ^{222}Rn activities in stream water sampled at S2 and S4 decreased approximately 40% (from 175-108 dpm/L at S2 and from 297 to 180 dpm/L at S4). At the same time stream water

sampled at S1 measured a near 88% decrease in ^{222}Rn activity (from 240 to 30 dpm/L). Measured ^{222}Rn activity at S1 remained low until T4.5 when it increased to 106 dpm/L, 56% of the measured baseflow activity at this stream sample site. Although measured ^{222}Rn activity S2 and S4 fluctuated between T1.2 and T8 there was a general trend of increasing activity after T1.2. By ~6.5 ^{222}Rn activity at S2 and S4 had returned to pre-event baseflow values. Unlike stream water samples, measured ^{222}Rn activity in groundwater sampled from W3 almost doubled at T1.2 increasing from an initial value of 405 at T0 to 752 dpm/L. Activity then remained more or less constant in all samples collected from this well.

3.3.4.4 Chemistry

Figure 10 displays temporal variations in stream water chemistry with discharge during E8 storm runoff. Except for K^+, all event water ion concentrations were significantly less than their respective baseflow concentrations. Approximately 30 minutes after peak runoff, all monitored ion concentrations in stream water, except K^+ decreased between 24 and 82% of baseflow values. Concentrations of K^+ displayed the opposite trend increasing by 81%. All ion concentrations, again with the exception of K^+ continued to increase thereafter approaching pre-storm baseflow values. Potassium concentrations decreased towards baseflow values. Electrical conductivity followed the trend of the majority

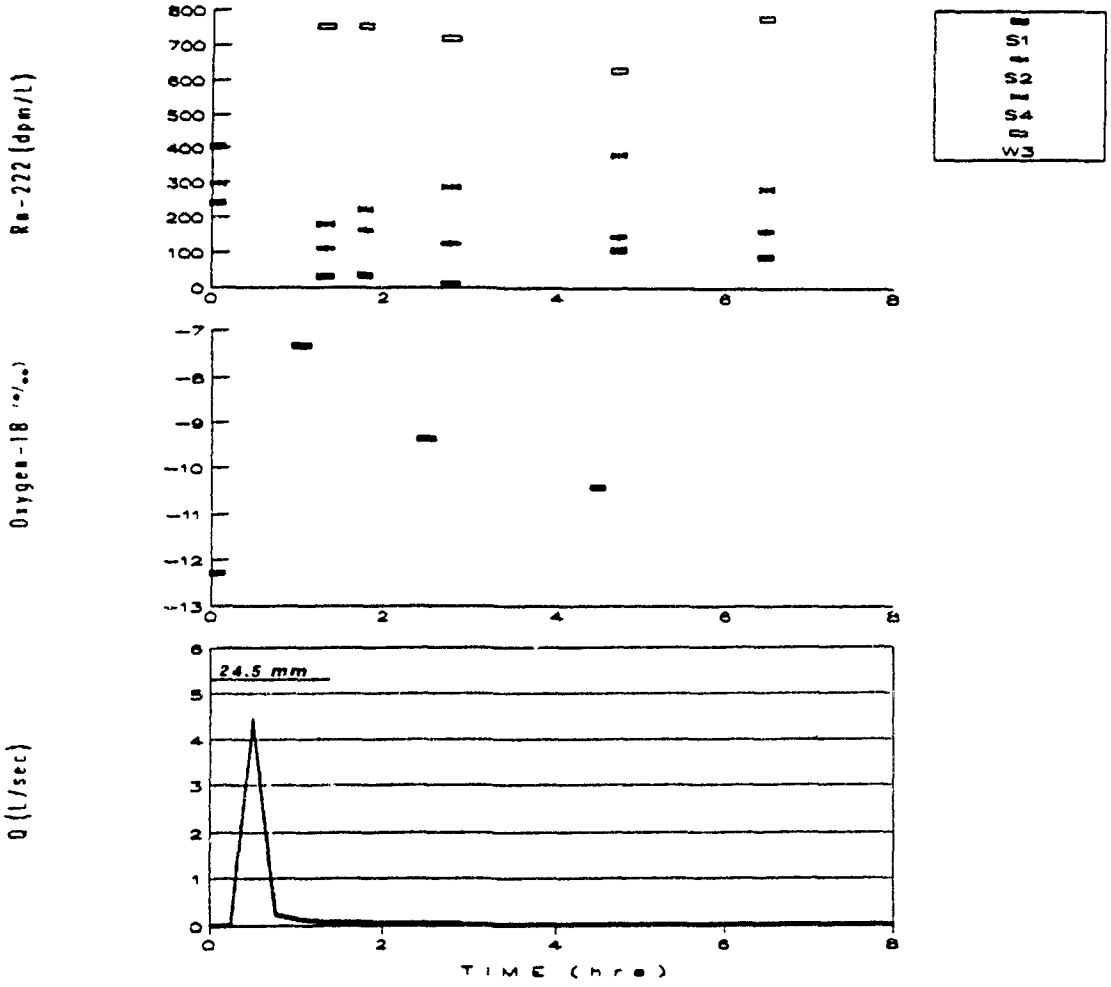

Figure 9. Temporal trends in stream ^{18}O at S1 and measured ^{222}Rn activity at S1, S2, S4 and in W3 with discharge (Q) during E8 storm runoff. Time "zero" corresponds to the commencement of rain at 16:45 hr, August 12. The solid black line above the hydrograph indicates precipitation duration and quantity.

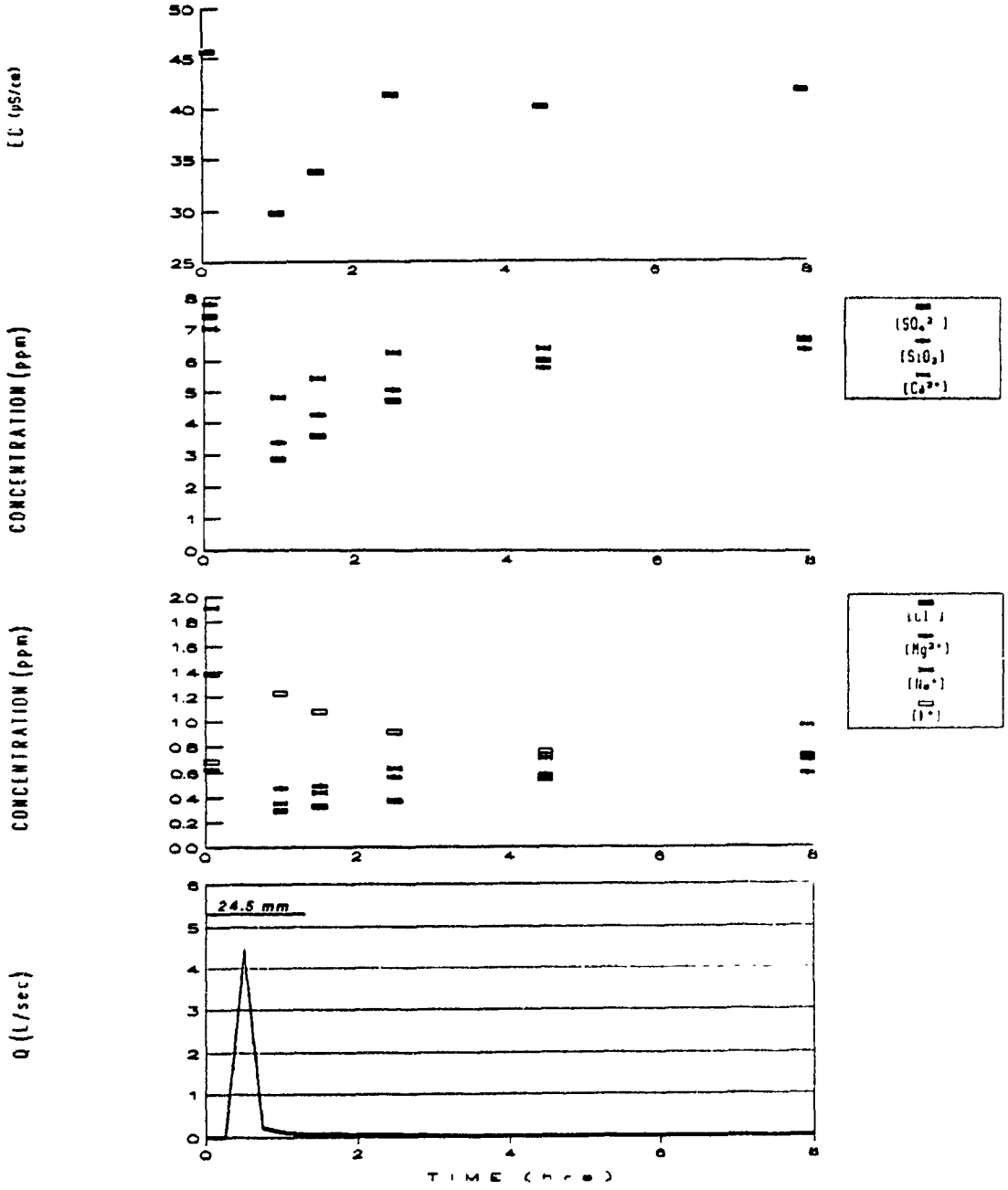

Figure 10. Temporal trends in stream water chemistry and EC with discharge (Q) at S1 during E8 storm runoff. Time "zero" corresponds to the commencement of rain at 16:45 hr, August 12. The solid black line above the hydrograph indicates precipitation duration and quantity.

of ions decreasing initially by 35% before returning to pre-storm values.

3.3.5 Rain Event 9; August 13-14, 1988

3.3.5.1 Introduction

Approximately 14-16 hours after cessation of the storm following E8, another severe thunderstorm moved into the area. This thunderstorm (E9) occurred between the hours of 20:30 on August 13 and 01:30 on August 14 (T0-T5, see Figures 11 and 12). By the end of the storm 73.6 mm of precipitation had fallen on Basin-35. As in Events 5 and 6, the bulk of this storm came in two pulses. The first pulse totalling 50.4 mm of rain occurred between T1 and T2. The second pulse T2.5-T4 dropped approximately 19 mm of water. The result was a double peaked hydrograph as shown in Figures 11 and 12.

Event 9 was a convective thunderstorm of moderate duration (5 hours) and high intensity; near 25 mm precipitation per hour between 21:30 (T1) and 00:39 (T4.15) hours. Primed from the 52 mm of rain deposited on August 12 and the early morning hours of August 13, stream discharge reached its greatest value all summer of 68 L/sec. At T3 high runoff within the TLW had caused several road washouts. As a result no stream or well data is available between sample times T3 and T18.

3.3.5.2 Isotopes: Oxygen-18

Throughfall samples collected and analyzed for this event had $\delta^{18}O$ values of -4.74 and -4.80‰, approximately 1 per mil less than E8 throughfall samples. Stream $\delta^{18}O$ response during E9 storm runoff is depicted in Figure 11.

3.3.5.3 Radon-222

During E9 ^{222}Rn samples were collected from sample sites S2, S4 and W3 continually and from S7, W10 and W24 when possible. Variations in ^{222}Rn activity at a variety of sample sites during E9 storm runoff is displayed in Figure 11.

At T3 (August 13) measured ^{222}Rn activities in stream water sampled at S2 had decreased from a baseflow value of 220 dpm/L to 127 dpm/L. Samples collected at T18.5, T23 and T37 remained more-or-less constant with activities ranging between 57 and 77 dpm/L. By T59.5 (August 16) ^{222}Rn activity remained below pre-storm baseflow activity with a value of 144 dpm/L.

Measured ^{222}Rn activity in stream water samples collected from S4 during E9 storm runoff responded similarly as those at S2. At T0.5, ^{222}Rn activity increased from 372 to 515 dpm/L. By T3 activity had decreased to 139 dpm/L. Values remained relatively constant in samples collected until T37 on August 15 when activity increased to 289 dpm/L. On August 16 at T59.5, S4 ^{222}Rn activity was 336 dpm/L,

approximately 12% less than ^{222}Rn activity in pre-storm baseflow samples and 35% less than peak activity measured at T1.

Variations in groundwater (as noted at W3) activities were quite different than those at S2 and S4. Groundwater sampled 3.5 hours prior to the onset of E9 (T-3.5) precipitation had an activity of 550 dpm/L. At T1, or one hour after the onset of precipitation, measured ^{222}Rn activity in groundwater increased to 735 dpm/L. Activity remained relatively constant in all samples collected until T23 on August 14 when it dropped to 407 dpm/L. By T36.5 values had again increased reaching 538 dpm/L, however, by T59.5 activity had decreased to approximately 390 dpm/L.

In W24, measured ^{222}Rn activity in groundwater decreased substantially from 117 dpm/L at T0 to 38 dpm/L by T3. Activity increased to 105 dpm/L by T18 and continued increasing reaching 215 dpm/L by T59.5.

No visible surface flow was observed at S7 prior to T3, however, the seep in proximity to S7 was saturated. During E9, five ^{222}Rn samples were collected and analyzed from S7. Sample collection times were T3, T18.5, T23, T37 and T59.5. En route to the field laboratory after samples were collected at T3, the S7 water sample to be used for determination of ^{222}Rn concentration was lost. Measured activities in the preceding two water samples collected at this site (T18.5 and T23) remained constant near 120 dpm/L.

Activity decreased to 87 dpm/L by T37 and by T59.5 activity had increased to 172 dpm/L.

During E9 subsurface pipe flow was observed in close proximity to W27 and S7. Radon-222 activity of the pipe water sampled in proximity to W27 at T23 was 106 dpm/L. Groundwater samples collected from W10 were infrequent and displayed minor variations.

3.3.5.4 Chemistry

Figure 12 displays variations in stream water chemistry during E9 storm runoff at S1. Ion concentrations in event water were all significantly less than their respective pre-storm baseflow concentrations except K^+ which was approximately 50% greater in event water. Between T0 and T3 all ion concentrations except K^+ decreased between 3 and 50% while K^+ concentrations measured a 23% increase. At T18, Ca+, Cl- and K^+ concentrations in stream water (S1) were notably less (approximately 6, 20 and 51 % respectively) than their respective concentrations in water sampled at T3. Concentrations of Mg^+ did not vary, however, SO_4^{2-}, SiO_2 and Na^+ concentrations all increased by approximately 12, 18 and 42% respectively over their concentrations measured at T3. At T59.5 all ion concentrations in stream water remained well below those of pre-storm stream water although the trend shows ion concentrations returning towards baseflow values.

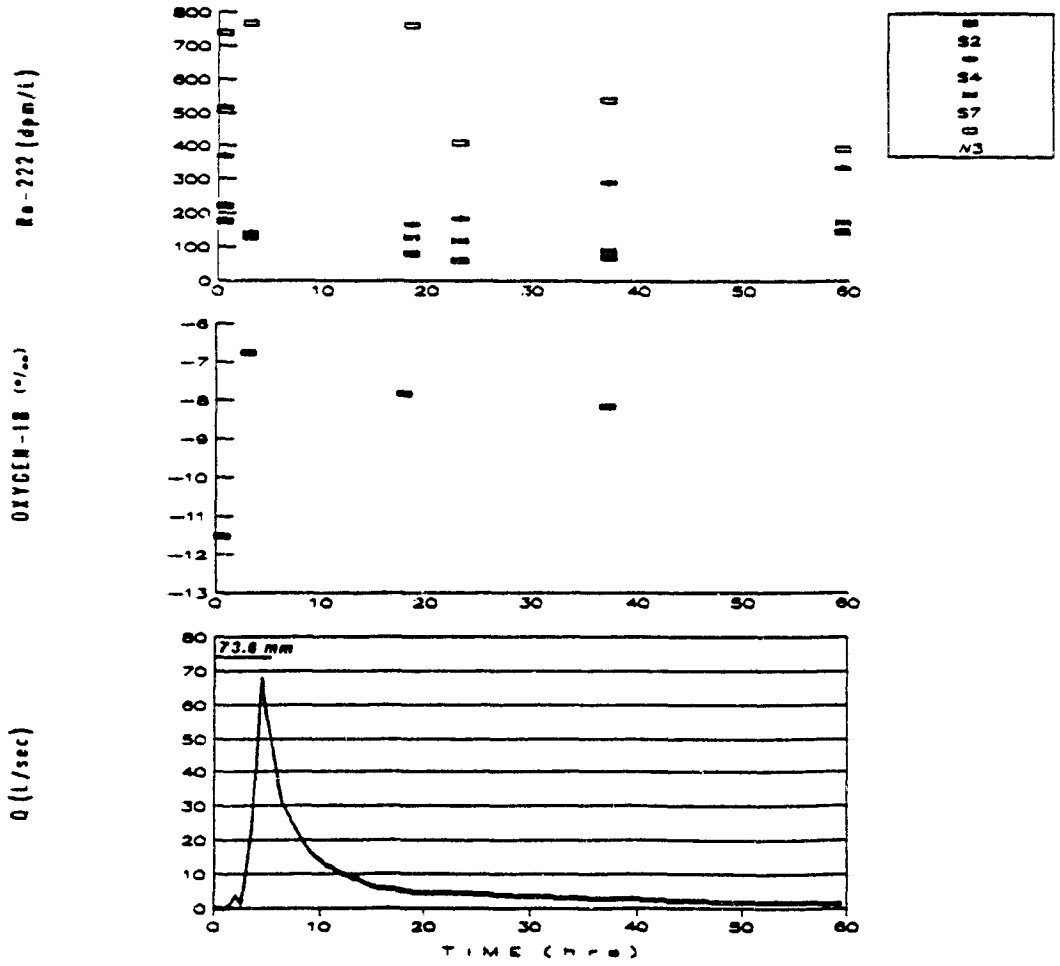

Figure 11. Temporal trends in stream ^{18}O at S1 and measured ^{222}Rn activity at S2, S4, S7 and in W3 with discharge (Q) during E9 storm runoff. Time "zero" corresponds to the commencement of rain at 20:30 hr, August 13. The solid black line above the hydrograph indicates precipitation duration and quantity.

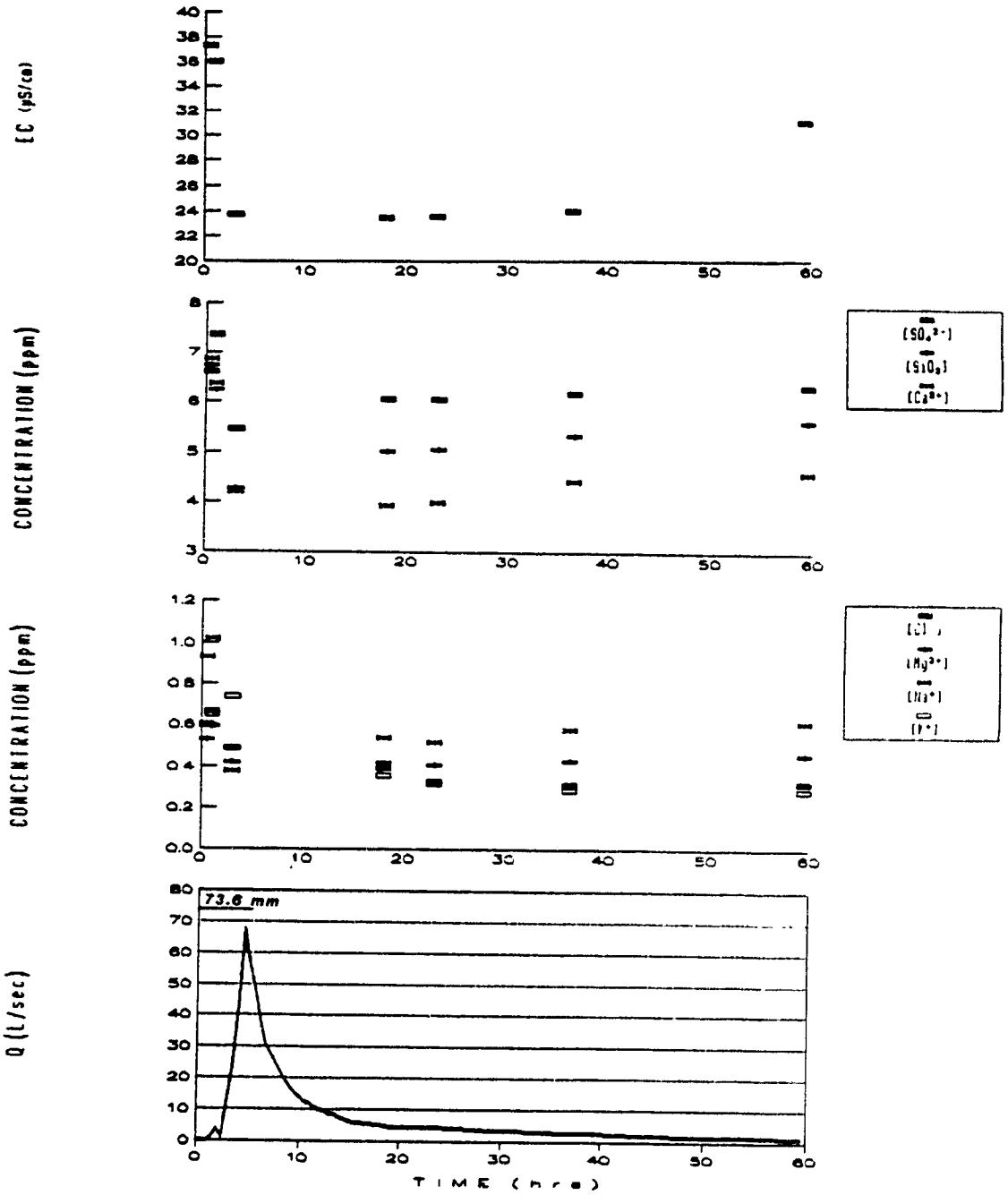

Figure 12. Temporal trends in stream water chemistry and EC with discharge (Q) at S1 during E9 storm runoff. Time "zero" corresponds to the commencement of rain at 20:30 hr, August 13. The solid black line above the hydrograph indicates precipitation duration and quantity.

Electrical conductivity decreased from an initial value of 39.7 to 23.7 µS/cm at T3 and remained constant near 23 µS/cm between T18 and T37. By T59.5, EC had increased to 31 µS/cm. With the exception of K^+ and Cl^- pipe water chemistry and EC at T23 was similar to the chemistry of water samples collected at both S1 and S7 at the same time. Chloride concentrations increased in a downslope direction having a concentration of 0.26 ppm at S7, 0.29 ppm at the pipe and 0.33 ppm at S1. Concentration of K^+ was 0.13 ppm in the pore water, 0.23 ppm at S7 and 0.32 ppm at S1.

Chemistry samples collected from S1 and S7 Between T3 and T59.5 varied similarly. Ion concentrations at S1, however, were generally slightly greater than those at S7 as were values of EC.

3.3.6 Rain Event 10; August 27, 1988

3.3.6.1 Introduction

Following E9 and an additional 25 mm of precipitation on August 17, cool sunny weather prevailed for four days with temperatures ranging between 18 and 21°C. During the week of August 22-27, overcast skies, intermittent light rain and drizzle prevailed at TLW. During this week minor rain storms of 5.8 and 7.6 mm occurred on August 24 and 25 in 2 and 6 hour intervals respectively. These minor storms were each sampled three times, once prior to, during and after event precipitation. Stream discharge during both of

these events remained relatively constant varying a maximum of 8%. Chemistry and ^{222}Rn samples collected throughout this week and during these minor events showed little variation. On August 27 a long duration low intensity storm depositing 45.8 mm of precipitation occurred between 10:00 and 23:00 hours (T0-T13, see Figures 13 and 14). At T0 visible surface streamflow only extended upstream to S6 (Figure 3b). High intensity rain occurred between T8.5 and T9.5 hours producing a distinctive peak above the slowly responding hydrograph to earlier less intense rain. Although rain ended approximately 12 hours after the initiation of precipitation, a second more pronounced peak was registered on the hydrograph after no additional rain was observed.

3.3.6.2 Isotopes: Oxygen-18

Temporal variations in $\delta^{18}O$ with discharge is displayed in Figure 14. Although event and pre-event water $\delta^{18}O$ values for E10 (-13.7 and -11.37°/$_{oo}$ respectively) are notably different than each other, during storm runoff most stream samples collected had $\delta^{18}O$ values heavier (less negative) than both event and pre-event water. As a result separation of E10 storm runoff components according to equations 5 and 6 (see Chapter 2) is not possible. Interpretation of the obtained $\delta^{18}O$ data is presented in chapter 4.

3.3.6.3 Radon-222

Temporal variations in ^{222}Rn activity at selected sample sites during E10 storm runoff are shown in Figure 13. During E10, ^{222}Rn samples were collected from stream sample sites 1, 2, 4 and 7 and groundwater wells 3, 10, 13 and 20. At T3, approximately 3 hours after the commencement of precipitation, measured stream ^{222}Rn activity decreased from 116 to 85 dpm/L. Activity remained constant until the initial peak in discharge. At this time activity had decreased to 60 dpm/L. Between the initial (T8.5) and secondary peak in discharge (T14.5-T16.5) ^{222}Rn activity increased slightly to 81 dpm/L. Samples collected at T22, approximately 6.5 hours after the second peak in discharge recorded the lowest activity of 28 dpm/L. Activity remained low (33 dpm/L) when sampled approximately 10 hours later, however, returned to 83 dpm/L when sampled at T46.

At S2 and S4 measured ^{222}Rn activities in stream water fluctuated. Between T0 and T3 water samples collected at both S2 and S4 measured significant increases in ^{222}Rn activity. At S2 measured ^{222}Rn increased from 283 to 871 dpm/L while at S4 activity increased from 369 to 523 dpm/L. At both S2 and S4, the obtained value at T3 was the peak activity measured at each respective site during E10 runoff sample collection. At T9, shortly after the initial discharge peak, ^{222}Rn activity at S2 and S4 reached the lowest measured values during E10 storm runoff of 426 and

263 dpm/L respectively. By T12 activities had increased to 570 and 447 dpm/L at S2 and S4 respectively. Samples collected from S2 between T12 and T46 registered a continual decrease in activity reaching 479 dpm/L at T46. Samples collected from S4 between T12 and T32 also measured a continued decrease in activity reaching 283 dpm/L by T32. Radon activity at S4 then increased to 390 dpm/L by T46.

At S7 no baseflow ^{222}Rn activity was measured. Eleven stream water samples collected from S7 during the time period of August 18-25 had a mean activity of 264.8 dpm/l (1σ= 60). Thus it is presumed that at T3 the measured ^{222}Rn activity of 193 dpm/L reflects a relatively minor decrease (between 5.5 an 27%) in stream water activity between T0 and T3. At T4.5 ^{222}Rn activity had increased to 266 dpm/L, however, by T12 it had decreased reaching the lowest recorded activity (at S7) during E10 storm runoff of 139 dpm/L. The last stream sample collected at S7 at T46 measured a ^{222}Rn activity of 199 dpm/L, a value similar to that measured at T3.

After an initial increase in activity from 386.6 (at T0) to 703 dpm/L (at T4.25) ^{222}Rn activity in W3 decreased to 375 dpm/L. Thereafter ^{222}Rn activity remained relatively constant ranging between 425.1 and 492.8 dpm/l.

In groundwater sampled from W10, ^{222}Rn activity decreased from a baseflow activity of 390 dpm/L to 292 dpm/L at T3. Activity increased to 412 dpm/L by T9. Between T12

and T46 measured activity remained relatively constant fluctuating between 210 and 265 dpm/L.

In groundwater well 13, ^{222}Rn activity fluctuated little between T0 and T6.5 (between 213 and 279 dpm/L). A peak activity (318 dpm/L) in groundwater sampled from this well was noted at T9. By T22 ^{222}Rn activity had decreased to 148 dpm/L. Activity continued to decrease reaching 92 dpm/L at T46.

Measured activity in groundwater sampled from W20 decreased from 435 dpm/L at T0 to 333 dpm/L at T3. Between T4.5 and T9 activity remained constant between 265 and 278 dpm/L. By T22 activity had decreased slightly to 207 dpm/L and remained constant thereafter.

3.3.6.4 Chemistry

Figure 14 displays variations in stream water chemistry with discharge. During the initial peak in discharge stream water concentrations of SO_4^{2-}, SiO_2, Ca^{2+} and Mg^{2+} decreased by between 7 and 16% of their respective baseflow concentrations while Na^+ concentration remained constant. Potassium and Cl^- concentrations increased 10 and 44% respectively over their respective baseflow values at the same time. As discharge volume decreased, K^+, Cl^- and Na^+ ion concentrations decreased while SO_4^{2-}, SiO_2, Ca^{2+} and Mg^{2+} concentrations increased. At T22, approximately six hours after the second peak in discharge stream water ion

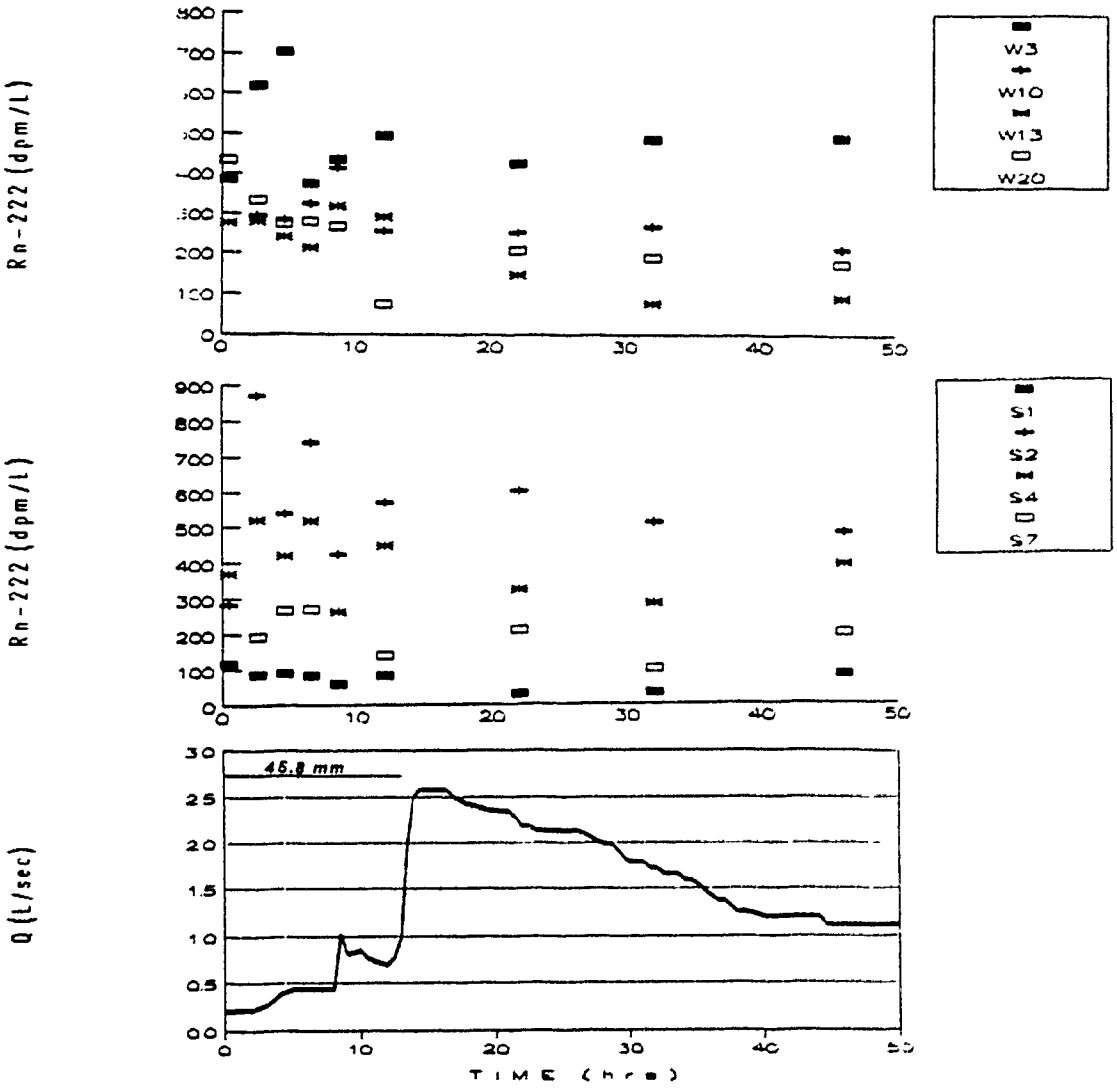

Figure 13. Temporal trends in measured ^{222}Rn activity at several sample sites with discharge (Q) during E10 storm runoff. Time "zero" corresponds to the commencement of rain at 10:00 hr, August 27. The solid black line above the hydrograph indicates precipitation duration and quantity.

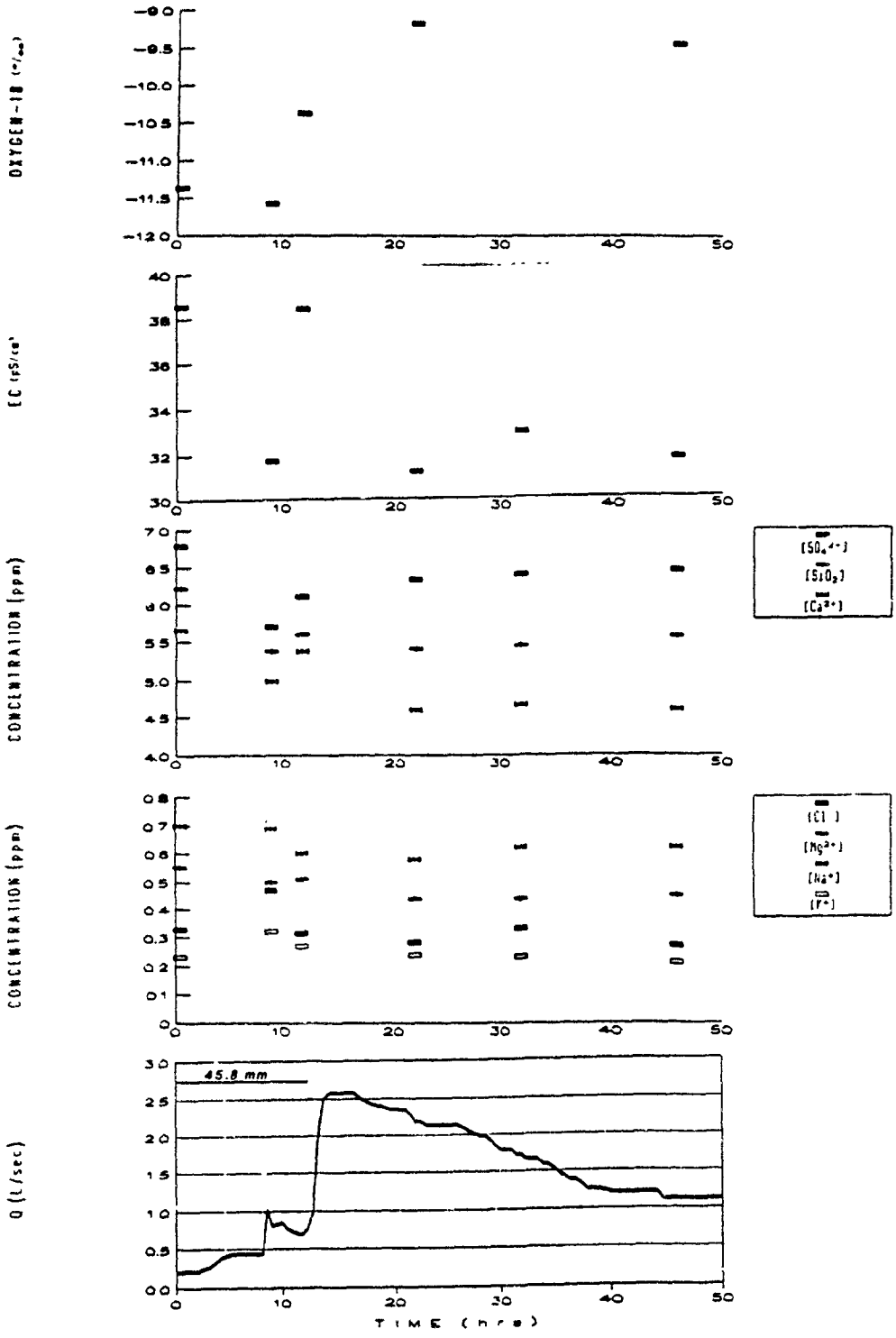

Figure 14. Temporal trends in stream water chemistry, ^{18}O and EC at S1 with discharge (Q) during E10 storm runoff. Time "zero" corresponds to the commencement of rain at 10:00 hr, August 27. The solid black line above the hydrograph indicates precipitation duration and quantity.

concentrations were all less than their respective concentrations measured in samples collected during the initial peak except SO_4^{2-} which increased by 4%. Water samples collected between T22 and T46 were very similar in chemistry.

Values of EC decreased from 38.6 to 31.7 µS/cm during the initial peak, increased to 38.4 µS/cm at T12 and then decreased to 31.2 µS/cm at T22. Values stayed relatively constant through the remaining duration of E10 sampling.

3.3.7 Rain Event 11; September 3, 1988

3.3.7.1 Introduction

For 6 days after event 10, generally clear and cool weather conditions prevailed. On September 3 overcast skies dominated resulting in light rain and drizzle. Between 17:10 and 01:10 hours (T0-T8; see Figures 15 and 16) on September 3 and 4, 19.6 mm of precipitation fell on the study basin. All parameters except $\delta^{18}O$ were sampled from a variety of sample sites including S7, W7, W16 and W20. Fluctuation in precipitation intensity resulted in the generation of a double peaked storm hydrograph.

3.3.7.2 Radon-222

Temporal variations in ^{222}Rn activity at selected sample sites during E11 storm runoff are shown in Figure 15. During E11, the most pronounced variations in ^{222}Rn activity

were noted in stream water samples collected at S2 and S4. Measured activity in samples collected from S2 fluctuated between 1156 and 844 dpm/L between T0 and T6. At T9 activity had decreased to 638 dpm/L. By T15 (the last sample collected), ^{222}Rn activity remained below baseflow activity (883 dpm/L) with a value of 655 dpm/L. At S4 measured stream water ^{222}Rn activity decreased from 547 to 445 dpm/L between T0 and T3. By T9 activity was 395 dpm/L. Unlike samples collected at S2, at T15 ^{222}Rn activity at S4 had returned to baseflow values.

At stream sample site 7, measured ^{222}Rn activity decreased from 398 dpm/L at T0 to 175 dpm/L by T6.7. Between T6.7 and T15.5 activity increased continually reaching 306 dpm/L at T15.5.

Between T0 and T1.5 measured ^{222}Rn activity in groundwater sampled from W3 increased from 404 to 595 dpm/L. Activity remained between 22 and 61% above baseflow activity through the duration of E11 sampling (T1.5-T15.5). Radon activity measured in groundwater sampled from W27 decreased from 376 to 265 dpm/L between T0 and T2. Activity fluctuated little (between 228 and 285 dpm/L) in all samples collected thereafter. In groundwater well 16, measured ^{222}Rn activity in groundwater increased from 195 to 266 dpm/L between T0 and T2. At T15.5 measured activity was 167 dpm/L. In W20, measured ^{222}Rn activity increased from a baseflow value of 418 dpm/L to 500 dpm/L at T2. At T15.5 measured activity had

decreased to 206 dpm/L.

3.3.7.3 Chemistry

Figure 16 displays variations in stream water chemistry and EC during E11 storm runoff. Although there had been six days of clear and cool weather since precipitation last fell in Basin-35 ion concentrations in pre-storm baseflow remained between 7 and 54% less than average summer baseflow concentrations (Table 2). During the initial peak in discharge Ca^{2+} and SiO_2 concentrations decreased by 10 and 16% respectively; Mg^{+} and Na^{+} concentrations remained constant. Samples collected at selected intervals thereafter showed increasing SiO_2 and Ca^{2+} concentrations towards average summer baseflow concentrations with minor fluctuations during the second peak in discharge. Sulphate, Cl^{-} and K^{+} concentrations increased with the initial discharge peak by 6, 27 and 57% respectively. Potassium concentrations slowly decreased to baseflow concentrations throughout event sampling while Cl^{-} concentration decreased below its' baseflow concentration by 8% at T15. Variations in EC were minor.

3.4 Summary

Although differences among storm events are numerous (i.e. antecedent basin characteristics, event water chemistry, storm duration and intensity, etc.) many

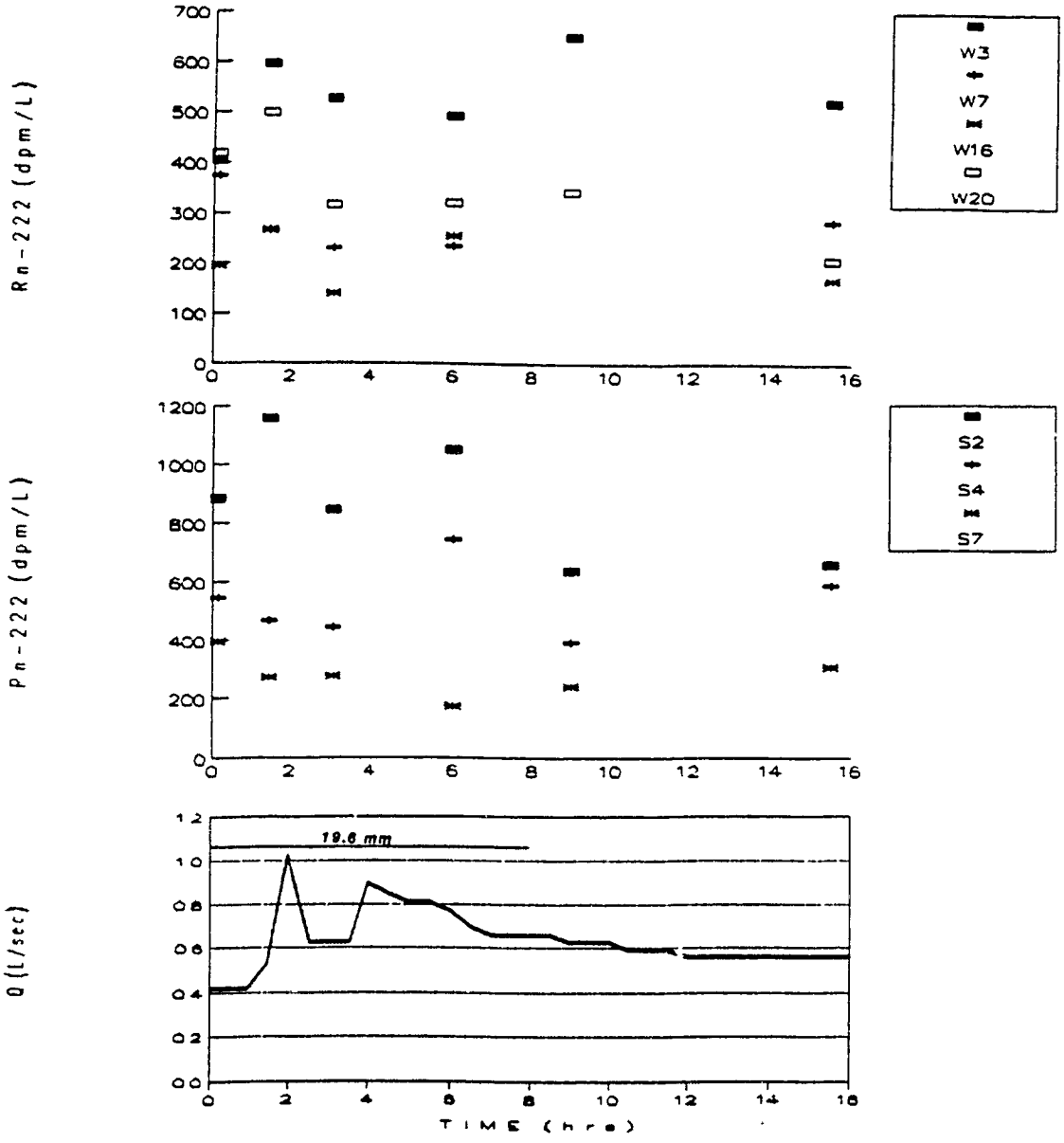

Figure 15. Temporal trends in measured ^{222}Rn activity at several sample sites with discharge (Q) during E11 storm runoff. Time "zero" corresponds to the commencement of light rain from drizzle at 17:10 hr, September 3. The solid black line above the hydrograph indicates precipitation duration and quantity.

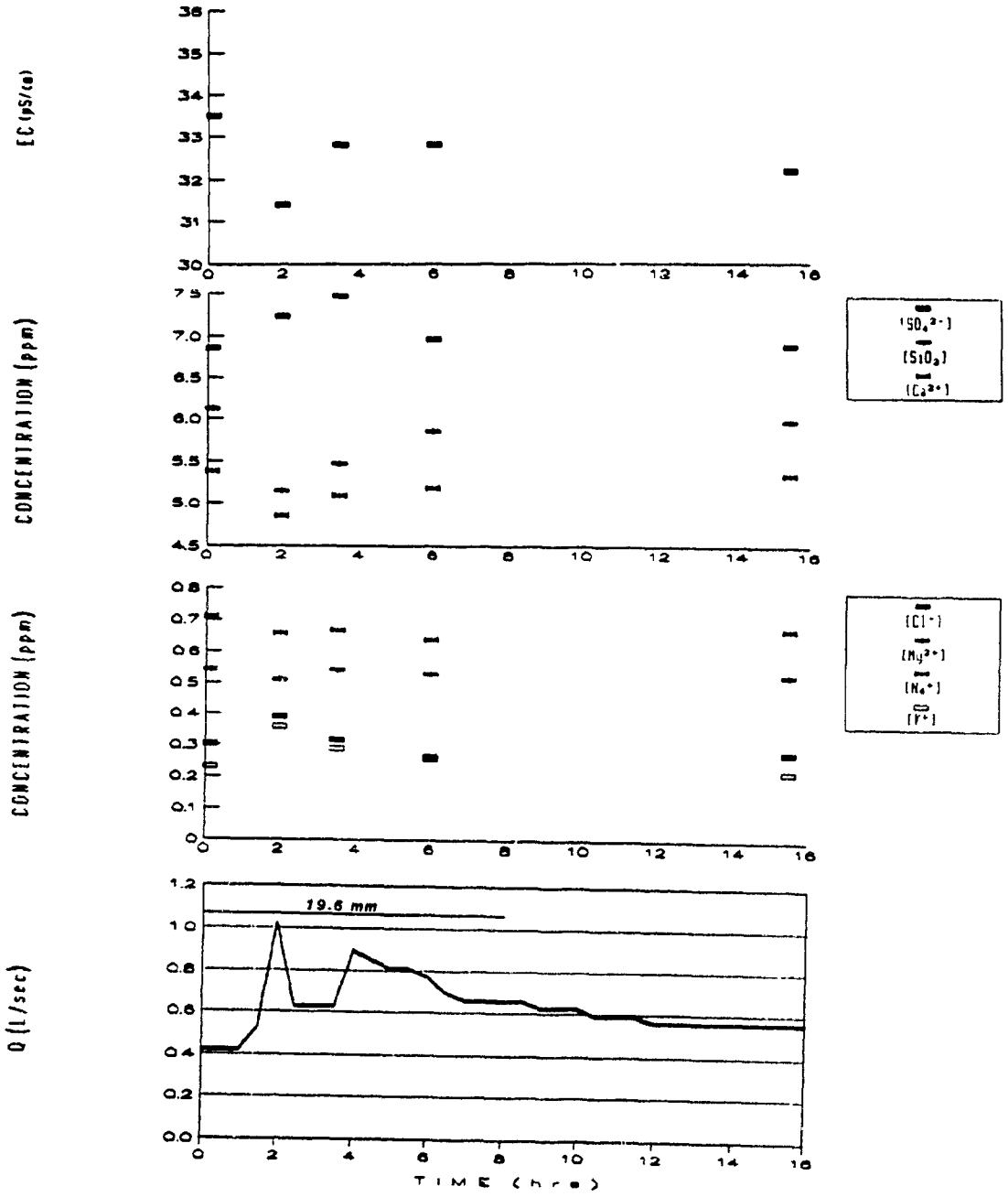

Figure 16. Temporal trends in stream water chemistry and EC at S1 with discharge (Q) during E11 storm runoff. Time "zero" corresponds to the commencement of light rain from drizzle at 17:10 hr, September 3. The solid black line above the hydrograph indicates precipitation duration and quantity.

similarities are notable. Pre-event stream water is generally high in dissolved constituents and representative of average baseflow concentrations. Discharge and concentrations of SO_4^{2-}, SiO_2, Ca^{2+} and Mg^{2+} in stream water are generally inversely related; that is, with an increase in discharge dilution occurs. Potassium, Na^+ and Cl^- concentrations, on the other hand, often increase with discharge. Magnesium ion concentrations varied least among and within individual events.

Radon-222 activities for individual sample sites varied both during and among individual storm events, spatial trends are noticeable and will be discussed in the following chapter. The highest ^{222}Rn activities were continually measured at S2, S4 and in W3 while the lowest activities were commonly measured at S1.

Trends in EC generally follow those of major ions decreasing with increases in discharge and generally being highest in stream baseflow and phreatic zone groundwater.

CHAPTER 4
INTERPRETATION AND DISCUSSION

4.1 INTRODUCTION

The primary purpose of this chapter is to discuss and identify (using results presented in chapter three and Appendix 1) the mechanisms responsible for generating summer surface storm runoff in Basin-35 of the Turkey Lakes Watershed (TLW).

4.2 Factors Regulating Runoff Generating Mechanisms and Percent Component Contributions to Surface Storm Runoff in Basin-35

It is understood that several parameters such as antecedent soil moisture, physical storm characteristics, topography, soil characteristics, vegetative cover, climate, land use, and hydrologic conditions can directly and/or indirectly affect the mechanisms generating stormflow (and therefore the components of stormflow runoff) in any given basin. Several recent studies (Kirkby, 1978; Blowes and Gillham, 1987; Pearce et. al., 1986; Myrabø, 1986; and Dewalle et. al., 1988), however, stress the importance of antecedent soil moisture and physical storm characteristics as key parameters directly governing mechanisms responsible for generating storm runoff in humid region catchments.

Through both interpretation of data collected and infield physical observations made during the course of this study, it is known that several runoff generating mechanisms

operate in Basin-35. These mechanisms vary both temporally and spatially, the extent of which is in large part (yet not exclusively) related to antecedent basin moisture conditions and physical storm characteristics.

4.3 Antecedent Basin Conditions; Wet or Dry?

Because of the limited number of storm events monitored the entire range of combinations of antecedent basin and physical storm characteristics cannot be discussed. Variations in physical storm characteristics were large, ranging from low intensity, short duration to high intensity, long duration storms. The antecedent basin conditions under which each of the storms occurred, however, was either wet or dry. These terms are described below.

Although the literature is replete with statements regarding wet, dry and/or average antecedent conditions in any specific study basin, few papers have actually defined this terminology. In a paper by Myrabø (1986) antecedent soil conditions were correlated to physical measurements of saturated area and stream discharge. Thus at a given discharge delineation of antecedent basin conditions (ie. wet/dry or average) was possible. Whipkey (1966) used less complex means to label antecedent conditions. In his study antecedent conditions were considered dry if more than four days had passed since the last rain or wet if less than four

days had passed since the last rain. For this study, dry antecedent conditions were considered prevalent when stream discharge, as measured at the V-notch weir (Figure 3b), decreased below .02 L/sec. Under such conditions, several common observations were made and include the following; 1) visible surface stream discharge did not extend upslope of stream sample site 3, (or less than approximately 35% of the stream channel length between S1 and S7 was wet, see Figure 3b); 2) all groundwater wells except those in the extreme lower reaches of the basin (W3, W22, W27 and W28) were dry; and 3) the percentage of observed saturated area in the two seeps located in the lower reaches of Basin-35 (one in proximity to S2 and the other in proximity to S4, see Figure 3b) was reduced significantly and approaching zero.

Conversely, antecedent conditions were considered wet when stream discharge was greater than 0.03 L/sec. Under such conditions several common observations were made and include the following; 1) visible surface stream discharge extended upslope of S3 commonly ranging between S5 and S7, (or greater than 35% of the stream channel length between S1 and S7 was wet); 2) groundwater wells located in proximity to the upper reaches of the stream channel (i.e. W9, W10, W11, W13 and W14) had standing water; and 3) observed saturated areas within the confinements of the seeps in proximity to S2 and S4 were significant and commonly resulted in observable overland flow along

preferred pathways to support surface stream discharge. Note also that during wet antecedent conditions the seep near S7 was generally wet, though not necessarily contributing to visible surface flow.

During the sampling period of this study, average or intermediate antecedent basin conditions were observed. Under such conditions baseflow discharge generally ranged between 0.02 and 0.03 L/sec, however, groundwater wells in the upper reaches of the basin were dry and visible surface stream discharge generally did not extend upslope of S5. None of the seven intensively monitored storm events took place during such conditions.

4.4 Storms Occurring Under Dry Antecedent Condition

4.4.1 Introduction

Based on the classification system outlined above, four of the seven intensively monitored storm events (E3, E5, E6, and E8) occurred during dry antecedent conditions. Each of these events was unique and characterized by different physical storm characteristics. As a result, discussion of events on an individual basis is warranted. Because no isotopic data was collected for either E5 or E6 and basin response to event precipitation, as interpreted through water chemistry data, was similar between these two events, discussion of E5 and E6 results are presented together.

4.4.2 Storm Event 3; June 24

Stream $\delta^{18}O$ response during E3 (Figure 5) indicates that storm runoff was dominated by pre-event water (94-99%) with minor event water contributions (Table 4). Between T0 and T2 (see Figures 5 and 6) a surge in pre-event groundwater (vadose and/or phreatic zone water) in the lower reaches of the basin is indicated by increased ^{222}Rn activity in stream water samples collected at S1 and groundwater samples collected from W3. At S1 and in W3, measured activity increased by 56% and 141% respectively. Between T2 and T13 measured ^{222}Rn activity in stream water remained between 16 and 33% above baseflow activity. In groundwater sampled from W3, activity remained between 82 and 119% above baseflow groundwater activity. Stream samples collected from S4 between T0 and T3 show no significant change (<10%) while between T2 and T13 measured activity decreased and remained between 12 and 44% below baseflow activity. This suggests that for the entire duration of E3 storm runoff (T0-T13) pre-event water was being displaced continually at least in proximity to W3 by a "piston-flow" type mechanism (Seip and Seip, 1985). The dilution of ^{222}Rn in stream water discharging at S4 indicates a mixture of both event and pre-event waters; however, the fact that ^{222}Rn activity did not decrease by as much as 50% at any of the sampled times indicates that at S4, pre-event water composed greater than 50% of the passing flow at all sample

Table 4: Percentage of Pre-event Water in E3 Storm Runoff

Date (M/D)	Actual Time	Graphical Time	% Pre-event Water* $\delta^{18}O$
06/24	05:30	T0.0	100
06/24	07:30	T2.0	98.2
06/24 (P)	11:00	T5.5	NA
06/24	12:00	T6.5	94.0
06/24	18:30	T13.0	98.5

P = peak storm runoff
NA = not available
* calculated according to equation 5 (see page 25) and a baseflow $\delta^{18}O$ of -13.5°/$_{oo}$

times of E3 and therefore likely throughout the entire E3 storm runoff.

Because event 3 baseflow Cl^- concentration (0.58 pm) resembled that of event water Cl^- concentration (0.53 ppm), interpretation of Cl^- data is questionable. Groundwater Cl^- concentration, as measured in water sampled from W3 was 0.33 and 0.28 ppm at T0 and T2 respectively. As a result it is postualated that the measured stream baseflow Cl^- concentration is incorrect. Between T2 and T13 stream Cl^- concentration varied little (<18%) remaining near 0.3 ppm. This suggests that event water contributions to E3 storm runoff were minimal and supports the environmental isotope data results presented.

Between T0 and T13 values of pH, EC and the concentrations of SO_4^{2-}, SiO_2, Ca^+ and Mg^{2+} in stream water varied little (<8%). This supports $\delta^{18}O$ results signifying that event water (characterized by low ion concentrations, see Table 3) contributions to E3 storm runoff were minor.

4.4.3 Storm Events 5 and 6; July 11 and 13

Because isotope and hydrometric data are not available for either of these two storm events, discussion of results is based solely on variations in water chemistry. Due to unknown contact time relationships between water and Basin-35 soil for the chemical parameters measured, results are considered less conclusive than those that could be obtained from environmental isotope data.

4.4.3.1 Storm Event 5

In order to determine the percent pre-event water contribution to E5 storm runoff using stream chloride concentration variations in equation 5 (see Chapter 2), a representative baseflow concentration must be used. On July 10, approximately 30 hours prior to E5 precipitation initiation, 9 mm of precipitation fell on Basin-35. As a result the measured baseflow Cl^- concentration for event 5 is not considered representative. In its place the mean of five baseflow samples collected between the time period July 5-8 has been used as the representative Cl^- concentration for "old water" (C_o) in equation 5. Table 5 displays the percent pre-event water contributions at selected times during E5 storm runoff.

At T1.5 (the initial and larger of the two discharge peaks, see Figure 7) pre-event water contribution to surface runoff was approximately 75%. Variations in other water

chemistry parameters support this figure. All monitored ion concentrations in storm event water (with the exception of K^+) were significantly less than their respective pre-storm baseflow concentrations (see Table 4 and Figure 7). A 10-30% decrease in SO_4^{2-}, SiO_2, Ca^+ and Mg^{2+} concentrations and a 16% decrease in EC between T0 and T1.5 support a notable event water input to storm runoff during this time period. (Table 5 indicates that 25% of total runoff at T1.5 was event water). Because event water concentration of K^+ was greater than pre-event water concentration the 133% increase in K^+ concentration in the surface stream between T0 and T1.5 is also indicative of a notable event water contribution to storm flow during this time period. However, the fact that stream K^+ concentration was only 33% of event water concentration at this time supports the notion that pre-event water was the dominant contributor to storm runoff at this time. According to Table 5 (using Cl^- concentration in equation 5), at T4.5 (approximately one hour after the second peak in discharge) 57.2% of discharge at the weir was pre-event water. Continued dilution in the concentrations of SO_4^{2-}, SiO_2 and Ca^+ between 13 and 37% below baseflow concentrations indicates that event water contributions to stormflow were significant and could possibly have contributed the 42.8% to total flow at this time. With stream K^+ concentration remaining approximately 70% above baseflow concentration it too indicates continued and

Table 5: Percentage of Pre-event Water in E5 Storm Runoff

Date (M/D)	Actual Time	Graphical Time	% Pre-event Water* Cl^-
06/11	12:00	T0.0	100
06/11	13:00	T1.0	84.3
06/11 (P)	13:30	T1.5	75.0
06/11	15:00	T3.0	49.3
06/11 (P)	15:30	T3.5	NA
06/11	16:30	T4.5	57.2
06/11	18:00	T6.0	32.0
06/11	20:30	T8.5	80.0
06/12	08:00	T20.0	67.5

P = peak storm runoff
NA = not available
* calculated using equation 5 (see page 25)

notable event water contributions to stormflow at this time. By T20, the various ion concentrations measured in the stream were approaching their respective baseflow values even though pre-event water contribution at this time was 67.5% (Table 5). This may be indicating that the event water supporting the remaining 32.5% of discharge at T20 had been ionically enriched because of the increased residence time and percolation through Basin-35 soils and till or that the chloride ion cannot confidently be used as a conservative tracer for this event.

4.4.3.2 Storm Event 6

Unlike E5, Cl^- cannot confidently be used as a conservative chemical tracer in equation 5 to determine the percent pre-event water contribution to E6 storm runoff at specific sample times. Prior to E6, baseflow Cl^-

concentration was 0.42 ppm (0.08 ppm less than E5 baseflow and 0.19 ppm less than the mean Cl^- concentration of the five baseflow samples collected between July 5 and 8). Mean E6 throughfall Cl^- concentration was 0.52 ppm. During storm runoff measured stream water Cl^- concentration increased (peaking at T5.5 with 0.58 ppm) and remained above baseflow concentration at all sampled times. If the baseflow Cl^- concentration of 0.42 ppm is considered a good representation of actual groundwater concentration, then at T5.5 when stream Cl^-concentration was 0.58 ppm, (0.06 ppm greater than mean event water concentration), total storm runoff at this time must have been composed of event water contributions. At the same time (T5.5, approximately one hour after the second and most significant peak in discharge) SO_4^{2-}, SiO_2, Ca^+ and Mg^{2+} concentrations were 3.3, 18.7, 13.5 and 8.8% respectively less than their respective baseflow concentrations. Sodium and K^+ concentrations were 7 and 59% respectively greater than their respective baseflow concentration. As in E5, all ion concentrations in event water (Table 3), with the exception of K^+ were significantly less than their respective concentrations measured in pre-storm baseflow (Figure 8). Thus if event water contributions to storm runoff at this time were near 100%, it is likely that stream water chemistry would resemble event water chemistry. The above shows that this is not the case. Because of unknown contact

time relationships, this cannot be substantiated.

Because E6 precipitation initiation was only 44 hours after cessation of E5 precipitation (which measured 26.8 mm) it is quite probable that the E6 baseflow Cl^- concentration was not representative of actual groundwater Cl^- concentrations due to dilution from E5 event water contributions. If a baseflow Cl^- concentration of 0.61 ppm (that which was used for E5) is considered representative of E6 baseflow Cl^- concentration, then because both event and pre-event water Cl^- concentrations are greater than the noted baseflow concentration of 0.42 ppm yet similar to each other (0.52 and 0.61 ppm), substitution of the appropriate numbers into equation 5 yields erroneous results. Based on the noted minor variations at T5.5 of E6 stated above, it is most probable that E6 storm runoff was dominated by contributions of pre-event water.

Because of the nature of data available for precipitation events 5 and 6 conclusions are presented with caution. It appears there were two mechanisms responsible for generating surface storm runoff during both E5 and E6. A displacement of pre-event water (a combination of vadose and phreatic water) by a piston flow type mechanism was responsible for delivering most of the water to support peak storm runoff. The remainder of water supporting storm runoff was event water delivered to the stream by direct precipitation and/or via rapid throughflow.

Contributions of event water to storm runoff were notable during both E5 and E6 while the magnitude of contribution appears larger during E5. This could be attributed to both storm intensity and the total quantity of precipitation falling during each event in approximately the same time period (i.e. during E5 between T0 and T4.5, 100% of precipitation had fallen while during E6 between T0 and T4.5, 94.5% of event precipitation had fallen). Rain event 5 precipitation quantity (26.8 mm) was greater than that of E6 (12.7 mm). Direct precipitation of event water onto the seeps and stream channel is responsible for the contribution of some event water to storm runoff during both storms. The exact means by which significant volumes of event water contributed to storm runoff during these events is unknown, however, based on the noted rapid response of Basin-35 to both E5 and E6 precipitation and no observed overland flow, it is postulated that rapid throughflow (rapid subsurface downslope movement of water through or along preferred pathways) delivered sufficient volumes of event water, at least during E5 to cause the noted variations in stream water chemistry.

4.4.4 Storm Event 8; August 12, 1988

At T0, when E8 baseflow samples were collected, there was no visible channel flow and the seep in proximity to S2 was dry. As a result the measured Cl^- concentration (1.39

ppm) in stream water sampled from the ponding basin behind the weir is not considered representative of actual baseflow concentrations. Instead the mean of three baseflow samples (0.73 ppm) collected at S1 on August 8 (when both seeps in the lower reaches of the basin had visible yet limited saturated areas and stream discharge at the V-notch weir was positive) has been used for the E8 baseflow Cl^- concentration. Table 6 displays percent contributions of pre-event water to E8 storm runoff at selected times as determined using stream Cl^- and $\delta^{18}O$ variations in equation 5. Results indicate storm runoff was dominated by event water contributions.

Water chemistry data support the above conclusion. Sharp decreases in EC and all ions monitored (between 24 and 82%) and sharp increases in K^+ at T1 (81%) suggest an instantaneous and significant input of low ion concentration event water. Decreasing K^+ concentrations and increases in all other ion concentrations after peak discharge is indicative of the increasing addition of pre-event water as indicated in Table 6.

Between T0 and T1, ^{222}Rn activities measured at S1 decreased from 240 to 30 dpm/L. Although increased stream turbulence (due to the significant increase in stream discharge from 0 to 4 L/sec at peak runoff) may be responsible for some ^{222}Rn gas loss between this time period, water chemistry fluctuations and stream $\delta^{18}O$

Table 6: Percentage of Pre-event Water In E8 Storm Runoff

Date (M/D)	Actual Time	Graphical Time	% Pre-event Water	
			$\delta^{18}O$	Cl^-
08/12	16:45	T0.0	100	100
08/12 (P)	17:15	T0.5	NA	NA
08/12	17:45	T1.0	25.1	17.7
08/12	18:15	T1.5	NA	24.3
08/12	19:15	T2.5	55.9	32.5
08/12	21:15	T4.5	72.2	64.0
08/13	00:45	T8.0	NA	99.1

P = peak storm runoff
NA = not available

response indicate that the ^{222}Rn activity of 30 dpm/L corresponds largely to a negligible pre-event water contribution. At T2.5 stream $\delta^{18}O$ and Cl^- response (Figures 9 and 10 respectively and Table 6) indicate that pre-event water contributions to storm runoff had increased. Variations in Cl^- suggest that 32.5% of total storm runoff was pre-event water while $\delta^{18}O$ indicates that 56% of runoff was pre-event water. At the same time measured ^{222}Rn activity in the stream was 10 dpm/L. This supports the notion that storm runoff was still dominated by event water contributions. It also suggests that at this time the percent pre-event water contribution to stormflow as determined using Cl^- concentration variations in equation 5 may be more correct than that value determined using $\delta^{18}O$. The reason for the measured ^{222}Rn activity at T2.5 being less than that measured at T1 is unknown. By T4.5 ^{222}Rn activity had increased to 106 dpm/L indicating that pre-

event water contributions were again substantial as indicated by both $\delta^{18}O$ and Cl^- in Table 6.

Although E8 results support the notion that storm runoff was dominated by event water contributions, variations in ^{222}Rn activity in groundwater samples collected from W3 (located in the lower part of the basin) indicate a continued displacement of pre-event water during E8. Between T0 and T1, measured ^{222}Rn activity in groundwater sampled from W3 had increased by nearly 86%. Between T1 and T8 activity remained between 55 and 91% greater than pre-storm activity. This indicates that higher activity groundwater (presumably phreatic water) was being displaced throughout the entire duration of E8 storm runoff.

From this discussion it is suggested that mechanisms capable of generating a near-instantaneous basin response to event precipitation must have occurred. Because storm runoff was dominated by event water contributions and the high intensity of precipitation it is likely that three mechanisms operated simultaneously to deliver event water to the stream channel. Direct precipitation on the stream channel and saturated areas, overland flow from partial areas and rapid throughflow are the only viable mechanisms, according to the variable-source-area concept, that could produce the noted hydrograph response. Because of the small area of land constituted by the seeps and stream channel with respect to total basin area, it is unlikely that direct

precipitation onto the seeps and stream channel was responsible for significant event water contributions to storm runoff. During E8 storm runoff little overland flow was observed elsewhere than within the stream channel itself. Thus the assumption that overland flow from partial areas was largely responsible for the noted basin response is unlikely. Rapid throughflow of event water is therefore the presumed mechanism which was responsible for delivering the bulk of event water to the stream channel during E8 storm runoff. The means by which this could have occurred is discussed in later sections of this chapter. Pre-event water contributions to storm runoff, although minor, were likely the result of a piston-flow type mechanism as evidenced by measured groundwater activity in W3.

4.4.5 Summary of Storms Occurring Under Dry Antecedent Conditions

For each of the storms monitored under dry antecedent conditions it is postulated that a piston flow type mechanism delivering pre-event water to the stream channel was operative throughout the entire storm event. The relative importance of this mechanism as the key mechanism responsible for generating surface stormflow runoff in Basin-35 during dry antecedent conditions decreases with increasing precipitation duration and intensity. During low intensity storm events a piston flow type mechanism operates in the lower reaches of the basin. With prolonged and high

intensity precipitation events rapid throughflow delivers significant quantities of event water to the stream channel from the upper reaches of the basin.

4.5 Storms Occurring Under Wet Antecedent Conditions

4.5.1 Introduction

Based on the classification system outlined earlier in this chapter, the remaining 3 intensively monitored storm events (E9, E10 and E11) occurred during wet antecedent conditions. Again due to different physical storm characteristics among these storms, discussion of each separate event is warranted.

4.5.2 Storm Event 9; August 13-15:

Table 7 displays percent pre-event water contributions to E9 storm runoff. Because of the short time period (<13 hours) between cessation of the storm following E8 and the initiation of E9 precipitation, pre-storm baseflow $\delta^{18}O$ and Cl^- concentrations from both E8 and E9 have been used in the mass balance equations. Using the E9 baseflow Cl^- concentration (0.60 ppm; see Figure 12) in equation 5 indicates that at T0.5, 120% of water discharging at the weir was of pre-event origin (see Table 7). This obvious error validates the use of E8 baseflow Cl^- concentration (0.73 ppm which indicates that at T0, 38.2% of water discharging at the weir was event water from E8) as the

Table 7: Percentage of Pre-event Water In E9 Storm Runoff

Date (M/D)	Actual Time	Graphical Time	% Pre-event Water			
			$\delta^{18}O^{A}$	$\delta^{18}O^{B}$	Cl^{-C}	Cl^{-D}
08/13	20:30	T0.0	90.0	100	71.8	100
08/13	21:00	T0.5	NA	NA	85.8	120
08/13	22:30 (P)	T2.0	NA	NA	NA	NA
08/13	23:30	T3.0	26.5	29.5	49.0	68.4
08/14	01:00 (P)	T4.5	NA	NA	NA	NA
08/14	14:30	T18.0	40.8	45.3	28.0	39.5
08/14	19:30	T23.0	NA	NA	15.4	21.5
08/15	09:30	T37.0	45.4	50.4	12.5	17.4
08/16	08:00	T59.5	NA	NA	14.2	19.8

[A] using the pre-event $\delta^{18}O$ value of -12.77 $^{o}/_{oo}$ from E8 baseflow
[B] using the pre-event $\delta^{18}O$ value of -11.52 $^{o}/_{oo}$ from E9 baseflow
[C] using the pre-event $[Cl^{-}]$ of .731 ppm from E8 baseflow
[D] using the pre-event $[Cl^{-}]$ of .67 ppm from E9 baseflow
P = peak storm runoff
NA = not available

representative of actual E9 baseflow Cl^{-} concentration and supports use of the $\delta^{18}O$ baseflow value from E8.

Due to the immense quantity of precipitation that fell on Basin-35 during E9 precipitation (73.6 mm in approximately 5 hours) it is reasonable to expect substantial event water contributions to storm runoff. Stream $\delta^{18}O$ and Cl^{-} response during E9 indicate such an occurrence. Variations in water chemistry and ^{222}Rn concentrations support the dominance of event water contributions to storm runoff. At the same time they indicate that there were several mechanisms responsible for the generation of E9 storm runoff and that these mechanisms varied both spatially (within the basin) and temporally. The

following discussion identifies mechanisms operating in Basin-35 during E9 substantiating each process with water chemistry and environmental isotope data.

In the early stages of E9 precipitation (T0-T0.5), the minor increase in stream discharge can be directly related to the displacement of pre-event water in the lower reaches of the basin. This process is substantiated by noted increases in both Cl^- and ^{222}Rn concentrations. At stream sample site S1, Cl^- concentration increased from 0.59 ppm at T0 to 0.66 ppm at T0.5. Because mean event water concentration of Cl^- was 0.26 ppm and mean baseflow Cl^- concentration (as determined for E8) was 0.73 ppm, the increase in concentration reflects a displacement of pre-event water. Table 6 indicates (using the E8 baseflow Cl^- concentration as C_o in equation 5) that between T0 and T0.5 pre-event water contributions to stream flow increased by approximately 14%. This displacement process is further substantiated by increased ^{222}Rn activity in water samples collected from S4 and W3 by 38 and 64% respectively during the same time period. Baseflow ^{222}Rn activity in water samples collected from S2 were not determined. Relatively minor variations in water chemistry, pH and EC between T0 and T0.5 by less then 11% generally supports the conclusion that event water input to streamflow during this time was minimal.

Between T0.5 and T3 (during which time approximately 55

mm of precipitation fell) event water contributions to storm runoff increased substantially (see Table 6). All monitored ion concentrations, except K^+, decreased from baseflow values between 26 and 63%. Potassium concentrations increased by 23%. Because all ion concentrations in event water (with the exception of K^+) were significantly less than their respective baseflow concentrations (as well as stream water concentrations at T0.5), a large event water contribution to stormflow between this time period is substantiated. At T3 all groundwater wells had standing water and overland flow was noted in the immediate upslope areas of S2 and S4. Measured ^{222}Rn activities in water samples collected at S2 and S4 were 127 and 135 dpm/L respectively; 27 and 73% respectively less than the activity measured at T0.5. At S4 this activity was approximately 63% less than baseflow activity. This indicates that event water contributions to the noted overland flow were significant. At the same time measured ^{222}Rn activity in groundwater samples collected from W3 displayed little variation (<4%) over measured activity at T0.5 and remained approximately 64% above baseflow activity. This indicates that a displacement of pre-event water was still occurring at least in proximity to W3 and that the overland flow observed immediately upslope of S2 and S4 was likely the product of the displacement of pre-event water, return flow of event water which had infiltrated in upslope reaches of Basin-35

and direct precipitation onto the saturated areas. Thus the overland flow noted at T3 was variable-source-area overland flow.

Further evidence to support the assumption that event water contributions to storm runoff at T3 were increasing, yet did not totally dominate runoff is derived from water chemistry variations between S1 and S7. Water samples collected from S7 and S1 at T3 were, with the exception of Cl^- concentrations, chemically similar. At S7 Cl^- concentration was 0.23 ppm while at S1 it was 0.49 ppm. Because water samples collected from S7 had Cl^- concentrations resembling that of throughfall event water (0.26 ppm), it is thought that water discharging at S7 was composed primarily of event water. Because no overland flow was observed in the vicinity of S7, this water must have reached S7 by either direct precipitation on the sample site and/or by return flow of event water which had infiltrated upslope areas of the basin. As this water proceeded downstream increased input of pre-event water resulted in the increased concentration of Cl^- of 0.49 ppm noted at S1.

Although no water samples were collected between T3 and T18 due to road washouts in the TLW, it is reasonable to assume that the significance of pre-event water contribution to storm runoff during peak discharge (68 L/sec at T4.5) was less than that at T3 when discharge was only 17.6% of peak discharge (12 L/sec). At T18 (approximately 13 hours after

precipitation cessation and when stream discharge had decreased to 4.9 L/sec) between 28 and 45.3% of total storm runoff was pre-event water (as determined using Cl^- and $\delta^{18}O$ respectively, see Table 7). At this time macropore flow (rapid throughflow) was observed in two locations; in the vicinity of W27 and immediately upslope of S7. This observation demonstrates that rapid throughflow via macropores was one process responsible for delivering event water to the stream channel and seepage areas. At the same time groundwater recharge measurements indicated that for any given groundwater well, less than two minutes was required for complete recharge. This indicates that rapid throughflow via macropores was not the only mechanism contributing event water to storm runoff. Because hydraulic conductivity in TLW decreases with depth (Craig et. al., 1988), as the water table rises it penetrates into a zone of higher hydraulic conductivity. Thus rapid throughflow was occurring through upper soil horizons which were saturated from below by the rising water table. This resulted in large contributions of event water to stormflow and explains the short time period required for groundwater wells to recharge at T18.

Measured ^{222}Rn activity in water samples collected from S2 and S4 remained approximately 56 and 68% less than activity measured at these sites at T0.5 suggesting that the still visible overland flow was largely composed of return

flow. (At S4 this activity was 58% less than baseflow activity.) In W3, groundwater ^{222}Rn activity at T18 was identical to that measured at T3 signifying that pre-event water was still being displaced at this time and that event water contributions in this well were still negligible.

At T23 water samples collected concurrently from S7, the macropore near W27 and at S1 were chemically similar in most respects except for Cl^- and K^+ concentrations. Chloride concentrations in stream water sampled at S7, the macropore near W27 and S1 were 0.26, 0.29 and 0.33 ppm respectively. At the same time $\delta^{18}O$ content of the pore water was -7.30°/$_{oo}$ while at S1 $\delta^{18}O$ of water samples collected at T18 and T36.5 were -7.83 and -8.18°/$_{oo}$ respectively. Radon-222 activities measured in water samples collected from S7 and the pore near W27 at T23 were 118 and 107 dpm/L respectively. At both S2 and S4, ^{222}Rn remained below their respective activity measured at T0.5 by approximately 65% (58 and 183 dpm/L respectively). (At S4 this activity was approximately 50% less than baseflow activity). In W3 measured groundwater activity had decreased substantially for the first time since E9 precipitation initiation. Activity was 408 dpm/L, 19% below baseflow activity and approximately 45% below measured activity at T0.5. All of the above results signify that by T23 rapid throughflow of event water was now operative through the entire reach of the basin and that the displacement of pre-event water was

diminishing. By T59.5, all monitored ion concentrations in stream runoff (including K^+) remained below the pre-storm baseflow concentrations (ranging between 4 and 46%). This again suggests that event water contributions to runoff were still significant as noted in Table 7 using Cl^- as a conservative tracer. The fact that ^{222}Rn activity at S2, S4 and in W3 remained 19, 35 and 47% below activity at T0.5 and at S4 and W3 activity remained 10 and 23% less than baseflow support the above that event water contributions in stormflow at T59.5 were significant.

4.5.2.1 Summary of Event 9

Based on the above discussion there were several stormflow generating mechanisms operating during E9 storm runoff, the spatial and temporal allocation of each mechanism appears directly related to storm intensity and duration and proximity to the water table in this basin. With the onset of precipitation a piston flow type mechanism displaced pre-event water to support the initial and small increase in stream discharge. Minor event water contributions reached the stream by direct precipitation. As precipitation continued and the water table rose into a zone of higher hydraulic conductivity rapid throughflow via macropores and/or along saturated soil horizons delivered large quantities of event water to the stream channel from the upper reaches of the basin. At the same time in the

lower reaches of the basin direct precipitation onto the stream channel and seeps was also contributing event water to stormflow. Displacement of pre-event water was continuing at this time in the lower reaches of the basin. As infiltration continued and the wetting front migrated downslope, rapid throughflow of event water was the primary mechanism operating to generate the descending limb of the hydrograph.

4.5.3 Rain Event 10; August 27, 1988

During E10 storm runoff stream $\delta^{18}O$ values increased significantly above both baseflow and event water $\delta^{18}O$ values (-11.58 and -13.7°/$_{oo}$ respectively). Also during E10 storm runoff, stream Cl^- concentrations increased and decreased respectively above and below baseflow concentration. As a consequence, determination of the percent contribution of individual source components to storm runoff using either of $\delta^{18}O$ or Cl^- as a hydrological tracer is not possible (see Table 8). Despite the above, several interesting and important observations regarding the components contributing to and mechanisms responsible for generating E10 storm runoff can be made. These observations are discussed below.

Although no $\delta^{18}O$ or stream water chemistry samples were collected at T3, ^{222}Rn data indicates that at this time increased stream discharge was primarily the result of a

Table 8: Percentage of Pre-event Water in E10 Storm Runoff

Date (M/D)	Actual Time	Graphical Time	% Pre-event Water		
			$\delta^{18}O$	Cl^{-A}	Cl^{-B}
08/27	10:00	T0.0	100	100	13.0
08/27 (P)	18:30	T8.5	NA	NA	NA
08/27	19:00	T9.0	90.8	382.3	49.6
08/27	22:00	T12.0	NA	74.5	9.7
08/28 (P)	00:30-02:30	T14.5-T16.5	NA	NA	NA
08/28	08:00	T22.0	195.6	13.7	1.8
08/28	18:00	T32.0	NA	109.8	14.2
08/29	08:00	T46.0	184.3	-15.7	-2.0

[A] using E10 pre-storm S1 baseflow [Cl^-] of 0.33 ppm
[B] using average S1 baseflow [Cl^-] of 0.67 ppm (Table 3)
P = peak storm runoff
NA = not available

displacement of pre-event water. Between T0 and T3, during which time 8.6 mm of precipitation fell, measured ^{222}Rn activity in water samples collected at S2, S4 and W3 increased 207, 42 and 60% respectively. This indicates that at this time pre-event water was in fact being displaced to support storm runoff.

Between T3 and T8.5 stream discharge increased slowly. At T9, approximately 30 minutes after the initial peak in runoff (1.02 L/sec), stream $\delta^{18}O$ was -11.58°/$_{oo}$. Because this value is similar to E10 baseflow $\delta^{18}O$ (-11.37°/$_{oo}$) it indicates that at T9 storm runoff was still dominated by pre-event water contributions. Both ^{222}Rn and Cl^- data support this presumption.

At T9 measured ^{222}Rn activity in stream samples collected from S2 and groundwater samples collected from W3

remained 50.2 and 12.4% respectively above baseflow activities measure at these respective sites. This indicates that groundwater was being displaced in proximity to S2 and W3 at this time supporting $\delta^{18}O$ results. At S4 at T9, measured stream water ^{222}Rn activity decreased below baseflow activity by 29%. This suggests that at T9 event water contributions were significant at S4, however, pre-event water still represented the majority of water passing S4 at this time. In groundwater wells 10 and 13 (see Figure 3b) measured ^{222}Rn activity was representative of pre-storm activity measured in the same wells. This suggests that the displacement of pre-event water was generally limited to the lower reaches of the basin.

Measured stream water Cl^- concentration at T9 was 0.47 ppm. Event 10 baseflow and throughfall Cl^- concentrations were 0.33 and 0.28 ppm respectively. This suggests that the baseflow Cl^- concentration was not representative of actual groundwater Cl^- concentration and that at this time there must have been a displacement of, presumably phreatic water, to support both the increase in discharge and the noted increase in Cl^- concentration.

By T12 precipitation had ceased and overland flow was noted in the vicinity immediately upslope of S2 and S4. Although no $\delta^{18}O$ samples were collected at this time, both ^{222}Rn and Cl^- data indicate that storm runoff was still dominated by pre-event water contributions. Measured ^{222}Rn

activity in stream water samples collected from S2 and S4 and in groundwater sampled from W3 was 101.3, 21 and 27.5% greater than measured baseflow activity at these respective sample sites. At T12 measured Cl^- concentration at S1 was 0.32 ppm; more or less the same as recorded baseflow concentration. This indicates that at T12, storm runoff was still dominated by pre-event water contributions and that the overland flow noted upslope of S2 and S4 was variable source area overland flow (displacing pre-event water).

Between T14.5 and T16.5 stream discharge peaked for the second time during this storm event. Water samples were not collected during this time.

At T22 stream $\delta^{18}O$ was $-9.18^{o}/_{oo}$. Because this water is isotopically heavier than both throughfall and pre-storm baseflow $\delta^{18}O$ (-13.7 and $-11.37^{o}/_{oo}$ respectively) it is postulated that vadose water contributions at this time were significant. Although $\delta^{18}O$ of vadose water is unknown, it is a presumed mixture of infiltrated and stored E9 precipitation which had a $\delta^{18}O$ near $-5^{o}/_{oo}$ and throughfall precipitation which fell during the week prior to E10 and had a $\delta^{18}O$ range between -13.58 and $-15.66\ ^{o}/_{oo}$). Thus at T22 storm runoff in Basin-35 was a composite mixture of phreatic and vadose waters and E10 throughfall precipitation, however, the dominant contributor to streamflow at this time was vadose water. Both ^{222}Rn and Cl^- data support this postulation. At T22 measured ^{222}Rn

activity in stream water sampled at S2 remained 117% above baseflow activity while at S4 activity was representative of baseflow. Groundwater sampled in W3 at the same time was also representative of E10 baseflow activity with a value of 425 dpm/L. In groundwater sampled from W10 and W13, ^{222}Rn activity was respectively 35 and 46% below their respective baseflow activities. This suggests that event water contributions to storm runoff were negligible in the lower reaches of the basin but were now increasing in the upper reaches.

Stream Cl^- concentration at T22 was 0.28 ppm (identical to event water Cl^- concentration). Although this Cl^- concentration suggests that storm runoff at this time was dominated by event water, both the $\delta^{18}O$ value and ^{222}Rn data refute this assumption. Based on the above, the noted stream Cl^- concentration at this time was likely representative of a mixture of phreatic water (characterized by a baseflow Cl^- concentration of 0.38 ppm) and vadose water (which was composed of E9 throughfall precipitation which had a Cl^- concentration of 0.26 ppm and throughfall samples collected during the week prior to E10 which generally had Cl^- concentrations near 0.2 ppm). Based on the above cited Cl^- concentrations, the presumption that at T22 storm runoff was still being dominated by pre-event water which was composed largely of vadose water is supported.

At T46 stream $\delta^{18}O$ and Cl^- concentration were -9.44°/$_{oo}$

and 0.27 ppm respectively; suggesting that pre-event water (composed largely of vadose water) was still dominating storm runoff. Similar ^{222}Rn activity among the various sample sites between T22 and T46 support the above (see Figure 13). Minor variations between baseflow ion concentrations and EC and stream water chemistry and EC throughout E10 storm runoff (generally less than 23%, see Figure 14) support the above discussion suggesting that event water contributions to streamflow were minimal.

4.5.3.1 Event 10 Summary

Based on the above discussion there were two primary runoff generating mechanisms operating in Basin-35 during event 10. Throughout event precipitation a piston-flow type mechanism was continually operative within the basin and was responsible for a displacement of pre-event water, primarily phreatic zone water. This displacement is believed limited to the lower reaches of the basin where at T3 and T9 ^{222}Rn concentrations increased relative to baseflow concentrations. As the storm progressed and finally ceased, infiltration resulted in a significant rise in the water table. In the lower reaches of the basin a rising water table resulted in the generation of variable source area overland flow. This overland flow was composed primarily of pre-event water, largely phreatic water during continued event precipitation changing to a mixture of phreatic and

vadose zone water in the latter stages of runoff after precipitation had ceased. It is further postulated that in the upper reaches of the basin the rising water table had penetrated into a zone of high hydraulic conductivity which resulted in rapid throughflow. The composition of this throughflow was predominantly vadose and phreatic water with minor contributions of event water. Determination of the relative percent contribution of phreatic and vadose zone waters to storm runoff during E10 storm runoff is not possible.

4.5.4 Event 11; September 3-4

Relatively minor variations in stream water chemistry (with the exception of K^+ and Cl^-) and EC (<16%) suggest the dominance of pre-event water in E11 storm runoff. This assumption is based on the premise that if event water contributions to storm runoff were significant, stream water chemistry would be diluted relative to baseflow values. This, however, is not the case. Table 9 displays the percent contribution of pre-event water at selected times to E11 storm runoff as determined by variations in stream Cl^- concentration.

At T2, approximately 30 minutes after the initial peak in discharge, pre-event water contributions to storm runoff was 62.8%. At the same time, SiO_2, Ca^{2+}, Na^+ and Mg^{2+} concentrations in stream water decreased between 6 and 16%

Table 9: Percentage of Pre-event Water in E11 Storm Runoff

Date (M/D)	Actual Time	Graphical Time	% Pre-event Water (Cl^-)
09/03	17:10	T0.0	100
09/03 (P)	19:10	T2.0	62.8
09/03	20:10	T3.0	95.2
09/03 (P)	21:10	T4.0	NA
09/03	23:10	T6.0	117
09/04	08:40	T15.5	111

P = peak storm runoff
NA = not available

while K^+, Cl^- and SO_4^{2-} concentrations increased 6, 27 and 57% respectively. Throughfall concentrations of K^+, Cl^- and SO_4^{2-} were greater than their respective concentrations in E11 baseflow. Dissolved silica, Ca^{2+}, Na^+ and Mg^{2+} event water concentrations, however, were significantly less than their respective concentrations in baseflow (Table 3, Figure 14). Thus the above noted dilutions and increases in stream water ions at T2 suggests that event water contributions to storm runoff was responsible for the variations. Increased ^{222}Rn activity in samples collected from S2 and W3 by 31 and 47% respectively between T0 and T2 indicate a displacement of pre-event water during this time period. Water samples collected from S4 at the same time indicated a 15% decrease in ^{222}Rn activity. This indicates that although event water was being discharged at S4, the bulk of this discharge was of pre-event origin and that the percent of pre-event water in total discharge at this time was largely the result of a displacement of stored water. At S7, ^{222}Rn activity

decreased by 32% between T0 and T2. This suggests that event water contributions to subsurface stormflow were notable, and that in the upper reaches of the basin contributions of event water to the stream channel flow were pronounced.

At T3, all ion concentration trends reversed except SO_4^{2-}. This indicates that event water contributions to storm runoff were decreasing and supports the results displayed in Table 9. Between T6.7 (shortly after the second peak in discharge) and T15.5, all ion concentrations approached baseflow concentrations (Figure 14). This suggests that event water contributions were still diminishing even though discharge had just recently peaked for the second time. According to Table 9, pre-event water constituted 117 and 110% of total runoff at T6.7 and T15.5 respectively. Although these values are erroneous, they suggest that groundwater was the dominant contributor to stormflow at these times. Groundwater samples collected from W3 at T6.7 and T15.5 measured ^{222}Rn activities 23 and 28.7% respectively above baseflow groundwater activity. At S4, measured stream water ^{222}Rn activity at T6.2 and T15.5 was 35.6 and 7% respectively above baseflow stream activity at S4. At S2 at T6.7 activity was 19% above baseflow activity, however, by T15.5 this activity was 15% below baseflow activity at the same stream sample site. Apart from the minor (15%) decrease in ^{222}Rn activity at S2 at T15.5, the above ^{222}Rn data indicates that between T6.7 and T15.5 there

was a continued displacement of pre-event water to support storm runoff at these times. At S7 by T15.5 ^{222}Rn activity was 23% below baseflow activity. This indicates that at S7, most of the water discharging was of pre-event origin, however, event water contributions were notable.

From this data it is suggested that pre-event water dominated E11 storm runoff with event water contributions to stormflow being small and limited to the early stages of the event when precipitation intensity was greatest. The composition of E11 baseflow, however, is in question. The increase in ^{222}Rn activity in the lower reaches of the basin with the initiation of precipitation suggests that phreatic zone water is being displaced at this time. After precipitation ended there was a second peak in discharge. This peak was also dominated by pre-event water, however, at this time stream Cl^- concentrations decreased below pre-storm baseflow concentrations even though event water concentrations are greater than baseflow concentrations. This suggests that the pre-event water responsible for supporting storm runoff in the later stages of E11 runoff is likely a mixture of phreatic and vadose waters. The vadose water may be stored E10 precipitation water which had a mean Cl^- concentration of 0.28 ppm, a value which is similar to E11 stream Cl^- concentrations of 0.27 and 0.28 ppm at T6.7 and T15.5 respectively.

4.5.5 Summary of Storms Occurring Under Wet Antecedent Conditions

Under wet antecedent conditions mechanisms primarily responsible for generating surface storm runoff in Basin-35 include piston flow and rapid throughflow. With the initiation of precipitation, piston flow, operating in the lower reaches of the basin, delivers pre-event water to the stream channel. Throughflow occurs in the upper reaches of the basin. As a storm progresses rapid throughflow occurs throughout most of the basin and the relative importance of piston flow decreases. Note, however, that under wet antecedent conditions vadose water contributions to stormflow are significant while under dry antecedent conditions vadose water contributions can be considered negligible.

4.6 SUMMARY

This study accepts and supports the commonly recognized variable source area concept mechanisms of stormflow generation. Results indicate, however, that the subsurface flow mechanisms of rapid throughflow via macropores or pipes or along saturated soil horizons and displacement of old water by a piston-flow type mechanism are largely responsible for the generation of summer-storm runoff in Basin-35 at Turkey Lakes Watershed. The relative importance of each mechanism is directly dependent upon antecedent soil moisture (and depth to the water table) and physical storm

characteristics. Unquestionably basin topography and soil structure and composition are also limiting factors affecting response to precipitation events in Basin-35.

Table 10 summarizes each of the seven storm events monitored. During each of the monitored storm events, be it under wet or dry antecedent conditions and having any physical storm characteristic, a piston flow type mechanism was operative. The relative importance of this mechanism as it pertains to the generation of surface stormflow apparently increases with decreasing soil/till moisture content in the vadose zone. Under dry antecedent conditions, soils possess greater water retention capacities. As a result, during low to intermediate intensity storms, much of the incident precipitation will be retained in storage and a displacement of pre-event water in the lower reaches of the basin will be largely responsible for the increase in stream discharge as noted for events 3, 5 and 6. As volume of precipitation increases and soils become sufficiently saturated it is reasonable to expect increasing inputs of event water to runoff. For the noted response of Basin-35 during E8 it is postulated that the high intensity of precipitation determined the primary mechanism operating in Basin-35 to generate the noted storm hydrograph. Although rapid throughflow has been observed under both saturated and unsaturated conditions (Beven and Germann, 1982) near saturated soil layers tend to give the greatest throughflow

(Kirkby, 1985). During E8, it is postulated that the high intensity precipitation percolated rapidly through the upper, highly permeable topsoil. As this water infiltrated deeper, decreasing hydraulic conductivity (such as that created by a zone of less permeable soil) resulted in the formation of a temporary zone of saturation. Rapid throughflow then took place through this saturated soil zone. In this study basin the till layers likely acted as the impeding layer by reducing hydraulic conductivity significantly.

Under wet antecedent conditions and high intensity storms the relative importance of a capillary fringe effect diminishes, although not completely. Initial increases in discharge will usually be the result of the displacement of pre-event water; however, increasing precipitation quantity and intensity will often result in the generation of rapid throughflow via macropores or subsurface flow along saturated soil horizons. If precipitation quantity is sufficient to significantly raise the water table, the resulting saturation into zones of increasing hydraulic conductivity will generate rapid throughflow of both event and pre-event water throughout large reaches of the drainage basin (i.e. events 9, 10 and 11). The relative percentage of event and pre-event water is dependant upon total storm volume and antecedent water table level. Because under wet antecedent conditions soils presumably possess less water

Table 10: Summary of Storm Events Monitored (NDA means No Data Available and CI means data Cannot be Interpreted)

Event	Event Date	Event Description	Hydrograph Section	Percent Pre-event Water Chloride	Oxygen-18	Stormflow Generating Mechanisms or Synopsis
E3	06/24	-dry antecedent conditions -8.6 mm of rain in 12.5 hrs	a) ascending limb b) peak c) descending limb d) post-storm baseflow	NDA NDA NDA NDA	≈90% NDA ≈94% ≈99%	-piston flow throughout entire storm with minor direct throughfall precipitation contributions
E5	07/11	-dry antecedent conditions -26.8 mm of rain in 4.5 hrs	a) ascending limb b) initial peak c) initial descending limb d) second descending limb e) post-storm baseflow	≈84% ≈75% ≈49% 32-57% 60-80%	NDA NDA NDA NDA NDA	-piston flow operating in the lower reaches of the basin throughout the entire storm -rapid throughflow of primarily event water in the upper reaches of the basin after prolonged precipitation
E6	07/13	-dry antecedent conditions -12.7 mm of rain in 5.5 hrs	---	CI	NDA	-it is postulated that basin response was was similar to that noted for E5
E8	08/12	-dry antecedent conditions -24.5 mm of rain in 1.3 hrs	a) ascending limb b) peak c) descending limb d) post-storm baseflow	NDA <25% 18-33% >72%	NDA <18% 25-56% ≈99%	-although a piston flow type mechanism was operating throughout the entire duration of E8, rapid throughflow and direct precipitation of event water were the dominant mechanisms responsible for generating E8 stormflow runoff
E9	08/13- 08/14	-wet antecedent conditions -73.6 mm of rain in 5 hrs	a) pre-storm baseflow b) ascending limb c) peak d) descending limb e) post-storm baseflow	72-100% 50-60% NDA 13-39% 14-20%	90-100% 27-30% NDA 41-50% NDA	-with the initiation of precipitation phreatic zone water was displaced by a piston flow type mechanism operating in the lower reaches of the basin -with prolonged precipitation rapid throughflow and direct precipitation onto the stream channel resulted in the domination of event water in surface storm runoff
E10	08/27- 08/28	-wet antecedent conditions -45.8 mm of rain in ≈12 hrs	a) initial peak b) second peak c) descending limb d) post-storm baseflow	CI CI CI CI	CI CI CI CI	-during the initial peak of E10 storm runoff, piston flow, operating in the lower reaches of the basin delivered much of the water required to generate the noted basin response -after prolonged precipitation, rapid throughflow (composed of both phreatic and vadose zone waters and event water) occurred throughout the entire reach of the basin
E11	09/03	-wet antecedent conditions -19.6 mm of rain in 8 hours	a) initial peak b) descending limb c) second peak d) descending limb e) post-storm baseflow	≈63% ≈95% NDA ≈100% ≈100%	NDA NDA NDA NDA NDA	-the initial peak in storm runoff was the result of a displacement of pre event water in the lower reaches of the basin by a piston flow type mechanism and rapid throughflow in the upper reaches of the basin of event water -the second peak appears to be the result of rapid throughflow of primarily pre event water throughout the entire reach of the basin

storage capacity, vadose water response will increase and (as in E10, E11 and possibly E9) contribute substantially to storm runoff by rapid throughflow or by a translatory flow type mechanism.

4.7 Conclusions

Based on isotopic and chemical results presented and physical observations made in the field, the following conclusions concerning stormflow generation in a small Precambrian Shield catchment are presented:

1) Results indicate that the percent component contribution and the mechanism(s) responsible for stormflow generation within the study basin are largely dependant upon antecedent basin conditions and physical storm characteristics. The variable source area subsurface flow mechanisms of rapid throughflow and piston flow were the two major processes operating in Basin-35 during the monitored storm events.

2) Mechanisms responsible for the generation of summer surface stormflow runoff in Basin-35 vary both spatially and temporally. Generally speaking, shortly after initiation of precipitation under any given antecedent condition a piston flow type mechanism operates in the lower reaches of the basin delivering pre-event water (primarily phreatic zone water) to the stream channel. Rapid throughflow of water from the upper reaches of the basin occurs during intense precipitation events as well as during wet antecedent

conditions. During prolonged rainfall events or under wet antecedent conditions when the water table is close to ground surface, rapid throughflow may occur throughout the entire reach of the basin.

3) The composition of throughflow varies. During dry antecedent conditions throughflow is largely composed of event water. Under wet antecedent conditions throughflow is generally a mixture of event and pre-event waters. In this case pre-event water is a mixture of both vadose and phreatic zone waters.

4) The use of ^{18}O as a conservative hydrological tracer in this study has proven beneficial in differentiating the components and mechanisms responsible for generating storm runoff. However, by using the two component ^{18}O tracer model (equations 5 and 6 and assuming vadose and phreatic water are characterized by the same $^{18}O/^{16}O$ ratio) the importance of soil water to stormflow generation is masked. Under dry antecedent conditions when soil water retention capacity is great, the two component model may suffice; during average or wet antecedent conditions when a soils water retention capacity is generally reduced, a 3- component model incorporating vadose water $\delta^{18}O$ should be utilized.

5) The use of ^{222}Rn as a tool in hydrological studies has been demonstrated. Radon-222 is a reliable indicator of groundwater seepage into surface streams. Because of its demonstrated sensitivity and degassing properties caution

must be used when results are interpreted. In many rainfall events ^{222}Rn data has indicated surges in groundwater (both phreatic and/or vadose waters) a phenomenon not detectable by variation in water chemistry or ^{18}O content, especially during periods of intense rainfall and high runoff.

4.8 Future Research and Recommendations

Further research is required in Precambrian Shield catchments to investigate mechanisms and components responsible for stormflow generation. Future work should include;

1) Comprehensive studies should continue throughout the fall, winter and spring seasons to assess the impact of seasonal variations on stormflow components and mechanisms of generation;

2) A three component model incorporating vadose water as an integral component of stormflow (such as that used by Dewalle et. al., 1989) should be utilized under wet antecedent conditions instead of the two-component model utilized in this study;

3) If ^{222}Rn is to be used in this type of investigation; i) the gas exchange rate or rate of gas loss to the atmosphere during different stages of stream discharge should be determined and related to channel geometry; ii) analysis of ^{222}Rn production from soils collected from various locations throughout the study site should be performed in order to

relate variations in water samples to site specific soil characteristics; and iii) individual ^{222}Rn samples should be counted at least twice in order to reduce error.

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APPENDIX 1

Note: Missing values indicate no data available.
[ ] = concentration in ppm or mg/L
^{222}Rn is measured in dpm/L
$\delta^{18}O$ is measured in ‰

EVENT	SAMPLE DATE	SAMPLE SITE	SAMPLE TIME	GRAPH TIME	$[SO_4^{2-}]$	$[SiO_2]$	$[Cl^-]$	$[Ca^{2+}]$	$[Mg^{2+}]$	$[Na^+]$	$[K^+]$	pH	EC	$[^{222}Rn]$	$\delta^{18}O$
E3	06/23	S1	18:00	T0	7.64	6.37	0.58	6.05	0.56	0.9	0.31	6.49	45.1	92.4	-13.49
	06/24		07:30	T2	7.57	6.24	0.34	6.37	0.59	0.69	0.23	6.51	43.4	143.9	-13.36
	06/24		09:00	T3.5	7.49	5.96	0.36	6.1	0.57	0.73	0.35	6.52	42.7	107.1	-13.06
	06/24		12:00	T6.5	7.26	5.95	0.37	6.26	0.59	0.62	0.3	6.36	41.5	118.5	-13.38
	06/24		14:30	T9	7.37	6.07	0.3	5.99	0.57	0.66	0.26	6.51	42.3	113.4	
	06/24		18:30	T13	7.42	6.22	0.32	6.22	0.58	0.7	0.26	6.55	42.9	122.8	
		S2	18:00	T0	7.86	6.77	0.29	7.2	0.62	0.71	0.17	6.39	47.5	298.4	
			07:30	T2	7.92	6.8	0.29	7.18	0.61	0.7	0.17	6.39	48.0	280.7	
			09:00	T3.5	7.84	6.7	0.27	6.98	0.61	0.39	0.17	6.36	46.3	250.7	
			12:00	T6.5	7.76	6.55	0.39	6.64	0.6	0.81	0.22	6.36	46.4	654.3	
			14:30	T9	7.66	6.63	0.27	6.94	0.61	0.69	0.18	6.41	47.2	293.7	
			18:30	T13	7.55	6.61	0.29	6.95	0.61	0.73	0.20	6.41	47.4	354.9	
		S3	18:00	T0	7.18	5.68	0.26	5.75	0.55	0.61	0.18	6.31	39.8		
			07:30	T2	7.19	5.87	0.27	5.9	0.56	0.63	0.18	6.36	42.7		
			09:00	T3.5	7.25	5.63	0.30	5.43	0.55	0.58	0.23	6.33	39.7		
			12:00	T6.5	7.17	5.68	0.31	5.6	0.55	0.61	0.25	6.4	40.5		
			14:30	T9	7.19	5.75	0.27	5.6	0.55	0.6	0.23	6.39	39.9		
			18:30	T13	7.18	8.79	0.26	5.48	0.54	0.63	0.23	6.35	39.9		
		S4	18:00	T0	7.19	5.7	0.24	5.74	0.55	0.59	0.18	6.27	40.1	940.1	
			07:30	T2	7.14	5.67	0.25	5.86	0.55	0.61	0.18	6.28	39.9	1024.7	
			09:00	T3.5	7.2	5.72	0.33	5.62	0.57	0.61	0.22	6.3	44.2	821.6	
			12:00	T6.5	7.14	5.69	0.27	5.7	0.54	0.59	0.23	6.19	40.6	601.7	
			14:30	T9	7.1	5.74	0.26	5.7	0.56	0.61	0.22	6.33	40.3	523.7	
			18:30	T13	7.08	5.78	0.27	5.39	0.55	0.63	0.21	6.28	41.0	606.1	
		W3	18:00	T0	7.67	6.91	0.33	6.52	0.61	0.78	0.23	6.19	44.7	298.4	
			07:30	T2	7.76	6.93	0.28	7.1	0.63	0.76	0.22	6.23	47.9	718.8	
			09:00	T3.5	7.74	6.9	0.39	6.9	0.62	0.8	0.49	6.22	47.9	542.9	
			12:00	T6.5	7.78	6.77	0.49	6.95	0.63	0.98	0.38	6.19	50.8	558.0	
			14:30	T9	8.04	6.79	0.6	7.22	0.64	1.1	0.46	6.2	51.2	564.8	
			18:30	T13	7.79	6.8	0.48	7.48	0.65	0.94	0.33	6.17	50.1	652.2	
		W22	18:00	T0	7.8	7.08	0.36	6.46	0.68	0.83	0.35	6.18	49.1		
			07:30	T2	7.83	7.07	0.34	6.69	0.68	0.84	0.32	6.12	47.8		
			09:00	T3.5	7.88	7.08	0.4	6.3	0.68	0.9	0.8	6.24	48.3		
			12:00	T6.5	7.85	7.1	0.53	6.64	0.69	0.93	1.13	6.31	50.2		
			14:30	T9	7.81	7.09	0.49	6.55	0.67	0.92	0.83	6.18	49.7		
			18:30	T13	7.8	7.09	0.76	6.32	0.66	0.99	1.93	6.18	47.8		

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EVENT	SAMPLE DATE	SAMPLE SITE	SAMPLE TIME	GRAPH TIME	$[SO_4^{2-}]$	$[SiO_2]$	$[Cl^-]$	$[Ca^{2+}]$	$[Mg^{2+}]$	$[Na^+]$	$[K^+]$	pH	EC	$[^{222}Rn]$	$\delta^{18}O$
E3	06/23	W27	18:00	T0	7.34	6.47	0.59	5.99	0.67	1.49	0.35	6.3	44.4	633.8	
	06/24		07:30	T2	7.48	6.45	0.54	5.9	0.67	1.36	0.34	6.37	43.7	197.7	
	06/24		18:30	T13	7.07	6.19	0.52	5.55	0.66	1.47	0.38	6.58	43.0	378.6	
E5	07/10	S1	18:45	T0	7.91	7.01	0.49	7.47	0.51	0.84	0.36	6.22	43.5		
	07/11		13:00	T1	7.8	6.8	0.55	6.85	0.54	0.91	0.47	6.27	44.1		
	07/11		13:30	T1.5	5.59	5.46	0.51	5.6	0.46	1.37	0.84	6.4	36.6		
	07/11		14:10	T2.1		5.32		5.95	0.51	0.92	0.67	6.33	35.6		
	07/11		15:00	T3	5.39	6.0	0.4	6.64	0.6	0.71	0.56	6.3	40.9		
	07/11		16:30	T4.5	5.01	5.39	0.43	6.53	0.56	0.85	0.61	6.36	37.9		
	07/11		18:00	T6	5.63	6.04	0.32	6.75	0.6	0.69	0.49	6.37	40.8		
	07/11		20:30	T8.5	6.8	6.23	0.53	6.94	0.6	0.78	0.46	6.32	42.0		
	07/12		08:00	T20	7.35	6.76	0.47	7.29	0.63	0.79	0.38	6.25	48.8		
		S2	18:45	T0	7.86	6.8	0.41	7.59	0.57	0.8	0.24	6.2	44.0		
			13:00	T1	7.48	6.47	0.48	7.42	0.57	0.77	0.3	6.15	44.1		
			13:30	T1.5	6.72	5.98	0.53	7.73	0.56	0.76	0.37	6.2	44.7		
			14:10	T2.1	7.07	6.33	0.48	7.8	0.56	0.8	0.3	6.17	44.3		
			15:00	T3	5.4	5.68	0.42	7.14	0.57	0.76	0.33	6.08	41.2		
			16:30	T4.5	6.6	5.98	0.39	7.72	0.61	0.73	0.32	6.12	43.4		
			18:00	T6	6.83	6.21	0.39	7.46	0.61	0.74	0.34	6.17	44.7		
			20:30	T8.5	7.01	6.27	0.39	7.45	0.62	0.77	0.38	6.16	45.9		
			08:00	T20	7.0	6.16	0.45	7.14	0.61	0.79	0.48				
		S3	13:00	T1	7.29	5.79	0.39	6.25	0.52	0.67	0.33	6.26	37.8		
			13:30	T1.5	4.88	5.24	0.36	6.22	0.49	0.63	0.65	6.24	36.1		
			14:10	T2.1	5.02	5.93	0.32	7.18	0.58	0.64	0.71	6.2	40.5		
			15:00	T3	5.09	5.35	0.38	5.9	0.56	0.64	0.54	6.17	37.5		
			16:30	T4.5	5.29	5.7	0.25	6.79	0.61	0.63	0.58	6.24	40.0		
			18:00	T6	6.61	5.81	0.42	6.3	0.61	0.65	0.5	6.19	40.2		
			20:30	T8.5	6.17	5.94	0.29	6.42	0.59	0.7	0.4	6.19	39.6		
			08:00	T20	7.1	5.87	0.32	6.01	0.58	0.67	0.3	6.24	43.1		
		S4	18:45	T0	7.41	5.98	0.33	6.34	0.53	0.7	0.25	6.28	37.8		
			13:00	T1	7.32	5.75	0.42	6.59	0.53	0.72	0.28	6.16	38.1		
			13:30	T1.5	5.05	5.64	0.48	6.93	0.53	0.63	0.7	6.2	37.1		
			14:10	T2.1	5.05	5.75	0.45	6.29	0.57	0.7	0.57	6.13	38.1		
			15:00	T3	6.5	5.33	0.5	6.37	0.56	0.7	0.46	6.16	36.9		
			16:30	T4.5	5.55	5.62	0.32	6.36	0.57	0.62	0.53	6.12	38.3		
			18:00	T6	6.84	5.73	0.43	6.36	0.58	0.75	0.45	6.12	38.9		
			20:30	T8.5	6.94	5.75	0.35	6.01	0.57	0.65	0.37	6.08	39.1		
			08:00	T20	7.09	5.8	0.31	5.84	0.55	0.7	0.29	6.23	42.2		

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EVENT	SAMPLE DATE	SAMPLE SITE	SAMPLE TIME	GRAPH TIME	$[SO_4^{2-}]$	$[SiO_2]$	$[Cl^-]$	$[Ca^{2+}]$	$[Mg^{2+}]$	$[Na^+]$	$[K^+]$	pH	EC	$[^{222}Rn]$	$\delta^{18}O$
E5	07/10	W3	18:45	T0	7.92	7.1	0.45	7.91	0.55	0.86	0.3	6.06	45.0		
	07/11		13:00	T1	7.77	6.96	0.62	7.23	0.65	0.94	0.63	6.07	47.1		
	07/11		13:30	T1.5	8.13	6.77	0.86	7.6	0.69	1.29	1.05	6.03	51.7		
	07/11		14:10	T2.1	8.31	6.67	0.78	10.33	0.84	0.98	0.85	5.99	67.4		
	07/11		15:00	T3	8.11	6.73	0.85	9.38	0.82	1.25	0.89	5.96	59.5		
	07/11		16:30	T4.5	8.2	6.66	0.98	8.67	0.81	1.32	1.26	5.9	61.2		
	07/11		18:00	T6	7.95	6.64	0.61	8.59	0.81	0.89	0.69	5.92	57.8		
	07/11		20:30	T8.5	7.88	6.74	0.59	8.42	0.79	0.97	0.56	5.87	54.5		
	07/12		08:00	T20	7.72	6.94	0.48	8.44	0.73	0.78	0.42	5.9	54.5		
		W22	13:00	T1	7.74	7.07	0.38	7.21	0.67	0.85	0.25	6.01	46.4		
			14:10	T2.1	7.4	6.69	0.89	6.84	0.64	1.2	0.62	6.33	48.1		
			15:00	T3	7.53	6.76	0.87	7.13	0.66	1.35	0.43	6.37	47.6		
			18:00	T6	7.74	7.12	0.66	7.34	0.68	1.04	0.42	6.09	46.8		
			20:30	T8.5	7.74	7.07	0.50	7.27	0.68	0.92	0.3	5.98	46.5		
			08:00	T20	7.72	7.08	0.38	7.43	0.67	0.8	0.25	5.95	50.1		
E6	07/13	S1	11:00	T0	7.6	7.01	0.42	8.36	0.57	0.83	0.34	0.34	6.19		
	07/13		14:30	T2.5	7.75	6.69	0.48	6.76	0.58	0.86	0.44	6.3	43.6		
	07/13		16:00	T4	7.62	6.31	0.52	7.34	0.52	0.99	0.6	6.25	41.4		
	07/13		17:30	T5.5	7.35	5.7	0.57	7.23	0.52	0.89	0.54	6.33	41.1		
	07/13		19:00	T7	7.29	6.18	0.44	6.93	0.55	0.74	0.46	6.29	42.0		
	07/13		08:30	T20.5	7.63	6.77	0.49	8.23	0.58	0.78	0.43	6.2	49.4		
		S2	11:00	T0	7.8	6.8	0.34	8.85	0.59	0.82	0.39	6.23	46.2		
			14:30	T2.5	7.75	6.67	0.33	7.82	0.59	0.83	0.37	6.2	46.3		
			16:00	T4	7.31	6.26	0.34	8.52	0.56	0.69	0.39	6.11	44.6		
			17:30	T5.5	7.48	6.58	0.29	9.28	0.56	0.74	0.37	6.13	45.2		
			19:00	T7	7.45	6.57	0.33	8.95	0.57	0.75	0.38	6.18	45.7		
			08:30	T20.5	7.78	6.76	0.38	7.99	0.62	0.77	0.49	6.17	51.4		
		S3	11:00	T0	7.28	5.86	0.28	7.32	0.53	0.68	0.27	6.24	38.8		
			14:30	T2.5	7.33	5.97	0.28	6.75	0.51	0.68	0.3	6.19	38.7		
			16:00	T4	7.01	5.29	0.37	6.25	0.52	0.6	0.44	6.21	37.6		
			17:30	T5.5	6.97	5.93	0.36	8.24	0.51	0.62	0.47	6.16	39.1		
			19:00	T7	7.09	6.22	0.35	7.46	0.54	0.64	0.41	6.25	39.6		
			08:30	T20.5	7.32	6.0	0.35	6.5	0.57	0.7	0.33	6.19	44.1		
		S4	11:00	T0	7.28	5.88	0.29	6.57	0.54	0.72	0.28	6.1	39.0		
			14:30	T2.5	7.27	5.96	0.32	6.31	0.55	0.67	0.28	6.06	39.1		
			16:00	T4	6.99	5.79	0.43	7.61	0.52	0.62	0.43	6.15	38.7		
			17:30	T5.5	7.01	5.81	0.35	7.02	0.53	0.62	0.44	6.09	39.8		
			19:00	T7	7.16	5.86	0.34	7.67	0.53	0.63	0.39	6.09	39.3		
			08:30	T20.5	7.32	5.92	0.31	6.21	0.54	0.7	0.31	6.15	44.8		

APPENDIX 1

EVENT	SAMPLE DATE	SAMPLE SITE	SAMPLE TIME	GRAPH TIME	$[SO_4^{2-}]$	$[SiO_2]$	$[Cl^-]$	$[Ca^{2+}]$	$[Mg^{2+}]$	$[Na^+]$	$[K^+]$	pH	EC	$[^{222}Rn]$	$\delta^{18}O$
E6	07/13	W3	11:00	T0	7.2	7.01	0.38	7.91	0.68	0.81	0.39	5.85	47.9		
	07/13		14:30	T2.5	7.3	7.1	0.55	8.6	0.62	1.02	0.49	5.94	47.6		
	07/13		16:00	T4	7.34	6.92	0.63	8.68	0.62	0.96	1.12	5.95	49.0		
	07/13		17:30	T5.5	7.46	6.93	0.57	8.8	0.67	0.93	0.87	5.95	50.6		
	07/13		19:00	T7	7.3	6.89	0.43	7.71	0.65	0.87	0.4	5.92	48.9		
	07/13		08:30	T20.5	7.27	6.93	0.42	8.01	0.67	0.81	0.37	5.92	53.8		
		W22	11:00	T0	7.24	7.11	0.36	8.15	0.62	0.8	0.23	6.07	46.1		
			14:30	T2.5	7.24	7.25	0.39	8.06	0.62	0.85	0.28	6.03	46.8		
			16:00	T4	7.21	7.58	0.44	9.01	0.6	0.92	0.30				
			17:30	T5.5	7.25	6.99	0.41	8.24	0.63	0.91	0.29	6.18	46.6		
			19:00	T7	7.17	6.98	0.37	7.73	0.6	0.85	0.28	6.13	46.6		
			08:30	T20.5	7.36	7.16	0.34	8.53	0.65	0.8	0.24	5.93	52.0		
E8	08/11	S1	20:00	T0	7.44	7.82	1.39	7.03	0.62	1.92	0.68	6.16	45.7	240.1	-12.27
	08/12		17:45	T1	2.86	3.4	0.29	4.81	0.47	0.35	1.23	6.15	29.7	30.2	-7.34
	08/12		18:15	T1.5	3.59	4.27	0.33	5.45	0.49	0.44	1.08	6.27	33.8	33.2	
	08/12		19:15	T2.5	4.7	5.07	0.37	6.28	0.56	0.63	0.92	6.27	41.3	10.1	-9.37
	08/12		21:15	T4.5	6.02	5.78	0.54	6.4	0.58	0.71	0.76	6.31	40.2	106.1	-10.44
	08/13		00:45	T8	6.74	6.4	0.73	6.76	0.59	0.97	0.7	6.18	41.8	89.6	
		S2	17:45	T1	5.5	4.75	0.49	6.07	0.51	0.59	0.84	6.15	36.1	108.6	
			18:15	T1.5	5.84	5.17	0.46	6.82	0.52	0.63	0.7	6.24	38.5	161.0	
			19:15	T2.5	6.16	5.57	0.41	7.02	0.55	0.65	0.63	6.21	40.3	123.7	
			21:15	T4.5	6.5	5.95	0.41	6.85	0.59	0.71	0.56	6.18	42.3	143.9	
			00:45	T8	6.97	6.31	0.43	6.92	0.61	0.78	0.56	6.17	43.4	161.74	
		S4	20:00	T0	7.39	5.95	0.46	5.41	0.55	0.82	0.37	6.19	35.5	297.1	
			17:45	T1	3.37	3.97	0.27	5.12	0.43	0.41	1.25	6.2	29.8	179.9	
			18:15	T1.5	5.45	5.06	0.46	5.76	0.52	0.54	0.93	6.16	35.9	219.4	
			19:15	T2.5	6.56	5.79	0.36	5.92	0.53	0.61	0.65	6.23	37.1	285.6	
			21:15	T4.5	7.0	5.93	0.33	5.6	0.55	0.67	0.5	6.24	38.1	382.2	
			00:45	T8	7.21	6.12	0.29	5.78	0.53	0.71	0.49	6.22	37.8	382.1	
		W3	20:00	T0	7.89	7.08	0.36	8.34	0.68	0.78	0.35	5.92	43.0	405.1	
			17:45	T1	7.62	6.71	0.4	8.27	0.62	0.84	0.51	6.01	42.4	752.7	
			18:15	T1.5	7.0	6.29	0.36	9.01	0.7	0.76	0.65	5.87	46.3	751.8	
			19:15	T2.5	7.31	6.69	0.48	8.61	0.69	0.84	0.38	5.91	44.9	717.3	
			21:15	T4.5	7.19	6.94	0.37	8.46	0.67	0.89	0.36	5.90	45.1	628.9	
			00:45	T8	7.22	7.03	0.37	8.87	0.68	0.84	0.30	5.91	45.0	776.0	

APPENDIX 1

EVENT	SAMPLE DATE	SAMPLE SITE	SAMPLE TIME	GRAPH TIME	$[SO_4^{2-}]$	$[SiO_2]$	$[Cl^-]$	$[Ca^{2+}]$	$[Mg^{2+}]$	$[Na^+]$	$[K^+]$	pH	EC	$[^{222}Rn]$	$\delta^{18}O$
E8	08/11	W22	20:00	T0	7.74	7.22	0.36	8.14	0.64	0.89	0.23	6.06	44.2		
	08/12		17:45	T1	7.61	7.2	0.29	7.33	0.62	0.85	0.21	6.04	41.5		
	08/12		18:15	T1.5	7.41	6.9	0.36	7.96	0.61	0.82	0.24				
	08/12		19:15	T2.5	7.4	6.94	0.35	7.68	0.59	0.84	0.21	6.3	41.7		
	08/12		21:15	T4.5	7.47	6.98	0.32	8.16	0.61	0.86	0.2	6.25	41.6		
	08/13		00:45	T8	7.64	7.21	0.27	7.99	0.61	0.83	0.21	6.02	42.0		
		W24	17:45	T1	6.15	6.31	0.55	15.3	1.34	0.97	1.1	5.66	82.6		
			18:15	T1.5	5.92	6.43	0.54	15.3	1.35	0.9	1.0	5.67	78.9		
			19:15	T2.5	5.7	6.38	0.56	12.9	1.02	0.8	0.94	5.68	71.0		
			21:15	T4.5	5.74	6.67	0.54	10.8	1.01	0.83	0.84	5.72	69.4		
			00:45	T8	6.21	7.19	0.56	13.7	1.44	0.92	1.06	5.73	80.0		
		W27	17:45	T1	5.45	8.69	1.66	16.12	1.71	1.71	2.64				
			18:15	T1.5	5.59	9.39	2.02	18.54	2.01	1.89	1.37				
			00:45	T8	4.08	7.91	1.54	18.08	1.92	1.88	0.92	6.33	106.5		
		W28	20:00	T0	6.15	7.01	0.78	8.16	0.89	1.06	1.41	6.22	49.2		
			17:45	T1	5.99	7.32	0.62	7.6	0.73	0.81	0.86	6.52	45.7		
			21:15	T4.5	5.76	7.29	0.85	8.1	0.74	0.99	0.83				
			00:45	T8	5.75	7.26	0.61	7.36	0.62	0.85	0.69				
E9	08/13	S1	16:30	T0	6.62	6.74	0.59	6.88	0.53	0.93	0.6	6.33	37.3		-11.52
	08/13		21:00	T0.5	7.37	6.24	0.66	6.37	0.59	1.02	0.65	6.28	36.0		
	08/13		23:30	T3	5.44	4.26	0.49	4.18	0.42	0.38	0.74	6.02	23.7		-6.57
	08/14		14:30	T18	6.07	5.01	0.39	3.93	0.42	0.54	0.36	6.12	23.4		-7.33
	08/14		19:30	T23	6.08	5.05	0.33	3.98	0.41	0.52	0.32	6.08	23.5		
	08/15		09:00	T36.5	6.21	5.33	0.32	4.43	0.43	0.58	0.29	6.19	24.0		-8.18
	08/16		08:00	T59.5	6.36	5.63	0.33	4.6	0.46	0.62	0.29	6.09	31.2		
		S2	16:30	T0										220.2	
			21:00	T0.5										174.3	
			23:30	T3										127.3	
			14:30	T18										77.3	
			19:30	T23										57.5	
			09:00	T36.5										69.3	
			08:00	T59.5										144.9	
		S4	16:30	T0										372.0	
			21:00	T0.5										514.9	
			23:30	T3										139.3	
			14:30	T18										166.6	
			19:30	T23										183.1	
			09:00	T36.5										288.7	
			08:00	T59.5										335.9	

APPENDIX 1

EVENT	SAMPLE DATE	SAMPLE SITE	SAMPLE TIME	GRAPH TIME	$[SO_4^{2-}]$	$[SiO_2]$	$[Cl^-]$	$[Ca^{2+}]$	$[Mg^{2+}]$	$[Na^+]$	$[K^+]$	pH	EC	$[^{222}Rn]$	$\delta^{18}O$
E9	08/13	S7	23:30	T3	4.92	4.57	0.22	4.19	0.39	0.38	0.65	5.96	23.0		
	08/14		14:30	T18	6.05	4.97	0.3	3.76	0.38	0.54	0.24	5.78	22.6	127.7	
	08/14		19:30	T23	6.16	4.99	0.26	3.85	0.39	0.53	0.23	5.78	22.2	117.7	
	08/15		09:30	T37	6.2	5.11	0.24	3.97	0.42	0.52	0.22	5.76	23.1	87.3	
	08/16		08:00	T59.5	6.2	5.19	0.24	3.82	0.39	0.54	0.23	5.75	27.8	171.72	
		W3	16:30	T0										505.4	
			21:00	T0.5										739.6	
			23:30	T3										765.1	
			14:30	T18										761.2	
			19:30	T23										407.6	
			09:00	T36.5										538.2	
			08:00	T59.5										389.7	
		W10	23:30	T3	7.27	5.42	0.62	8.6	1.09	0.88	1.8	5.85	51.0		
			14:30	T18	6.17	5.27	0.31	6.15	0.63	0.62	0.83	5.79	31.5	189.1	
			19:30	T23	6.21	5.36	0.33	5.26	0.64	0.7	0.44	5.71	31.3	131.1	
			09:00	T36.5	6.28	5.46	0.29	5.34	0.62	0.61	0.38	5.85	30.7	224.9	
			08:00	T59.5	6.37	5.46	0.33	5.37	0.54	0.63	0.3	5.7	34.2	228.3	
		PORE	19:30	T23	5.57	4.87	0.29	3.4	0.4	0.51	0.13	5.66	20.7	106.1	-7.3
E10	08/26	S1	08:30	T0	6.8	6.22	0.33	5.66	0.55	0.7	0.23		38.6	116.6	-11.37
	08/27		13:00	T3										85.7	
	08/27		14:00	T4										89.1	
	08/27		16:30	T6.5										83.4	
	08/27		19:00	T9	5.7	5.37	0.47	4.99	0.5	0.69	0.32		31.7	59.9	-11.58
	08/27		22:00	T12	6.11	5.6	0.32	5.37	0.51	0.6	0.27		38.4	81.0	-10.38
	08/28		08:00	T22	6.33	5.4	0.28	4.59	0.44	0.58	0.24		31.2	27.8	-9.18
	08/28		18:00	T32	6.39	5.44	0.33	4.66	0.44	0.62	0.23		32.9	33.0	
	08/29		08:00	T46	6.44	5.56	0.27	4.59	0.45	0.62	0.21		31.7	82.9	-9.44
		S2	08:30	T0										283.3	
			13:00	T3										870.9	
			14:00	T4										536.7	
			16:30	T6.5										738.2	
			19:00	T9										425.8	
			22:00	T12										569.6	
			08:00	T22										598.8	
			18:00	T32										507.9	
			08:00	T46										478.9	

APPENDIX 1

EVENT	SAMPLE DATE	SAMPLE SITE	SAMPLE TIME	GRAPH TIME	$[SO_4^{2-}]$	$[SiO_2]$	$[Cl^-]$	$[Ca^{2+}]$	$[Mg^{2+}]$	$[Na^+]$	$[K^+]$	pH	EC	$[^{222}Rn]$	$\delta^{18}O$
E10	08/26	S4	08:30	T0										369.4	
	08/27		13:00	T3										522.9	
	08/27		14:00	T4										421.8	
	08/27		16:30	T6.5										519.2	
	08/27		19:00	T9										262.6	
	08/27		22:00	T12										447.3	
	08/28		08:00	T22										324.4	
	08/28		18:00	T32										282.8	
	08/28		08:00	T46										389.6	
		S7	08:30	T0											
			13:00	T3										193.4	
			14:00	T4										265.6	
			16:30	T6.5										269.6	
			19:00	T9											
			22:00	T12										138.5	
			08:00	T22										211.0	
			18:00	T32										97.8	
			08:00	T46										196.8	
		W3	08:30	T0										386.6	
			13:00	T3										619.7	
			14:00	T4										703.1	
			16:30	T6.5										375.2	
			19:00	T9										434.4	
			22:00	T12										492.8	
			08:00	T22										425.1	
			18:00	T32										483.3	
			08:00	T46										489.2	
		W10	08:30	T0										390.4	
			13:00	T3										292.3	
			14:00	T4										281.4	
			16:30	T6.5										323.3	
			19:00	T9										411.7	
			22:00	T12										254.5	
			08:00	T22										251.2	
			18:00	T32										265.7	
			08:00	T46										210.8	

APPENDIX 1

EVENT	SAMPLE DATE	SAMPLE SITE	SAMPLE TIME	GRAPH TIME	$[SO_4^{2-}]$	$[SiO_2]$	$[Cl^-]$	$[Ca^{2+}]$	$[Mg^{2+}]$	$[Na^+]$	$[K^+]$	pH	EC	$[^{222}Rn]$	$\delta^{18}O$
E10	08/16	W13	08:30	T0										276.6	
	08/27		13:00	T3										279.4	
	08/27		14:00	T4										240.4	
	08/27		16:30	T6.5										212.8	
	08/27		19:00	T9										317.8	
	08/27		22:00	T12										569.7	
	08/28		08:00	T22										148.1	
	08/28		18:00	T32										76.0	
	08/29		08:00	T46										91.6	
		W20	08:30	T0										435.2	
			13:00	T3										332.8	
			14:00	T4										271.7	
			16:30	T6.5										278.1	
			19:00	T9										265.5	
			22:00	T12										73.6	
			08:00	T22										207.1	
			18:00	T32										190.4	
			08:00	T46										175.3	
E11	09/03	S1	08:30	T0	6.85	6.12	0.31	5.38	0.54	0.71	0.23	6.41	33.5		
	09/03		19:10	T2	7.23	5.14	0.39	4.84	0.51	0.66	0.36	6.3	31.4		
	09/03		20:40	T3.5	7.48	5.47	0.32	5.1	0.54	0.67	0.29	6.27	32.8		
	09/03		23:10	T6	6.97	5.86	0.27	5.18	0.53	0.64	0.26	6.33	32.8		
	09/04		08:40	T15.5	6.91	5.99	0.28	5.36	0.53	0.68	0.22	6.29	32.2		
		S2	08:30	T0	7.13	5.55	0.29	5.6	0.57	0.71	0.23	6.13	36.0	882.6	
			19:10	T2	7.47	5.78	0.48	5.77	0.52	0.65	0.46	6.14	34.9	1156.5	
			20:40	T3.5	7.5	5.98	0.35	5.58	0.54	0.66	0.37	6.06	35.2	843.5	
			23:10	T6	7.01	6.13	0.32	5.63	0.53	0.69	0.33	6.06	35.5	1047.4	
			08:40	T15.5	6.95	6.21	0.27	5.36	0.54	0.68	0.25	6.05	33.7	654.8	
		S4	08:30	T0	6.92	6.15	0.3	5.63	0.55	0.74	0.19	6.11	34.2	547.1	
			19:10	T2	7.48	5.9	0.39	5.49	0.58	0.66	0.33	6.03	34.3	467.6	
			20:40	T3.5	7.33	5.88	0.38	5.35	0.55	0.7	0.3	6.16	34.6	444.6	
			23:10	T6	6.91	6.04	0.26	5.21	0.59	0.69	0.23	6.12	33.2	741.7	
			08:40	T15.5	6.93	6.15	0.25	5.4	0.55	0.72	0.2	6.07	33.7	583.8	
		S7	08:30	T0	6.61	5.41	0.28	4.28	0.47	0.65	0.28	6.05	27.3	397.9	
			19:10	T2	6.65	5.34	0.23	4.42	0.43	0.61	0.29	6.07	27.8	270.7	
			20:40	T3.5	7.13	5.09	0.26	4.59	0.43	0.59	0.3	5.93	28.2	276.2	
			23:10	T6	6.61	5.45	0.24	4.28	0.45	0.59	0.26	6.04	27.6	174.6	
			08:40	T15.5	6.58	5.43	0.25	4.39	0.44	0.62	0.27	6.06	27.6	306.3	

APPENDIX 1

EVENT	SAMPLE DATE	SAMPLE SITE	SAMPLE TIME	GRAPH TIME	$[SO_4^{2-}]$	$[SiO_2]$	$[Cl^-]$	$[Ca^{2+}]$	$[Mg^{2+}]$	$[Na^+]$	$[K^+]$	pH	EC	$[^{222}Rn]$	$\delta^{18}O$
E11	09/03	W3	08:30	T0	7.38	6.89	0.34	6.38	0.6	0.81	0.25	6.03	38.9	404.4	
	09/03		19:10	T2	7.52	6.97	0.32	6.62	0.6	0.78	0.25	6.14	39.0	595.4	
	09/03		20:40	T3.5	7.51	6.88	0.36	6.6	0.33	0.8	0.23	6.0	38.6	526.9	
	09/03		23:10	T6	7.52	6.78	0.41	6.47	0.56	0.85	0.26	6.0	38.5	492.7	
	09/04		08:40	T15.5	7.46	6.79	0.42	6.71	0.6	0.85	0.29	6.0	38.7	520.3	
		W7	08:30	T0	6.73	5.43	0.32	4.28	0.52	0.64	0.35	5.72	27.9	376.3	
			19:10	T2	6.74	5.46	0.29	4.47	0.52	0.62	0.37	5.77	27.5	265.5	
			20:40	T3.5	6.8	5.5	0.32	4.28	0.53	0.62	0.39	5.69	28.4	228.5	
			23:10	T6	6.73	5.33	0.34	4.25	0.51	0.67	0.33	5.62	27.7	233.6	
			08:40	T15.5	6.78	5.36	0.26	4.31	0.51	0.62	0.31	5.66	28.0	285.1	
		W16	08:30	T0	6.39	5.16	0.3	4.26	0.5	0.62	0.3	5.98	28.3	194.6	
			19:10	T2	6.58	5.3	0.29	4.39	0.5	0.65	0.27	5.91	28.2	266.0	
			20:40	T3.5	6.54	5.25	0.32	4.76	0.51	0.68	0.25	5.92	28.3	138.0	
			23:10	T6	6.57	5.32	0.25	4.53	0.5	0.63	0.22	5.79	27.5	255.4	
			08:40	T15.5	6.57	5.15	0.43	4.47	0.51	0.75	0.29	5.82	27.9	167.1	
		W20	08:30	T0	6.91	6.08	0.39	5.6	0.58	0.78	0.21	6.01	34.4	417.8	
			19:10	T2	6.99	6.11	0.32	5.85	0.61	0.71	0.16	5.98	33.9	500.0	
			20:40	T3.5	6.99	6.12	0.31	5.58	0.6	0.7	0.18	6.0	35.2	315.4	
			23:10	T6	6.98	6.12	0.36	5.83	0.61	0.7	0.17	6.05	33.9	321.1	
			08:40	T15.5	7.04	6.1	0.39	5.88	0.64	0.76	0.19	5.94	33.9	205.9	
BASE-	05/12	S1			6.42	5.21	0.18	4.45	0.46	0.61	0.20	6.23	43.5	159.8	
FLOW	06/24				7.57	6.24	0.34	6.37	0.59	0.69	0.23	6.51	38.1	144.0	
	07/05				7.77	6.89	0.84	6.75	0.57	1.11	0.37	6.34	47.5	178.2	
	07/08				7.95	7.36	0.67	7.38	0.56	1.0	0.4	6.33	48.9	207.0	
	07/26				8.12	7.59	0.61	7.04	0.6	0.9	0.4	6.33	37.9	127.7	
	07/27				8.25	7.66	0.63	6.91	0.6	0.89	0.41	6.39	40.7		
	08/11				7.44	7.82	1.39	7.03	0.62	1.92	0.68	6.16	37.6	240.1	
	05/12	S2			6.61	5.82	0.24	5.19	0.5	0.65	0.25	6.08	47.8	499.6	
	06/24				7.92	6.8	0.29	7.18	0.61	0.7	0.17	6.39	42.9	280.7	
	07/05				7.77	6.89	0.38	7.84	0.57	0.81	0.2	6.4	45.9	146.8	
	07/08				7.64	6.9	0.37	7.76	0.59	0.81	0.19	6.39	48.1	197.5	
	07/26				7.89	6.91	0.41	7.52	0.61	0.84	0.26	6.42	37.8	156.4	
	07/27				7.8	6.95	0.32	7.21	0.61	0.8	0.22	6.41	37.3		
	05/12	S3			6.45	5.07	0.23	4.58	0.47	0.63	0.19	6.13	42.7		
	06/24				7.19	5.87	0.27	5.9	0.56	0.63	0.18	6.36	35.1		
	07/05				7.07	5.82	0.24	6.25	0.53	0.69	0.21	6.38	38.4		
	07/08				7.17	5.87	0.3	6.08	0.52	0.68	0.21	6.38	40.7		
	07/26				7.49	6.0	0.29	5.56	0.57	0.73	0.25	6.36	31.3		
	07/27				7.44	5.97	0.28	5.63	0.57	0.74	0.23	6.43	33.0		

APPENDIX 1

EVENT	SAMPLE DATE	SAMPLE SITE	SAMPLE TIME	GRAPH TIME	$[SO_4^{2-}]$	$[SiO_2]$	$[Cl^-]$	$[Ca^{2+}]$	$[Mg^{2+}]$	$[Na^+]$	$[K^+]$	pH	EC	$[^{222}Rn]$	$\delta^{18}O$
BASE-	05/12	S4			6.57	5.26	0.21	4.98	0.51	0.64	0.16	6.07	45.6	452.4	
FLOW	06/24				7.14	5.67	0.25	5.86	0.55	0.61	0.18	6.28	34.8	1024.7	
	07/05				7.07	5.82	0.25	5.96	0.53	0.69	0.21	6.39	38.6	419.2	
	07/08				7.14	5.88	0.32	6.08	0.53	0.74	0.23	6.43	39.9	543.7	
	07/26				7.51	6.07	0.3	5.81	0.54	0.77	0.25	6.28	32.1	273.5	
	07/27				7.43	6.01	0.32	5.6	0.57	0.73	0.24	6.3	31.7		
	08/11				7.39	5.95	0.46	5.41	0.55	0.82	0.37	6.19	28.2	297.1	
	07/05	W3			7.73	6.98	0.4	7.53	0.57	0.94	0.28	6.2	45.9	857.1	
	07/08				7.5	7.1	0.34	7.22	0.6	0.78	0.26	6.13	48.8		
	07/26				7.85	7.15	0.37	7.01	0.64	0.82	0.28	6.13	36.8	637.7	
	08/11				7.89	7.08	0.36	8.34	0.68	0.78	0.35	5.92		405.1	
	07/05	W22			7.77	7.1	1.44	7.57	0.63	1.72	0.41	6.25	51.0	630.3	
	07/08				7.61	7.07	0.46	7.61	0.63	0.88	0.26	6.18	49.0		
	07/26				7.81	7.18	0.35	7.27	0.65	0.87	0.25	6.23	38.9	324.9	
	08/11				7.74	7.22	0.36	8.14	0.64	0.89	0.23	6.06		338.1	
	07/05	W27			7.56	7.23	1.46	6.09	0.71	2.26	1.28				
	07/08				6.94	7.11	0.71	6.55	0.69	1.87	0.66	6.61	48.8		
	07/05	W28			8.26	7.09	0.82	8.14	0.77	0.94	1.63	6.34	59.5		