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STUDIES OF THE AGRICULTURAL CONTRIBUTION TO NITRATE ENRICHMENT 0F GROUNDWATER AND THE SUBSEQUENT NITRATE LOADING TO SURFACE WATERS

PART III: MECHANISMS OF RUNOFF GENERATION AND NITRATE FLUX TO STREAMS DURING RUNOFF EVENTS

FINAL REPORT
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M.G. Sklash, R.W. Gillham, J.A. Cherry
Department of Earth Sciences
University of Waterloo
Waterloo, Ontario

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

SUMMARY

This report presents the results of an investigation into the origin of nitrate in stream discharge during periods of high runoff following snowmelt or storm events. Studies were conducted in the Hillman Creek (PLUARG AG-13) and Canagagigue Creek (PLUARG AG-4) watersheds during the period from February to June of 1977. The primary objectives of the study were: (1) to separate the groundwater and overland flow contributions of nitrate to the streams during high runoff periods through the analyses of the stream hydrographs, (2) to evaluate the accuracy of the environmental isotope mass balance technique for separating the stream nitrate into its source components. In conjunction with these goals, two other aims of the study were: (1) to identify the nitrate sources during high runoff periods in order to plan remedial measures, (2) to establish criteria for the extrapolation of the study results to larger areas.

The investigation involved a multi-technique approach to storm runoff studies which included the monitoring of groundwater levels, stream discharge, and analyses for oxygen-18, specific conductivity, and nitrate in the rain, snow, snowmelt, overland flow, drainage tile effluent, groundwater and the stream during both high and low runoff periods. The actual hydrograph separations were achieved through the use of the environmental isotope mass balance technique. The groundwater stage- groundwater discharge rating curve technique and a standard graphical technique were applied whenever possible to determine the performance of the isotope technique.

The most positive result of the study is that the isotope technique can provide excellent hydrograph separations. The correlation between the isotope and rating curve results is generally quite good.

Only in the case of bank storage are the results divergent and it is shown that the discrepancy stems from the inability of the rating curve technique to discriminate between stream water stored in the bank and groundwater in the stream bank. The standard graphical technique, as expected, generally yielded much lower groundwater components than the other two methods.

The isotope technique demonstrated that the groundwater and overland flow contributions to nitrate in the stream during periods of high runoff cannot be determined by the use of simple graphical techniques. Through isotopic and chemical analyses, a significant source of overland flow in the Hillman Creek watershed was proven to be mostly of groundwater origin during one event and mostly of event water origin during another event. No overland flow was produced from the area during a third event. The overland flow of groundwater origin contained a much higher nitrate content than the near stream groundwater, the baseflow, or the overland flow of event origin water. The implications of these findings are that the groundwater nitrate content cannot necessarily be assumed constant during a storm and that the pre-storm basin conditions, the nature of the runoff producing event, and the nature of the basin itself are controlling factors in the response of the basin to an event.

A snowmelt event on East Canagigue Creek was found to be mostly of groundwater origin until the day of peak discharge when vast quantities of snowmelt caused the stream to become influent. Nitrate concentrations in the stream had remained near the baseflow level (less than 3 mg/L NO_3 -N) until the peak discharge day when the nitrate doubled from 3 to 6 mg/L NO_3^--N.

A rain event on the same basin only produced a 68% nitrate increase from baseflow. The stream remained effluent and groundwater dominated the hydrograph but to a lesser extent than on the east branch. As on the west branch, either high nitrate overland flow or drainage tile effluent caused the nitrate increase. The larger nitrate increase and smaller groundwater component on the west branch may reflect the influence of the hydrogeologic differences between the east and west branches.

The study has demonstrated that the quantitative extrapolation of these results to future events and other basins would be quite tenuous at this time. Also, it has shown that simple graphical techniques to determine nitrate sources may lead to serious errors. Much more effort of this type must be expended in order to make any attempt at quantitative extrapolations.

1. INTRODUCTION

During the April 1975 to March 1977 period, as part of the PLUARG Task Group C activities, the Department of Earth Sciences at the University of Waterloo undertook detailed studies of the occurrence and migration of nitrate in groundwater. During those studies it was observed that the nitrate concentration in Hillman Creek, the stream draining watershed AG-13, increased as the stream discharge increased. Data collected by the Ontario Ministry of the Environment suggested similar relationships in other PLUARG watersheds. These observations suggest that a very significant proportion of the annual nitrate load to the stream occurs during periods of high runoff.

Little quantitative information exists in the literature regarding the relative importance of the groundwater and overland flow contributions to the nitrate content of storm or snowmelt runoff in streams. Identification of the nitrate sources during runoff events is essential in the planning of fertilization practices which will minimize the nutrient loading of surface drainage systems.

1.1 Purpose and Scope

This report examines the roles of the water which existed in the basin prior to a storm (or snowmelt event) and the water added by the event in determining the nitrate concentrations of streams during high runoff events. The environmental isotope mass balance technique (oxygen-18 in this study) is used to separate the stream runoff hydrograph into its component parts. The value of this method is established via comparisons with other techniques commonly found in the literature. Three small watersheds with diverse hydrogeologic and land use characteristics provide the case studies in the comparisons.

In areas where topographic and hydrogeologic conditions preclude significant amounts of subsurface storm flow in storm or snowmelt runoff, the bulk of the nitrate load in a stream during snowmelt or storm runoff events can be attributed in part to the groundwater flux and in part to the overland flow flux to the stream. Several storm runoff and snowmelt hydrographs recorded between March and June, 1977 on Hillman Creek, Upper West Canagagigue Creek, and Upper East Canagagigue Creek, are examined. Subsurface storm flow is probably negligible in these basins.

1.2 Present Concepts of Storm Runoff Generation

The chemical behaviour of a stream during a runoff event (either due to a storm or snowmelt) is largely a function of the relative contributions of the components responsible for producing that event. The literature is replete with theories which attempt to explain the mechanisms which generate the runoff but most of these theories are weak in interpreting the temporal variations in stream chemistry which usually accompany the discharge variations.

Most of the popular theories for runoff generation are summarized in a paper by Freeze (1974). Freeze lists three basic mechanisms of storm runoff generation:

1. Partial area-overland flow in which soils become saturated from above during high-intensity storms. Only certain areas of the watershed, usually controlled by soil distribution, respond in this manner. Further explanations of this theory can be found in Betson (1964).
2. Variable source area-overland flow where overland flow is generated from areas saturated from below by a rising water table. Contributing areas grow and shrink with rainfall and are controlled mainly by topography and hydrogeology. Dunne and Black (1970a,b) provide a comprehensive field study which suggests this mechanism as being important.

3. Variable area-subsurface storm flow in which water is delivered directly to the stream channel via an expanding intermittent channel network. The water from the unsaturated zone is displaced by translatory flow and delivered to the channel through a near-stream saturated zone. Hewlett and Nutter (1970) described this mechanism in a report on a watershed study performed in the Appalachians.

Although Freeze suggests that: "...groundwater flow is seldom the cause of the major runoff during storms...," much evidence, mostly based on isotopic and chemical mass balance studies, indicates that groundwater is also an important contributor to storm runoff.

When considering snowmelt or rain runoff over frozen ground, classical Hortonian overland flow (Horton, 1933) becomes a viable concept for storm runoff generation. This situation is not at all uncommon in Canada and is particularly relevant in the study of nitrate export in light of the high stream discharges involved. Direct channel precipitation may also be a major runoff component in certain instances.

Storm or snowmelt runoff, then, can be generated by one or
more of the following generation mechanisms:

1. Partial area-overland flow
2. Variable area-overland flow
3. Variable area-subsurface storm flow
4. Groundwater flow
5. Hortonian overland flow
6. Direct channel precipitation

The first three mechanisms are defined as before. An outline of the last three mechanisms follows:

1. Hortonian overland flow is produced throughout a watershed when the rainfall rate

exceeds the infiltration capacity and the rainfall duration is sufficiently long to produce surface saturation. These conditions are rarely met except in special situations such as: rock outcrop; frozen, recently disturbed, or unvegetated soils; arid zones; and pavement.

2. Increased groundwater discharge during runoff events is a consequence of rapidly increasing hydraulic gradients near the stream and the growth of the groundwater discharge area in response to snowmelt or rainfall events.
3. Direct channel precipitation may be responsible for small storm hydrograph peaks in cases such as a short duration, high intensity storm following a period of prolonged drought.

If a basin produces storm runoff primarily by partial area-overland flow and the base flow has a high total dissolved solids content (TDS), then a storm occurring just after fertilization would probably result in greatly increased nitrates and markedly decreased TDS in peak runoff. If, however, increased groundwater discharge near the stream is the major source of storm runoff, then the TDS and nitrate concentrations in peak runoff would not be very different from those of base flow.

This example illustrates the need for identifying the manner in which runoff is produced and the source areas involved in its production. Fertilization practices designed to maintain or achieve low nitrate concentrations in surface drainage must consider this information to be effective.

1.3 Present Methods for Storm Runoff Studies

The following general categories of storm runoff study methods encompass most of the techniques found in the literature:

1. hydrograph separations based on empirical graphical techniques
2. hydrograph separations based on mass balance techniques using tracers.
3. hydrometric mass balance studies involving the measurement of parameters such as: stream discharge, precipitation, groundwater levels, soil moisture, etc.
4. physically-based mathematical models amenable to computer adaptation.
5. physical basin models

Each method has inherent weaknesses based either on unrealistic assumptions or limitations on data acquisition. Graphical techniques commonly assume groundwater to be insignificant and overland flow to be dominant. Physically-based mathematical models are generally restricted to hypothetical basins by their need for large amounts of hard-to-obtain physical data and computer space limits. Hydrometric measurements may be subject to considerable error stemming from the extremely heterogeneous nature of even the most 'homogeneous' research basins.

Physical basin models are often unrealistically simple. Mass balance techniques involving ionic species are subject to some error due to the spatial and temporal variations in overland flow and groundwater chemistry. Mass balance techniques involving stable isotopes require labour-intensive research or expensive automatic sampling equipment. Often storms or snowmelt events are isotopically unsuitable for hydrograph separation.

2. METHODS OF INVESTIGATION

The principal method in this study is the isotope mass balance technique with the stable isotope oxygen-18, as the tracer. Measurements of specific conductivity in conjunction with the oxygen-18 analyses were used to assist in the interpretation of the isotope data.

Hydrometric measurements, namely the groundwater and stream stages, and a standard graphical technique are also presented for comparative purposes.

2.1 Environmental Isotope Mass Balance

The environmental isotope mass balance, technique involves the use of naturally occurring stable and radiogenic isotopes such as: oxygen-18, deuterium, tritium, and radon; as tracers in basin-wide tracer tests. Dincer *et al.* (1970), Mook *et al.* (1974), Martinec *et al.* (1974), Martinec (1975), Fritz *et al.* (1975), and Sklash *et al.* (1976) have attempted to apply the environmental isotope mass balance technique in runoff studies. All of these efforts except that of Mook *et al.* (1974) (whose results are somewhat questionable) indicate large groundwater contributions to storm and snowmelt runoff. Consistently high groundwater contributions have led to some doubts about the method, however, the present study contains physical evidence which corroborates the results of the isotope technique.

The fundamental principle of the approach lies in the tracer-like nature which snowmelt and rainfall assume when their oxygen-18 contents deviate markedly from the oxygen-18 content of water already stored in the basin (groundwater and soil moisture).

The oxygen-18 content of a vapour mass is highly dependent on its place of origin and its temperature at condensation (Dansgaard, 1964). In addition, successive precipitations from the same vapour mass, altitude, local moisture sources and other factors all have effects on the isotopic nature of precipitation thereby creating seasonal, storm to storm, and intra-storm oxygen-18 variations. Groundwater in small basins, however, tends to acquire a temporally and spatially uniform oxygen-18 character which is closely related to the weighted mean oxygen-18 content of the water which recharges the basin over a period of years (Brinkmann *et al*., 1963).

Since the analytical accuracy of mass spectroscopic determinations of oxygen-18 contents in water is ±0.2 ^{o}/oo and the local temporal variations in the oxygen-18 content of precipitation may range from 10 to 20^{o}/oo in continental areas, the probability of experiencing runoff events in which the oxygen-18 contents of the rainfall (or snowmelt) and the water already in the basin (groundwater and soil moisture) are markedly different, is quite substantial. Part I of this report contains a further discussion on oxygen-18 for hydrogeologic studies.

The accuracy of these natural tracer experiments is a function of the degree to which the event fulfils the following criteria:

1. the oxygen-18 content of the rain (or snowmelt) is significantly different from that of the groundwater. Accuracy increases as the difference increases.
2. single-value concentration of oxygen-18 during the entire event; or excellent sampling control of the variations; or very short, high intensity storms.
3. temporally and spatially uniform oxygen-18 contents in the groundwater and unsaturated zones; or excellent sampling control of the variations; or topographic and hydrogeologic environments which preclude significant unsaturated zone contributions to runoff.

4. minimal runoff contributions from surface storage water. If these conditions are closely met, a clear-cut distinction between rain (or snowmelt) runoff (to be termed event water) and groundwater (and soil moisture)(to be termed pre-event water) in the runoff hydrograph (event hydrograph) can be achieved.

The main advantages associated with environmental isotopes such as oxygen-18, deuterium, and tritium in mass balance studies for hydrograph separations are that they are conservative (tritium decay is negligible over the period of a runoff event) and they are constituent atoms of water molecules. The isotopes are added to the watershed naturally by the hydrologic cycle.

Their concentrations change only in response to physical processes such as diffusion, dispersion and mixing. Non-conservative tracers, on the other-hand, may be subject to concentration changes resulting from chemical reactions and therefore spatial and temporal variability in groundwater and overland flow (Nakamura, 1971) is common. Even relatively conservative ions such as chloride can be ineffective in basins where road salt applications have been made.

If one considers only two sources of water in the runoff hydrograph, water added by the event (event water), and water which existed in the basin prior to the event (pre-event water), then for a specific time and location, the following two mass balance equations hold true:

$$Q_T = Q_P + Q_E \qquad [1]$$

and

$$Q_T \delta_T = Q_P \delta_T + Q_E \delta_E \qquad [2]$$

where: Q is discharge (L^3/T), δ is the oxygen-18 content ($^O/oo$), and the subscripts T, P, and

E refer to total, pre-event, and event water, respectively. If the stream discharge is known for the stream sampling site and oxygen-18 analyses are made on the groundwater, stream water, and event water, then equations [1] and [2] can be solved:

$$* \; Q_P = Q_T \frac{\delta_T - \delta_E}{\delta_P - \delta_E} \qquad [3]$$

It usually suffices to substitute base flow oxygen-18 for groundwater oxygen-18 (Sklash *et al.*, 1976).

Once the pre-event and event water contributions have been determined, substitution of these values into nitrate and water mass balance equations yield the overland flow (derived from event water) nitrate concentration:

$$N_E = \frac{Q_T N_T - Q_P N_P}{Q_E} \qquad [4]$$

where: N is the nitrate concentration of the components. Again, the groundwater nitrate concentration is approximated from base flow nitrate measurements and this value is assumed to remain constant during the course of a runoff event.

2.2 Hydrometric Technique

The main hydrometric technique applied in this study involves the establishment of groundwater stage-groundwater discharge rating curves for hydrograph separation purposes (Schicht and Walton, 1961; Rasmussen and Andreason, 1959; Visocky, 1970; Stevenson, 1967). Curves relating groundwater stage to stream discharge during baseflow periods (when stream discharge is totally groundwater) are assumed to hold true during high runoff periods. During a runoff event, measurements of groundwater stage sited on

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* Qg is used (rather than Qe) when groundwater is the only pre-event water considered.

the rating curve yield estimates of groundwater discharge. Overland flow is simply the difference between the groundwater and total discharges at any time. The nitrate concentration of the overland flow is then determined as in the isotope mass balance technique.

Generally, average groundwater stages over the entire basin are calculated for the determination of the groundwater stage -groundwater discharge rating curves (Schicht and Walton, 1961; Visocky, 1970; Stevenson, 1967). This is the common practice since observation well networks are rarely designed primarily with this type of rating curve in mind. In the Hillman Creek study, however, two recording groundwater wells were installed near the stream expressly for the purpose of establishing the groundwater stage-groundwater discharge rating curves. The assumptions involved here are that not all areas of the basin are sensitive to runoff events and that the groundwater discharge increases in response to runoff producing events are largely the result of rapid, near-stream, hydraulic head increases.

The observation wells in this study were 9 and 10 cm in diameter while those used in the studies in Illinois by Schicht and Walton (1961) and Visocky (1970) included wells in excess of 90 cm. in diameter. The effect of well storage would be much larger for the Illinois studies than for the Hillman Creek study.

The groundwater stage-groundwater discharge rating curve technique is subject to errors introduced by the heterogeneous nature of groundwater discharge along a stream. Responses may reflect either above or below average groundwater discharge for the sites. The isotope mass balance technique integrates inputs from throughout the basin and therefore should give a better indication of the weighted average response of the entire basin.

2.3 Graphical Technique

This method is included solely for comparative purposes. Many techniques are available, all of which are arbitrary and empirical.

The method chosen is one of the simplest and most commonly practiced. The runoff hydrograph is plotted on semi-logarithmic paper (discharge on the logarithmic axis) and the groundwater component is separated by extending the straight line portion of the recession limb back under the peak discharge (see Linsley *et al.*, 1959). Overland flow is the difference between the total and groundwater discharges. Nitrate concentrations in overland flow are determined as discussed previously.

3. THE STUDY AREAS

Hillman Creek, Upper West Canagagigue Creek, and Upper East Canagagigue Creek in southwestern Ontario were monitored during the spring of 1977. Discharge data for Upper East Canagagigue Creek are limited to several observations on a staff gauge as the stage recorder at the site was not in operation.

Hillman Creek was intensively monitored at the site where it changes direction from predominantly southward to predominantly eastward (Figure 1). Instrumentation at that site consisted of an automatic stream sampling device (North Hants Engineering Mark 4B), water level recording devices for stream stage and groundwater stage (a water table well approximately 3 metres from the stream and a piezometer in the stream open between 0.8 and 0.9 metres below the streambed), several piezometers ranging from 1.5 to 6.0 metres deep and sited from less than 1 to more than 60 metres from the stream, two standard rain gauges, and several rain collectors (for isotope analyses). A recording rain gauge approximately 2 km from this site provided hyetographs for the study area.

The drainage area is approximately 0.7 km^2 and the main stream length to the gauging site is about 1.1 km. Land use is entirely agricultural with livestock density very low to nil. Surface soils are generally sandy and the relief is for the most part low. Tile drainage is practiced but no drains are located upstream of the gauging site.

Upper West Canagagigue Creek was monitored at the federal gauging site (#02GA036). Instrumentation was limited to an automatic stream sampler, a standard rain gauge, and a rain collector. Piezometers near the stream were monitored only in the late portion of the study during which time no appreciable runoff events occurred.

The drainage area served by the gauging station is 18.9 km^2 and the main channel length is approximately 7 km. Land use is primarily dairy farming and the watershed is entirely agricultural. The topography is undulating and surficial material is commonly loam soil. Base flow in the stream ceases in the late spring and flows only intermittently following summer storms. Tile drainage is common through the watershed.

Upper East Canagagigue Creek was monitored where it flows southwesterly beneath Waterloo County Road 21. Instrumentation consisted of an automatic stream sampling device, a standard rain gauge, a rain collector, a staff gauge in the stream, and several piezometers ranging in depth from 1 to 7 metres and located from 2 to 50 metres from the stream.

The drainage area is approximately 9.4 km^2 and the main channel length is about 4.5 km. Land use in the undissected parts of the watershed is mainly dairy farming. The areas adjacent to the stream commonly consist of kame deposits. These sands and gravels have been incised by the stream to a depth of approximately 30 m and are characterized by dense stands of cedar. Unlike the west branch, flow in the east branch is strong even in the summer and the stream does not freeze during the winter. Local farmers have a saying that, 'the west branch carries the name but the east branch carries the water.

4. RESULTS AND DISCUSSION

4.1 General Observations

In this section, the base flow relationships between the groundwater and the surface water systems are examined with reference to baseflow discharge, oxygen-18, conductivity, nitrate characteristics, and the physical hydrogeology of the basins. It is desirable to have at least one full year of oxygen-18, conductivity and nitrate data in order to discuss the baseflow characteristics of basin but due to the time constraints of the study, this information is not available. The results to be presented, therefore, must be reviewed with these time limitations in mind.

Analyses of oxygen-18, conductivity, and nitrate for all samples are given in Appendix A. Data pertinent to individual events are listed in tables in the text.

4.2 Baseflow Characteristics of Hillman Creek

4.2.1 Isotopes and Chemistry

Baseflow oxygen-18 at the gauging site on Hillman Creek fluctuated between -6.3 and -8.4 ^{o}/oo during the interval from April 11 to June 10, 1977. A general trend from lighter to heavier values of δO^{18} from April to June is evident. These variations may be largely a result of changes in the relative contributions of the deep and shallow groundwater.

Spatial variations in oxygen-18 content are also evident. Values of δO^{18} in samples from the weir (approximately 1 km downstream from the gauging site), tended to be lighter than values for the gauging site (to be termed Verbeke's Bridge or VB) by about 1 to 2^{O}/oo. For example, on April 26, 1976, the values at Verbeke's Bridge and the weir were -6.6 and -8.1^{O}/oo, respectively (Cherry *et al.*, 1976). On April 16, 1977, the values were -6.9 and

-8.1°/oo, respectively.

Baseflow conductivity at Verbeke's Bridge was most commonly found to be near 760 µS but frequent deviations to as high as 800 µS and to as low as 450 µS were noted. Conductivity values at the weir site were approximately 100 µS less than at Verbeke's Bridge. The cause of this dilution may be as in the isotopic spatial variations, due to a relative increase in the downstream direction of the locally-derived, shallow groundwater contributions.

Nitrate (NO_3^--N) in baseflow varied both temporally and spatially. Early April (1977) values of nitrate at Verbeke's Bridge fluctuated between 3.5 and 6.5 mg/L and at the weir, between 2.5 and 4.5 mg/L. Baseflow shortly before and after the May 4 storm had between 4 and 6 mg/L nitrate at Verbeke's Bridge but between May 7 and 13, values ranged from 2 to 11 mg/L.

Groundwater samples taken from piezometers located away from the stream maintained a fairly uniform oxygen-18 content while near-stream piezometers showed more temporal and spatial variations (Table 1).

Groundwater nitrate values seemed to increase with distance from the stream. Temporal variations in groundwater nitrate concentrations were significant (Table 2).

4.2.2 Physical Hydrogeology

A rating curve relating stream discharge and stream stage was established for the gauging site at Verbeke's Bridge. Discharge measurements were made with an OTT CI TYPE current meter on a section of natural channel just upstream from Verbeke's Bridge. Units of litres per second are used since discharges are generally low. Stream stage records were obtained with a Stevens Type F Model 68 recorder mounted on a 9 cm diameter slotted steel pipe placed in midstream. The rating curve is based on eight stream discharge measurements (Figure 2a). A quadratic equation was fitted to these points so that other discharges could be extrapolated or interpolated easily.

Groundwater stage-groundwater discharge curves were determined for H44WT8 and GWW. H44WT8 is a 10 cm diameter water table well located approximately 3 metres from the stream bank. GWW is a 9 cm diameter piezometer situated in the streambed itself, open between 8D and 90 cm below the streambed. These wells were equipped with continuous stage recorders. Water levels in the other piezometers were periodically measured with an electric tape and correlated with the prevailing base flow discharge. Quadratic equations were fitted to each of the rating curves, two of which are shown in Figure 2B.

Water levels in the near stream groundwater installations appeared to parallel stream stage fluctuations more closely than the water levels in the distant piezometers.

The recession coefficient for baseflow for Hillman Creek varied between 0.83 and 0.98 during the study period. The larger recession coefficients usually corresponded to low discharges.

The differences in hydraulic head between H44WT8 and the stream and GWW and the stream for baseflow discharge at several times during the study period are listed in Table 3. These differences represent hydraulic gradients of approximately 0.03 and 0.12, respectively, where the former is essentially a horizontal gradient and the latter, a vertical gradient.

4.3 Baseflow Characteristics of Upper West Canagagigue Creek

4.3.1 Isotopes and Chemistry

Baseflow oxygen-18 values for Upper West Canagagigue Creek ranged from -13.5^{O}/oo on March 28, 1977 to -6.3^{O}/oo on June 2, 1977. Bank storage of snowmelt water and residual snowmelt may be in part responsible for the light March values and evaporation and low baseflow discharge could have produced the heavier June values. As in Hillman Creek, baseflow oxygen-18 tended toward heavier values in the late spring.

Conductivity generally increased with time during the study period. Conductivities ranging from 400 to 550 µS were observed in April while May and June values were within 500 to 600 µS. The progressively higher conductivities correspond well with the oxygen-18 trend.

Baseflow nitrate exhibited a trend toward lower values with time. In late March, baseflow nitrate was approximately 4.0 mg/L while in April, it was about 1.5 mg/L. Baseflow nitrate values changed fairly slowly allowing reasonable estimates of average baseflow nitrate to be made.

4.3.2 Physical Hydrogeology

Groundwater stage-groundwater discharge curves were not obtained for this basin. The recession coefficient ranged from between 0.85 and 0.96. The creek remained frozen until mid-March and flow virtually ceased in mid-May. Units of cubic metres per second are used for discharge.

4.4 Baseflow Characteristics of Upper East Canagagigue Creek

4.4.1 Isotopes and Chemistry

Baseflow oxygen-18 maintained a fairly consistent level of about -11.2°/oo throughout the study period. The uniformity of the baseflow oxygen-18 value seems reasonable in light of the strong baseflow characteristics of the stream, namely its regular summer discharge and its ability to remain unfrozen all winter long.

The conductivity of the stream, approximately 550 µS, also remained quite constant during the study period. This is also characteristic of a baseflow dominant stream. Nitrate concentrations also were relatively uniform in time. Baseflow samples taken from February to March had approximately 2.7 mg/L NO_3--N.

4.4.2 Physical Hydrogeology

Groundwater stage-groundwater discharge rating curves were established for several piezometers using manual measurements of both groundwater and stream stage.

Descending springs were observed at several locations along the creek. The strongly effluent nature of the stream is manifested in its ability to remain unfrozen all winter long and its strong, summer baseflow discharge.

Cubic metres per second are the discharge units used for the East Canagagigue Creek study.

4.5 Runoff Events on Hillman Creek

Full instrumentation for the Hillman Creek watershed was not achieved until April 11, 1977. Field work was terminated on June 11, 1977. During this interval, three notable storms, including two storms of sufficient magnitude to induce overland flow, occurred. Event monitoring was less complete than desired due to the long distance to the research area (approximately 300 km), however, several significant observations were made.

Prior to full instrumentation, snowmelt and storm runoff events were sampled on a reconnaissance basis only. These results will be discussed briefly.

4.5.1 Snowmelt Event - February 22, 1977

During the first visit to the area for the runoff study, above-freezing temperatures instigated a snowmelt runoff event. The stream valley itself was filled with compacted snow and a shovel was needed to reach open water. No discharge records are available for the day as sub-zero (ºC) temperatures at night caused the stilling well to freeze. H44WT8 was activated and the resulting hydrograph is shown in Figure 3. The ground was frozen at this time.

While considerable variability in the oxygen-18 contents of snow samples was noted (-7.5 to -24.9°/oo), overland flow samples from two locations (at Verbeke's Bridge and near the weir) exhibited similar oxygen-18 values (-15.2 and -15.5°/oo, respectively). Groundwater samples taken that day had oxygen-18 values similar to those taken during the previous two years. Two stream samples were taken at the weir and two at Verbeke's Bridge (Table 4).

The 11:15 sample at the weir (-8.8%) is assumed to be baseflow oxygen-18 as snowmelt at the time did not seem to be quantitatively significant. A value approximately 1.2 $^{\circ}$/oo heavier is assumed to be the baseflow oxygen-18 for Verbeke's Bridge as this site is generally heavier by about that amount.

On the basis of these assumed isotopic values for baseflow, the percentages of groundwater in snowmelt runoff were calculated (Table 5). Groundwater apparently made a large contribution to this snowmelt runoff event.

Widespread overland flow was observed in the basin but this was not unexpected in view of the fact that the surface materials were generally still frozen and infiltration capacity was therefore probably low. The hydrograph of H44WT8 (Figure 3) indicates that at least the near-stream groundwater responded rapidly to the snowmelt episodes. Water levels in more distant piezometers apparently showed a much slower response to the snowmelt (Table 6). Groundwater seepage through the streambed, monitored by means of a seepage meter, indicated a significant upward gradient through the streambed at Verbeke's Bridge (Lee, personal communication).

4.5.2 Rain Event - March 4, 1977

Approximately 7 mm. of rain fell on the basin on March 4. The soil was still frozen and scattered patches of snow were common throughout the basin.

Overland flow was observed at the same sites as noted on February 22. Nitrate values in the stream at a site midway between Verbeke's Bridge and the weir (noted as weir 2, see Figure 1) increased during the storm (Table 7). Insufficient isotope data precludes any hydrograph separation attempts.

4.5.3 Rain Events on April 2 and April 4, 1977

These two events are treated together since the second closely followed the first. Rain events on April 2 (19 mm) and April 4 (6 mm) caused two distinct runoff events at the Verbeke Bridge gauging site (Figure 4). The hydrograph in Figure 4 was obtained from the recording rain gauge located approximately 2 km. east of the gauging site.

Ground frost was no longer present in the basin when the events occurred, however, the basin was quite wet from an accumulation of 28 mm. of rain in the previous week. The steep stream recession prior to April 2, even though no rain had fallen in the previous three days, is indicative of the wet basin conditions. The diurnal regularity of the groundwater and stream hydrographs prior to these events suggest that evapotranspiration at this time was insignificant.

Isotopic and chemical data for these storms are unavailable as the necessary equipment had not yet been installed. A number of general observations can be made regarding the physical interactions of the groundwater-stream system in response to the rainfall events:

1. Significant and distinct hydrographs were recorded for both the stream and the near-stream groundwater (Figure 4).
2. Hydraulic heads in the groundwater system remained above stream level even at peak discharge (Figure 4).
3. Groundwater levels near the stream responded quickly to the rain events (Figure 4).
4. Groundwater near the stream was more sensitive to the second storm than the first even though the second storm was 66% smaller. The rising limb slope is steeper for April 4 even though rainfall intensity was lower and the rise-to-rain ratio for GWW was greater on April 4 than on April 2 (7:1 and 2.1:1, respectively).
5. The hydraulic gradients between H44WT8 and the stream and GWW and the stream decreased only slightly at peak stream discharge and increased shortly thereafter (Figure 4).

6. Successively higher groundwater stages at GWW resulted from the two storms (Figure 4).
7. The hydraulic gradient between GWW and the stream was greater at peak discharge on April 4 than it was at baseflow on April 1 (Figure 4).

Hydrograph separations by use of the groundwater stage-groundwater discharge rating curve method for the April 2 and 4 storms yield 41 and 91% groundwater, respectively, in the excess runoff (Figure 5). Excess runoff is that discharge in excess of the runoff expected in the absence of a runoff producing event. These separations correspond to 63 and 88% groundwater at peak discharge for April 2 and 4, respectively, where these percentages are percentages of the total stream discharge at the time.

Using the graphical technique of hydrograph separation, groundwater was found to constitute 63 and 61% of the peak discharges on April 2 and 4, respectively (Figure 5).

Approximately 20.9 X 10^3 m^3 of rain fell on the basin on April 2 producing 962 m^3 of excess flow, a storm yield of 5%. The volume of rain in the excess runoff as calculated by the groundwater stage-groundwater discharge rating curve method was 674 m^3. This runoff could have been supplied by an area along the stream 51 m wide if that area had a storm yield of 100%.

On April 4, 6.6 X 10^3 m^3 of rain resulted in 980 m^3 of excess flow or a 15% yield. Only 90 m^3 of excess flow are attributed to the rain and this could have been supplied by a 21.4 m strip along the stream.

4.5.4 Rain Event - April 22 to April 26, 1977

Significant rainfalls of 38, 35, and 31 mm occurring on April 22, 23, and 25, respectively, produced dramatic responses in both the stream discharge and groundwater stages. These events were the first to be monitored with full instrumentation, however, isotopic and chemical data are available for April 25 only due to sampling difficulties.

No rain had fallen on the basin in the week prior to April 22 and on the basis of the stream hydrograph, it can safely be assumed that the base flow conditions prevailed prior to the storms. The stream and groundwater hydrographs also denote the insignificance of evapotranspiration at the time.

Two major runoff peaks were observed, the first occurred on April 23 and the second on April 25. The stream recorder faltered on the first peak and although H44WT8 failed prior to the first peak, its peak stage was recorded.

A number of general observations can be made regarding the physical response of the system:

1. Significant and distinct hydrographs were recorded for both the stream and the groundwater (Figure 6).
2. The hydraulic head in the groundwater system remained above the stream stage even at peak discharge (Figure 6); that is, the stream remained effluent.
3. Groundwater near the stream responded quickly to the rain events (Figure 6). Groundwater responsivness apparently decreased away from the stream (Table 8).

4. The hydraulic gradient between GWW and the stream was greater at the second peak (10.8 cm/L*) than at baseflow (8.6 cm/L). The hydraulic gradient at the first peak was 30% lower than at baseflow (Figure 6).
5. Significant amounts of overland flow were observed emanating from a low area on Roger Verbeke's property upstream from Verbeke's Bridge. Overland flow in other areas was common but not nearly as abundant.
6. The second groundwater peak (on April 25) occurred about 6 hours after the second discharge peak (Figure 6).

The April 25 portion of the rain was isotopically ideal for hydrograph separation. Figure 7 is a plot of the temporal and spatial variations of oxygen-18 and conductivity in the rain and overland flow. The temporal variations in stream oxygen-18, conductivity and nitrate are listed in Table 9.

Some general observations regarding the isotopic and chemical response of the watershed can be made:

1. The oxygen-18 content of the rain on April 25 ranged between -16.5 and $-20.0^{\circ}/oo$ with a weighted average value of $-18.1^{\circ}/oo$ (Figure 7). Since baseflow oxygen-18 prior to April 22 was $-6.9^{\circ}/oo$, the groundwater component could be estimated to within ±5%.
2. The rain conductivity was relatively low (less than 100 µS) (Table 9), whereas baseflow conductivity prior to April 22 was about 750 µS.

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* L is the horizontal or vertical distance between the well screen and the streambed.

3. Overland flow from north of Verbeke's Bridge and from Whittle's property had oxygen-18 and conductivity values similar to the rain values. A major source of overland flow just upstream from Verbeke's Bridge had oxygen-18 and conductivity values indicative of large groundwater contributions (Figure 7 and Table 9).
4. Nitrate values in the stream were similar to those in overland flow from just upstream of Verbeke's Bridge (Table 9).

The hydrograph separations based on groundwater stage-groundwater discharge rating curves and the oxygen-18 method give similar results (Figure 8) with both methods indicating large groundwater contributions. For the local discharge peak at 14:30 April 25, total stream discharge was 81 L/s. The estimated groundwater contributions were 66 and 67 L/s for the groundwater stage-groundwater discharge rating curve and oxygen-18 techniques, respectively. The graphical technique estimated 32 L/s groundwater (Figure 8). As percentages of total discharge, these are 81, 83, and 40%, respectively.

Using the mass balance equations for oxygen-18 [3] and assuming $\delta g = -9.0^{0}/oo$ for the shallow groundwater, approximately 70% of the overland flow emanating from the low area just upstream from Verbeke's Bridge was groundwater. Estimating the conductivity of the rain-overland flow component as 100 µS (reasonable in light of the observed values for overland flow on Whittle's and Verbeke's property north of the creek) and the groundwater as 750 µS (the same as baseflow), mass balance equations for conductivity also suggest 70% groundwater in the overland flow emanating from the area upstream of Verbeke's Bridge.

In order to compute the growth of the groundwater discharge area in response to a storm, one can invoke Darcy's law:

$$Q_1 = K_1 I_1 A_1 \qquad [4]$$

where: Q_1 is baseflow discharge in the stream, K_1 is hydraulic conductivity, I_1 us the hydraulic gradient and A_1 is the area of groundwater discharge (either directly into the streambed or through the seepage face above the stream). At high flows caused by a runoff producing event,

$$Q_2 = K_2 I_2 A_2 \qquad [5]$$

where: Q_2 is the groundwater component of the stream discharge, K_2 is the hydraulic conductivity (assume $K_1 = K_2$), I_2 is the hydraulic gradient, and A_2 is the area of groundwater discharge (including direct seepage into the streambed, the seepage face, and areas away from the stream discharging groundwater which is then delivered to the stream as surface runoff).

Since: $I = \Delta H / \Delta L$ [6]

where: ΔH is the hydraulic head difference and ΔL the distance between the two points of head measurement and since ΔL is a constant for two points, equation [4] divided by [5] reduces to:

$$A_2 = A_1 \frac{\Delta H_1}{\Delta H_2} \frac{Q_2}{Q_1} \qquad [7]$$

Q_2 can be determined by the isotopic mass balance technique and ΔH_1 and ΔH_2 are the differences between the groundwater stage at a point in the saturated zone and the stream stage at baseflow at the chosen time, respectively.

At baseflow prior to the April 22 storm, ΔH_1 was 8.6 cm for GWW and 7.0 cm for H44WT8. Q_1 was 6.4 L/s. At the local discharge peak which occurred at 14:30 April 25,

ΔH_2 was 10.7 cm for GWW and 12.3 cm for H44WT8. On the basis of the isotope separation, Q_2 was 67 L/s. Therefore:

$$A_2 = A_1 \frac{8.6}{10.7}\,\frac{67}{6.4} \sim 8 \quad A_1 \text{ for GWW} \qquad [8]$$

$$A_2 = A_1 \frac{7.0}{12.3}\,\frac{67}{6.4} \sim 6 \quad A_1 \text{ for H44WT8} \qquad [9]$$

Therefore, in order to account for the large groundwater component in the storm runoff, on April 25, one must assume that the area of groundwater discharge expanded to between 6 and 8 times the baseflow discharge area and that the hydraulic gradient near the stream increased by 24% to 76% of the baseflow gradient.

Computation of the nitrate flux in the stream due to the event water is complicated by the fact that several stated or implied assumptions are not valid for this event. The foremost problem is the variability of the groundwater nitrate inputs. Where baseflow nitrate in the stream could be characterized by 3 to 6 mg/L, the overland flow emanating from just upstream from Verbeke's Bridge had nitrate contents of about 8 mg/L.

This water was observed to be a quantitatively significant contributor to the storm flow and was isotopically determined to be approximately 70% groundwater. In view of the lesser nitrate concentrations in overland flow from other areas (3 to 6 mg/L, the high nitrate in the tile drain sample (63 mg/L), and the high storm flow nitrate in the stream (6 to 9 mg/L, the following scenario is suggested.

Storm runoff contributions on April 25 consisted primarily of groundwater discharged as variable source area-overland flow and groundwater discharge through/and just above the stream channel. The former source of groundwater attained high nitrate concentrations by flushing out nitrates from the shallow soil zone :rate contents. The latter source of groundwater maintained its lower nitrate content as the near-stream areas are generally not fertilized.

The rest of the overland flow was generated as partial area-and flow and was mostly of event water origin. Having a less intimate contact with the shallow subsurface soil zones, and a lower initial Concentration of nitrate, its nitrate content remained fairly low. The contribution of partial area-overland flow was observed to be quantitatively much smaller than the variable area-overland flow generated by the groundwater. The tile drain sample showed that extremely high nitrate concentrations exist in the shallow subsurface suggesting that the variable area-overland flow could have conceivably been much higher in nitrate content had it not been diluted by the rainwater.

As a result of the large variable area-overland flow groundwater contributes the stream attained high nitrate contributions during storm runoff.

Because the relative proportions of groundwater from the variable area-overland flow and from the near-stream area are not known, one cannot employ the isotope technique to quantify the nitrate concentration in the event water. The isotope technique, however, has added valuable insight into the mechanism of nitrate contributions to the stream for this runoff event.

4.5.5 Rain Event - May 4, 1977

On May 4, 1977, 17 mm of rain fell on the basin producing a distinct yet rounded runoff hydrograph.

The recession coefficient for May 3, 0.74, indicates that stream was still falling fairly rapidly and possibly was not quite baseflow discharge. Evapotranspiration, although still insignificant, had begun.

Isotopic and chemical data are available for this storm. A number of general observations pertaining to the physical response of the watershed can be made.

1. Distinct groundwater and stream hydrographs were recorded (Figure 9).
2. The hydraulic head in the groundwater system remained well above stream stage even at peak discharge (Figure 9).
3. Groundwater near the stream responded quickly to the event (Figure 9).
4. The hydraulic gradient between GWW and the stream decreased from 12.3 cm/L at baseflow to 11.5 cm/L at peak discharge, a change of 7%.
5. No overland flow was observed.
6. The hydrographs for GWW and the stream peaked almost simultaneously.

The oxygen-18 value of the rain was suitable for isotope mass balance separation of the stream hydrograph. Baseflow prior to the storm was -7.7^{o}/oo δO^{18} while the weighted average rain value was -5.4 ^{o}/oo. At peak discharge, the groundwater could be determined to within ±13%.

A number of general observations can be made regarding the isotopic and chemical behaviour of the system in response to the storm.

1. The baseflow oxygen-18 and conductivity values were slightly diluted by the rain event (Figure 9).
2. Peak dilution of oxygen-18 and conductivity preceded peak discharge by approximately four hours (Figure 9).
3. Nitrate concentrations in the stream fluctuated erratically however there seems to be a dilution trend coincident with the oxygen-18 and conductivity dilutions (Figure 9).

The hydrograph separations by all three methods give large groundwater components of peak and total discharge (Figure 10). At peak discharge, groundwater contributed 91% of the water (isotope technique) to 82% (graphical) and 80% (rating curve-GWW).

The total rain on the basin, 19 X 10^3 m^3, produced 2300 m^3 of excess runoff, a storm yield of 12%.The required width of a strip of land which would totally convert the event component to runoff would be from 20 (for the isotope method) to 45 metres (for the rating curve).

Based on the variations in hydraulic gradient between GWW and the stream and applying equation [7], the area discharging groundwater at peak discharge was 3 times larger than the area discharging groundwater before the storm.

The fluctuations in nitrate concentrations of the stream prior to, during, and after the storm make it difficult to estimate an average baseflow nitrate value. Therefore the calculation of the nitrate concentration in the event component is also difficult.

It is suggested that overland flow due to the event water was insignificant. This theory is based on several observations, namely: there was no observed overland flow; the oxygen-18 value of the stream was diluted only slightly; oxygen-18 and conductivity dilutions in the stream preceded peak discharge indicating that channel precipitation probably caused the dilution; and a plot of oxygen-18 versus conductivity for the stream (Figure 11) indicates a simple two component (rain and groundwater baseflow) mixing.

In summary, storm runoff on May 4 was generated mainly by channel precipitation and near-stream groundwater discharge directly into the channel bed or just above it (through a seepage face). Nitrate contributions to the stream were made only by these components (about 6.5 mg/L, by the groundwater and 0.5 mg/L by the channel precipitation) yielding stream nitrate values which fluctuated between 4 and 7 mg/L.

4.5.6 Rain Event on June 6, 1977

In the early morning hours of June 6, 1977, approximately 38 mm of rain fell on the basin in less than two hours. The basin was quite dry prior to the storm and baseflow conditions prevailed. Evapotranspiration effects along the stream bank were quite significant at the time.

Very prominent hydrographs were produced by the storm at GWW, H44WT8, and in the stream. Double peaks are present in each of the hydrographs. Conductivity isotope and nitrate data are available only for the time following the second peak.

A number of general observations can be made regarding the physical response of the system.

1. Significant and distinct hydrographs were recorded for the stream and groundwater (Figure 12)
2. A reversal of hydraulic gradient occurred briefly (about 15 minutes duration) causing the stream to become influent for the only time during the entire study period (Figure 12).
3. The near-stream groundwater system responded quickly to the storm (Figure 12).
4. Significant overland flow was observed emanating from the low area on Roger Verbeke's farm. Other traditional overland flow sources were also noted to be productive.
5. The second peak in the hydrograph was smaller than the first for the stream and

H44WT8 but larger than the first at GWW.

The storm was a poor one for the application of the oxygen-18 $_{o}$18 hydrograph separation technique. Baseflow prior to the storm was -6.8^{O}/oo δO^{18} and the rain had a value of -7.8^{O}/oo. These values yield groundwater values accurate to ±15%. Some general observations of the isotopic and chemical response of the watershed can be made.

1. At high discharges, the oxygen-18 value of the stream approached the rain value and conductivity was reduced significantly from baseflow (~ 50%). Oxygen-18 and conductivity rapidly changed toward the baseflow values at first but just before reaching them, the rate of change slowed considerably. Nitrate in the stream apparently had concentrations similar to the overland flow at peak discharge (4 to 5 mg/L) but concentrations of 0.00 mg/L were reached before climbing to 10 mg/L as the discharge subsided (Figure 13).
2. The overland flow from the low area on Verbeke's property had rain-like oxygen-18 (-7.8^{O}/oo) and a conductivity (238 µS) closer to the rain (<100 µS) than to the groundwater (>600 µS). The nitrate concentrations of this overland flow (4.5 mg/L) was similar to that of the local peak discharge (4.2 mg/L).
3. The groundwater discharge into the streambed remained fairly constant. Piezometers A and B (open 1.30 m and 2.00 m below the streambed) changed from -8.3 and -8.8^{O}/oo on June 1 to -8.1 and -8.2^{O}/oo on June 11.

Groundwater contributions to the first runoff peak were small. The groundwater stage-groundwater discharge rating curve method yielded 29% (for GWW) to 4% groundwater (for H44WT8) in peak discharge. For the second peak, groundwater contributed 58, 33, 20 and 7% to peak discharge for the rating curve (GWW and H44WT8), isotope, and graphical techniques, respectively (Figure 14).

The reversal in hydraulic gradient and the breaks in the stream conductivity trends

(Figure 13) suggest that bank storage occurred during the event.

Figure 15 is a plot of oxygen-18 versus conductivity in the stream from the second discharge peak to baseflow discharge. Three distinct phases in the plot can be recognized. These phases are also apparent in Figure 13. Phase I is characterized by a rapid change from peak flow conductivity toward baseflow conductivity while oxygen-18 in the stream remained at the peak flow value. Hydraulic gradients between GWW and the stream and H44TW8 and the stream were less than the baseflow hydraulic gradients. Phase II involves a less rapid trend toward baseflow conductivity until baseflow conductivity is reached as oxygen-18 in the stream slowly approaches its baseflow value. The hydraulic gradients near the stream are greater than or equal to the baseflow gradients during this phase. In Phase III, conductivity and oxygen-18 have stabilized at their baseflow values and baseflow discharge levels are restored.

Plots relating the stream conductivity to discharge and stream oxygen-18 discharge for the recession portion of the storm hydrograph are given in Figure 16 (the conductivity curve seems smoother than the oxygen-18 because of the smoother curve it gives in Figure 13). These plots are similar to the technique found in Nakamura (1971) to separate storm hydrographs into their components.

According to Nakamura, discharge in Phase I of Figure 16 would be due to water from overland flow, channel precipitation, interflow, and groundwater. Interflow in the Hillman Creek basin is probably negligible due to the high permeabilities and low gradients in the basin. Bank storage, however, probably contributed to Phase I as the stream was influent just a short time before. The peak discharge-type oxygen-18 during Phase I is also indicative of bank storage. Phase II then, is probably due to bank storage and groundwater and Phase III is due only to groundwater.

While the gentle slopes and high hydraulic conductivities in the watershed preclude significant amounts of interflow, the reversal of hydraulic gradients and slow return to baseflow oxygen-18 and conductivity imply that bank storage occurred. The water in bank storage would be similar to peak discharge in oxygen-18 but may obtain a higher conductivity due to a longer and more intimate contact with the subsurface. These characteristics could account for the slow progression toward baseflow oxygen-18 and conductivity.

The nitrate history of the stream runoff also suggests that bank storage occurred. The first nitrate analysis in Figure 13 is representative of the peak discharge for the second peak. It is similar to the overland flow sample taken at the same time. As the stage subsided, bank stored water from the first peak stage discharged. It is assumed that this water was also low in nitrate and this is reflected in the very low nitrate concentration in the stream. As the stream became more effluent and groundwater again dominated the hydrograph, high nitrate values (10 mg/L) appeared in the stream. These high nitrate values in the stream suggest that not only near-stream groundwater, but also (some high nitrate) variable area-overland flow discharged groundwater, were contributing to the stream.

Approximately 2.7 X 10^4 m^3 of rain fell on the basin producing 2.6 X 10^2 m^3 of excess runoff, a storm yield of 1%. Based on the hydrograph separations using the groundwater stage-groundwater discharge rating curve for GWW; an area the length of the stream and 3 m wide could have produced the calculated overland flow if the storm yield for the strip was 100%.

In summary, the June 6 storm runoff water was comprised largely of event water in the first peak and about equal amounts of pre-event and event water in the second peak. The high intensity, short duration storm initially induced partial-area overland flow from the Verbeke farm low area rather than producing variable-area overland flow. The dry pre-storm conditions probably contributed to this type of response.

Although the near-stream groundwater response was both rapid and large, the stream stage momentarily exceeded the groundwater stage and bank storage occurred. The reversed gradients persisted only for a short time, after which the stream again became effluent. The water stored as bank storage influenced the isotopic and chemical nature of the stream as it returned of baseflow. High nitrate concentrations in the stream occurred only after groundwater re-established itself as the major component of stream discharge.

4.6 Runoff Events on Upper East and Upper West Canagagigue Creeks

Only a few favourable events were monitored for Upper East and Upper West Canagagigue Creeks during the spring of 1977. Several factors contributed to this situation. March, April, and May were fairly dry months with few storms (52 mm rain in April, 69 mm in March compared to 135 and 76 mm at Hillman Creek). Of the storms which did occur, most were of low intensity and long duration, two characteristics which rendered the isotope technique difficult to use. Discharge data on the east branch is questionable as the recorder was inoperable leaving only isolated staff gauge measurements for discharge.

The widespread practice of tile drainage in the Canagagigue Creek watersheds introduces possible errors into the nitrate flux calculations during high runoff periods. The tile drains, which could conceivably carry large volumes of high nitrate shallow groundwater during periods of high runoff, would probably carry much less, if any, of the high nitrate discharge during low flow periods. Some of the assumptions made previously; that baseflow nitrate can be used to approximate the nitrate content of discharging groundwater and that this level of nitrate concentration remains constant throughout a runoff event, could easily become invalid in these basins.

As a result of these problems, the calculated nitrate fluxes for the Upper East and Upper West Canagagigue Creeks are somewhat less clear-cut than the presented results would indicate.

4.6.1 Snowmelt Runoff on Upper East Canagagigue Creek - March 7

Between March 7 and March 11, the Upper East Canagagigue Creek basin lost the majority of its snow cover by melting. The creek remained open and running throughout this period. Considerable quantities of overland flow, especially along roadsides and in unforested areas, were observed. As the surface soils were still frozen and infiltration capacity limited, overland flow was not unexpected.

Stream discharge data for the event was limited by a non-functioning stage recorded to a number of staff gauge measurements. Low temperatures on March 7 produced little snowmelt. Oxygen-18 in the stream was characteristic of baseflow conditions (-10.8 to -11.2 ^{O}/oo).

Nitrate concentrations were also indicative of baseflow discharge (1.5 to 2.6 mg/9, NO_3^--N) (Table 10). Discharge at 10:30 March 7 was approximately 0.12 m^3/s.

Snow and snowmelt samples were collected daily from March 8 to March 10 from the sampling sites shown in Figure 17. Snowmelt samples consistently had heavier δO^{18}

values than the nearby snow (Table 11). This finding prompted the choice of the snowmelt oxygen-18 value for the isotope hydrograph separations rather than snow values.

On March 8, the snow oxygen-18 ranged between -23.6 and -16.1^{O}/oo while the snowmelt ranged between -11.7 and -14.7^{O}/oo. The stream samples had oxygen-18 values near the baseflow mark (-11.1^{O}/oo to -11.3^{O}/oo). Nitrate in the stream increased from 1.8 mg/L at 00:45 to 3.1 mg/L at 16:45 then decreased to 2.5 mg/L by 22:45. Snowmelt runoff was observed to be restricted to roadsides.

On March 9, warm temperatures and sunny skies coupled to produce considerable melting. Stream discharge increased from 0.15 m^{3}/s at 12:00 to at least 0.30 m^{3}/s and possibly to as high as 0.6 m^{3}/s at 20:00. The stream hydrograph shown in Figure 18 is composed of both observed and estimated discharges. The sediment load in the stream visibly grew with the higher discharges.

Snow samples collected on March 9 had oxygen-18 contents ranging from -20.2 to -15.2^{O}/oo while the snowmelt samples had -16.5 to -13.4^{O}/oo oxygen-18. Snowmelt was often seen re-entering the snowpack. The stream oxygen-18 tended to approach the snowmelt value with the peak value of -12.8^{O}/oo occurring at 17:20 (Table 10). The nitrate content of the stream increased from 2.2 to 3.3 mg/L during the day.

On March 10, continued warm temperatures and sunny skies resulted in the production of considerable amounts of snowmelt and overland flow throughout the basin. One area near the stream gauge was especially prolific. Stream discharge increased from 0.47 m^{3}/s at 08:55 to more than 2.4 m^{3}/s at 20:05.

Snow samples taken during the day had oxygen-18 values of -19.2 to -17.5^{O}/oo and conductivities from 47 to 255 µS. Overland flow samples from the gauge area had oxygen-18 contents of -14.9^{O}/oo to -11.9^{O}/oo and conductivities ranging from 240 to 907. Nitrate analyses on three of the snowmelt samples yielded values of 4.1, 4.4, and 8.8 mg/L NO_3^--N.

The stream oxygen-18 content shifted toward the snowmelt value. At 01:20, the stream had -12.3^{O}/oo δO^{18} (discharge of approximately 0.5 m^3/s) but at 21:50, a value of -14.0^{O}/oo, the average snowmelt value on March 10, was found in the stream (discharge of approximately 2.4 m^3/s. During this time, conductivity decreased by 26% from 555 µS to 412 µS and nitrate increased by 100% from 2.9 to 5.9 mg/L.

Overland flow essentially stopped by 19:00 as the air temperatures decreased and darkness approached. Stream samples taken at 08:00 and 09:00 on March 11 had oxygen-18 values of -14.1 and -13.8^{O}/oo, respectively, a conductivity of about 468 µS, and approximately 6.1 mg/L NO_3^- -N. Stream discharge was about 1 m^3/s. Overland flow was not evident at the time.

The temporal variations in the stream oxygen-18 conductivity, nitrate, and stream discharge are given in Figure 18. These and other relevant analyses are listed in Tables 10 and 11. Trends toward the snowmelt oxygen-18, lower conductivities, and higher nitrate values in the stream are associated with higher discharges. The hydrograph separation of the snowmelt runoff event using -14.0 ^{O}/oo δO^{18} for the event component (snowmelt) and -11.2^{O}/oo δO^{18} for the pre-event component (baseflow/groundwater) is illustrated in Figure 18. Peak discharge on March 10 had a negligible groundwater component but groundwater was dominant in the runoff on March 7, 8 and 9.

The temporal variations in average nitrate and average conductivity of the event component (snowmelt) as calculated by equation [4] are plotted in Figure 19. The observed values of nitrate and conductivity in the overland flow near the stream are plotted on the same diagram for comparative purposes. A reasonable correlation can be seen for points 1, 2, and 3 for conductivity. Point 4 indicates the correct trend was calculated but it shows that the actual snowmelt conductivity at the site was 60 µS less than the calculated average snowmelt over the basin. The calculated nitrate contents for the snowmelt over the basin are also plotted in Figure 19. Points 6 and 7 are two observed values of nitrate for the overland flow near the gauge. These values are about 2.4 mg/L less than the calculated values (6.6 versus 4.2 mg/L). Another overland flow site near the stream is represented by point 5 for both conductivity and nitrate. At this site, the conductivity was 120 µS less than the calculated basin average and the nitrate was 2.2 mg/L greater than the calculated basin average.

The reasonable correlations between the observed and calculated values for conductivity and nitrate indicates that the method gives credible results, while at the same time the variations between the two sets of observed results and the calculated values provide evidence of the heterogeneity of the runoff process in a watershed.

The nitrate export from the basin was determined for the period between 01:00 March 10 and 08:00 March 11 (Figure 20). Both the total nitrate flux and the nitrate flux due to the event component are given. The total and event water nitrate fluxes were calculated from the following equations:

$$\text{TOTAL NITRATE FLUX} = \int_{t_1}^{t_2} Q_t \, N_t \, dt \qquad [10]$$

$$\begin{array}{l}\text{EVENT WATER}\\ \text{NITRATE FLUX}\end{array} = \int_{t_1}^{t_2} Q_e \, N_e \, dt \qquad [11]$$

where: Q_t, N_t, Q_e, N_e are as defined previously, t_1 and t_2 are the beginning and end of the study period, respectively; $\int$ is the integration symbol, and dt is the derivative of time (Table 12).

Approximately 780 kg. of NO_3^- -N were discharged past the gauging station in the period between 01:00 March 10 and 08:00 March 11. Of this flux, 88% or about 690 kg, were provided by the event water discharge. The peak nitrate flux rate of about 14 gm/s occurred at approximately 21:00 March 10. In contrast, baseflow nitrate flux is about 3 gm/s.

Figure 21 demonstrates the relationships between oxygen-18 conductivity, and nitrate in the stream with stream stage. Oxygen-18 approached the snowmelt value of -14.0^{O}/oo, conductivity decreased markedly, and nitrate concentrations almost doubled as the stream stage increased. When the stream stage began to subside, however, oxygen-18 and nitrate (and to a lesser extent, conductivity) remained at the peak stage values. One explanation for the temporary stabilization of oxygen-18 and nitrate at the peak stage values could be that the high stream stage induced bank storage and the water stored in the bank discharged only after the stream stage began to subside. The water would have oxygen-18, conductivity, and nitrate contents characteristic of the peak stage water. The conductivity variation may not be as large as it seems if the 5% error associated with its measurement is considered.

In summary, the snowmelt runoff event between March 7 and 11 consisted mostly of groundwater until March 10. On March 10, abundant snowmelt throughout the basin created extremely high stream stages which forced the stream to become influent. High nitrate concentrations in the event water discharge largely contributed to higher nitrate concentrations in the stream and the release of bank storage water subsequent to peak discharge helped to prolong the high nitrate discharge in the stream.

4.6.2 Rain Event on Upper East and Upper West Canagagigue Creeks, March 28-29, 1977

The only storm on Canagagigue Creek that was quite suitable for isotopic study and which produced good runoff hydrographs on both branches occurred on March 28 and 29. Approximately 12 mm of rain fell on the basins which were still quite wet from the spring snowmelt. Scattered patches of snow persisted in some shaded areas of the basin but these had an effect on runoff only in the late afternoon. The basin no longer contained frozen soils. Although significant runoff hydrographs were recorded for both branches, overland flow from the rain was not observed.

Both the east and west branches were essentially at baseflow prior to the storm however small daily snowmelt peaks were still occurring in the late afternoons. Baseflow oxygen-18 was -12.4^{O}/oo on the east branch and -13.5^{O}/oo on the west branch. The influence of the daily snowmelt and/or bank storage can be seen in the East Canagagigue Creek baseflow oxygen-18 (Figure 22) which is normally about -11.2^{O}/oo.

The rain was sampled at both stream gauge sites at two times. The weighted average oxygen-18 value of the rain was -5.1^{O} /oo. The piezometer nests near the gauging station on the east branch were monitored during the event. The locations of the piezometer nests are given in Figure 17 (site P).

Discharge in the streams in response to the storm increased from 0.4 to 2.3 m^3/s for the west branch and from less than 0.2 to at least 1.0 m^3/s for the east branch. Double peaks in both of the discharge hydrographs are probably in response to the time distribution of the precipitation (Figures 22 and 23). The third discharge peak in Figure 23 is most likely the result of the daily snowmelt peak for March 29. Because of the complexities which arise when dealing with two event components (snowmelt and rain), analyses of the hydrograph and water samples are restricted to the time before the third peak.

The temporal variations in oxygen-18, nitrate, and conductivity in response to the storm are given in Figures 22 (east branch) and 23 (west branch). Nitrate concentration increased by 68% in the east branch and by 83% in the west branch. Conductivity decreased by 8% in the east branch and by 21% in the west branch. Oxygen-18 was diluted by 4% in the east branch and by 11% in the west branch.

The weighted average rain oxygen-18 value of $-5.1^{o}/oo$ would yield groundwater component accuracies of approximately ±5 and ±6% for the west and east branches, respectively.

Table 13 lists the measured responses of the near-stream groundwater near the East Canagagigue gauge during the storm event. All of the piezometers indicated that the stream remained effluent throughout the event (the stream staff gauge is located approximately 50 metres upstream from the piezometers, therefore the hydraulic heads which would be deduced from Table 13 are somewhat higher than the actual heads). Both the near and distant piezometers had similar responses. As all the nests are located on the flat valley bottom near the Creek, similar responses were not unexpected.

The hydrograph separations for the streams are given in Figures 22 (east) and 23 (west).Separations were made using only the individual rain sample values of oxygen-18. In all cases, groundwater was the dominant runoff component. Using a standard graphical technique for the west branch hydrograph (Figure 24), the first and second peaks of the hydrograph consisted of 65 and 65% pre-event water, respectively. The isotope technique with the individual rain values resulted in 88 and 86% pre-event water in these peaks.

The nitrate flux hydrographs for the streams are given in Figures 25 (east) and 26 (west). Between 11:00 March 28 and 12:00 March 29, approximately 860 kg. of NO_3^--N were exported from the West Canagagigue basin. About 38% of this amount, or 324 kg., was provided by the event water discharge. Nitrate concentrations of up to 28 mg/L would be required in the event water discharge in order to account for this flux (Table 14).

Between 10:10 March 28 and 08:30 March 29, approximately 356 kg. of NO_3^--N were discharged past the gauging site on East Canagagigue Creek. Of this flux, about 96 kg. or 27%, can be attributed to the event water discharge. Nitrate concentrations of up to 58 mg/L would be required in the event water discharge to account for the calculated export (Table 15).

About 2.2×10^5 m^3 of rain fell on the West Canagagigue basin during the storm. Roughly 1.7×10^5 m^3 ran off as stream discharge of which approximately 2.3×10^4 m^3 were derived from event water. The volume of rain falling on the 1.8 km^2 of bottomlands adjacent to the stream was about 2.1×10^4 m^3. Although the bottom lands and swamps in the basin occupy less than 10% of the total basin area, they could have delivered nearly 91% of the event water discharge if they had totally converted rainfall to runoff.

In summary, this low intensity storm caused stream discharge to increase by factors of 8 and 5 for the west and east branches, respectively. The west branch experienced a greater increase in nitrate concentrations (85% versus 68%), a greater dilution in conductivity (21% versus 8%), and a greater oxygen-18 dilution (11% versus 4%) than the east branch. The hydrograph separations made by the isotope technique indicated that up to 12% event water was present in the first peak and up to 10% in the second peak for the west branch but there was never more than 5% event water in the east branch runoff.

The high nitrate concentrations calculated for the event water component (over 50 mg/L) may be over-estimates resulting from the assumption that the pre-event component maintained constant nitrate values during a storm. If tile drain effluent during the event was quantitatively significant and high in nitrate, the assumption just mentioned would be invalid. Tile drain effluent in Hillman Creek was found to contain 63 mg/L nitrate during one runoff event. Although no samples of drainage tile effluent were taken from the Canagagigue watersheds, the Hillman Creek sample indicates that tile drains may have a considerable effect on the nitrate flux in storm runoff.

4.6.3 Rain Event on West Canagagigue Creek, April 20-26, 1977

A sporadic and generally low intensity storm on April 22 and 23, 1977 dropped 19 mm. of rain on the West Canagagigue Creek basin. The basin was fairly dry prior to the storm (4 mm. in the seven days prior to April 22) and the stream discharge was very low. Discharge in the stream increased from 0.03 to 0.14 m^3 in response to the storm.

The oxygen-18 content of the rain ranged from -1.0 to -13.1^{O}/oo, a variation which rendered the storm less than ideal for isotope hydrograph separation. Nearly 70% of the rain had an isotopic value of -8.7^{O}/oo and the weighted average rainfall was -8.0^{O}/oo.

Baseflow oxygen-18, conductivity, and nitrate contents were approximately -10.6^{O}/oo, 480 µS, and 1.5 mg/L, respectively, prior to the storm. In response to the storm, nitrate increased (by approximately 85%), conductivity increased and oxygen-18 first became heavier then lighter (Figure 27). The increases in nitrate and conductivity and the decrease in oxygen-18 did not occur until peak discharge was attained (Figure 27). No overland flow was observed during the runoff event.

Using the weighted average or moving weighted average figure for rain oxygen-18, accuracies of between 13 and 15% can be obtained for the groundwater component of peak discharge.

The isotope hydrograph separation for the storm is given in Figure 27. At peak discharge, almost 80% of the runoff was groundwater according to the isotope method. The standard graphical technique would yield an even higher percentage of groundwater.

The increase in nitrate and lighter oxygen-18 values in the stream at peak discharge could have been the result of a pulse of fresh groundwater being injected into the stream, however, the conductivity trend does not follow this hypothesis.

This low intensity storm produced a subdued runoff hydrograph which consisted almost entirely of groundwater. Increased nitrate concentrations following peak discharge appear to be of groundwater origin.

5. INTERPRETATION OF THE RESULTS

Several important behavioural characteristics of the study basins have been noted during the course of the study. Physical evidence which corroborates the isotope technique for the use in non-point source pollution studies has been obtained.

5.1 The Role of Groundwater in Runoff Generation and Its Effect on the Nitrate Flux in a Stream During High Runoff Periods

The mechanisms of runoff production in the study basins seem to be controlled to a large extent by both the pre-event basin conditions and the nature of the runoff - producing event itself. The nitrate flux in the stream during a runoff event, therefore, cannot be generalized as being attributable to any single runoff source or any combination of sources. The pre-event basin conditions and the type of event must be considered in determining the nitrate sources. Examples from the study demonstrate these relationships.

1. A major overland flow producing area on Verbeke's farm in the Hillman Creek watershed was found to produce at least two types of overland flow. On April 25, 1977,several samples were taken from the runoff emanating from this site. Isotopic and chemical evidence clearly established this water to be predominantly groundwater in origin. Quantitatively, this water was observed to be significant in the runoff event. On June 6, this area again generated quantitatively significant overland flow. This time, however, the water proved to be predominantly of event origin on the basis of isotopic and chemical analyses.

   Since the runoff was generated in the same location both times, the control of the runoff mechanisms in these cases must lie in the pre-event basin conditions and/or in the nature of the runoff producing events.

In the former case, the basin was extremely wet after some 73 mm. of rain in the preceding three days. On April 25, 31 mm. of rain, with no more than 4 mm. of rain in any hour, fell on the basin. The water table at H44WT8 was at least 20 cm. higher than during baseflow conditions. The latter case, however, found the basin quite dry with the water table at H44WT8 some 25 cm. below the level on April 25. The storm of June 6 dropped 38 mm. of rain on the basin in less than two hours. In essence, then, the April 25 storm was of lower intensity on a wet basin and the June 6 storm was of higher intensity on a dry basin.

The April 25 storm produced runoff by the variable area-overland flow mechanism as the high water table and large groundwater component in the overland flow suggest surface saturation from below. The June 6 storm produced runoff by the partial area-overland flow mechanism. The relatively deep water table and the large event water component in the overland flow are indicative of surface saturation trom above.

The nitrate increase in the stream during the April 25 storm apparently resulted from an influx of high nitrate, variable area-overland flow discharged shallow groundwater. Partial area-overland flow on that date generally had low nitrate concentrations.

The nitrate increase in the stream during the June 6 storm occurred only after groundwater re-established itself as the dominant stream component. Again, variable area-overland flow discharged shallow groundwater seems to be the source of the high stream nitrates. Prior to the nitrate increase, the stream experienced very low nitrate concentrations. These low values coincided with event water-diluted conductivities and oxygen-18 values all of which suggest that partial area-overland flow of event water dominated the runoff in the early parts of the event.

2. The snowmelt runoff event of March 10 and the rain runoff event of March 28 and 29 for the Upper East Canagagigue Creek apparently had markedly different sources. In the first case, frozen soil conditions contributed to the production of significant amounts of high nitrate, event water origin, overland flow. Reversed gradients caused bank storage of peak flow thereby prolonging the high nitrate flux in the stream. In the second case, frozen soils were absent and overland flow was not observed. Groundwater dominated the runoff hydrograph. High nitrate event water caused increased nitrate concentrations in the stream. As mentioned earlier, the significance of tile drain effluent in this case is unknown, however, tile drainage effluent could have been responsible for the high calculated values of nitrate in the event water.
3. Rain events on Hillman Creek on April 25 and May 4 were shown to produce storm runoff hydrographs that proved to be mostly of groundwater origin. Physical, isotopic, and chemical evidence all support this hypothesis. Nitrate concentrations in the stream increased considerably in response to the April 25 storm but increases were negligible for the May 4 storm.

   The difference between the responses in the two storms seems to be that the April 25 had considerable contributions of high nitrate, shallow groundwater produced by variable area-overland flow. The May 4, runoff was produced mainly by low nitrate groundwater which discharged near or into the stream. A larger storm and wetter basin conditions probably are responsible for the variable area-overland flow production on April 25.

5.2 The Performance of the Isotope Technique of Hydrograph Separation

The isotope technique of hydrograph separation yielded results that generally correlated very well with the groundwater stage-groundwater discharge rating curve technique and the specific conductivity results. Where discrepencies between the techniques occurred, plausible explanations can be given.

The storms of April 25 and May 4 on Hillman Creek are examples of the excellent correlations between the isotope and rating curve techniques. The evidence showing that much of the overland flow on April 25 was indeed of groundwater origin further substantiates the isotope results.

The March 10 snowmelt event on East Canagagigue Creek and the June 6 storm on Hillman Creek left isotopic and chemical evidence of bank storage. Although there was no equipment on East Canagagigue Creek for physical measurements of bank storage, the author's observations of the quickly rising stream leave little doubt as to the validity of the conclusions made on the basis of the isotopic and chemical data. There is, however, physical evidence in the form of hydraulic gradient reversals which indicate that bank storage occurred along Hillman Creek during the June 6 storm. This information confirms the isotopic results.

The groundwater stage-groundwater discharge rating curve technique for the June 6 storm on Hillman Creek gave considerably larger groundwater components than those obtained by the isotope technique. Although these results seem divergent, they probably are not seriously so since the rating curve technique cannot discriminate between the bank storage water and groundwater while the isotope technique can. The difference between the two results, therefore, most likely can be attributed to bank storage. Physical and isotopic evidence suggest that this is a plausible explanation.

5.3 Calculation of Nitrate Fluxes of Overland Flow Using the Isotope Technique of Hydrograph Separation

While the isotope technique has been demonstrated to be reliable in separating hydrographs, its application to the calculation of the nitrate fluxes in overland flow has been only moderately successful. One of the problems incurred during the study involved the assumption that the groundwater contributions to storm runoff are temporally and spatially constant with respect to nitrate concentration. The present study has revealed that groundwater from several parts of the basin can contribute to storm runoff and that these sources may have quite different nitrate contents.

High nitrate drainage tile effluent may become a significant factor during periods of high runoff. This component may have oxygen-18 contents similar to the groundwater oxygen-18 discharged during baseflow periods but the assumption that the baseflow and high runoff period nitrate concentrations are the same may be tenuous. This problem is especially prominent in the Canagagigue study where tile drainage is widespread.

Another problem incurred in the study involves the implied assumption that overland flow is of event origin. The present study has demonstrated that this is not always the case.

The isotope technique for hydrograph separations for the calculation of the nitrate flux due to the groundwater and overland flow components of storm runoff has proven to be extremely effective in identifying the mechanisms and source areas of nitrate transport during runoff periods. The use of conventional techniques alone would have led to several gross errors in the description of the nitrate runoff during the storm events in the study basins. For example, conventional techniques would not have identified the overland flow emanating from Roger Verbeke's farm 'in the Hillman Creek basin during the April 25 storm as groundwater and would therefore have attributed the increased nitrate load in the stream to event water running off as partial area-overland flow. Conventional techniques would probably also have missed the distinction between the pre-event water overland flow on April 25 and the event water overland flow on June 6 emanating from the same spot oh Roger Verbeke's farm in the Hillman Creek basin.

The use of standard graphical techniques to calculate the nitrate flux in the stream during runoff periods would underestimate the groundwater contributions of nitrate to the stream in the majority of cases as graphical techniques are notorious for assuming that groundwater decreases (or increases only slightly) during runoff events. In the Hillman Creek watershed, groundwater was responsible for the nitrate increases in the stream in all the intensively monitored events.

5.4 Extrapolation of the Results to Other Basins and Future Runoff Events

This study has demonstrated how a single basin can respond to different runoff producing events in quite dissimilar fashions. The nature of the runoff producing event and the pre-event basin conditions were mentioned as two of the factors causing these variations. Behavioural variations between the adjacent Canagagigue watersheds to a single rainfall event are indicative of the control of watershed response by the hydrogeologic characteristics of basins. All of these findings serve to render the quantitative extrapolation of any of these results from past events on a few basins to past or future events on several basins, quite speculative. 0ne can only speak in qualitative terms if extrapolations are to be made and in order to make any meaningful generalizations, much more effort must be expended in the investigation of watershed response to runoff producing events.

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TABLE 1. TEMPORAL AND SPATIAL VARIATION OF GROUNDWATER OXYGEN-18 NEAR H44WT8

SITE	DISTANCE TO STREAM (m)	DATE	δO^{18} (^{O}/oo)
H2AP11	~ 5m	Feb 12/77	-9.1
		Mar 4/77	-9.1
		June 12/75	-8.6
		Aug 6/75	-8.2
H2AWT8	~ 5m	Feb 22/77	-8.3
		Mar 4/77	-8.4
H44P8	~ 1m	Feb 22/77	-8.9
		Mar 4/77	-9.4
H38P14	~65m	Feb 22/77	-9.4
		Mar 4/77	-9.7
		April 1976	-9.2
		Aug 6/75	-8.8
H38P20	~65m	Feb 22/77	-8.9
		Mar 4/77	-9.2
		Aug 6/75	-9.1
PIEZ A (1.3m)	0	May 13/77	-9.5
		June 1/77	-8.3
		June 11/77	-8.1
PIEZ B (2.0m)	0	May 13/77	-10.7
		June 1/77	-8.8
		June 11/77	-8.2
PIEZ C (2.6m)	0	May 13/77	-9.9
		June 1/77	-8.9

TABLE 2. TEMPORAL AND SPATIAL VARIATIONS OF GROUNDWATER NITRATE NEAR H44WT8

SITE	DISTANCE TO STREAM (m)	DATE	NO_3-N (mg/L)
H38P14	~65	MAY 19/77	20.1
		APR 14/77	3.3
		MAR 30/77	2.0
		MAR 4/77	2.0
		AUG 10/76	35.0
		JULY 6/76	40.5
		JUNE 3/76	56.7
		APR 26/76	64.3
		NOV 13/75	6.5
		SEPT 12/75	21.0
		AUG 6/75	22.6
H38P20	~65	APR 14/77	0.1
		MAR 30/77	0.0
		MAR 4/77	0.2
		AUG 10/76	0.2
		JULY 6/76	0.0
		JUNE 3/76	1.8
		APR 26/76	0.0
		NOV 13/75	0.1
		SEPT 12/75	0.0
		AUG 6/75	1.2
H2AP8	~ 5	APR 14/77	0.3
		MAR 30/77	0.8
		MAR 4/77	0.1
		AUG 10/76	0.0
		JULY 6/76	0.4
		JUNE 3/76	0.4
		APR 26/76	0.1
		NOV 13/75	0.1
		SEPT 12/75	0.0
H2AP8	~ 5	AUG 6/75	0.0
		JUNE 12/75	0.4
H2AP11	~ 5	MAY 19/77	0.3
		APR 14/77	0.2
		MAR 30/77	4.0
		MAR 4/77	0.2
		AUG 10/76	0.2
		JULY 6/76	0.A
		JUNE 3/76	6.1
		APR 26/76	0.2
		NOV 13/75	0.0
		SEPT 12/75	0.1
		AUG 21/75	0.2
		JUNE 12/75	0.1

TABLE 2 (CONTINUED)

SITE	DISTANCE TO STREAM (m)	DATE	NO_3-N (mg/L)
H2AWT8	~ 5	MAY 19/77	0.1
		APR 14/77	1.8
		MAR 4/77	0.2
H44PA	~ 1	APR 14/77	0.1
		MAR 30/77	0.3
		MAR 4/77	0.1
H44P8	~ 1	APR 14/77	0.0
		MAR 30/77	0.1
		MAR 4/77	0.1

TABLE 3. TYPICAL HYDRAULIC HEAD DIFFERENCES BETWEEN H44WT8 AND THE STREAM AND GWW AND THE STREAM DURING BASEFLOW PERIODS - SPRING 1977.

H44WT8 - STREAM

DATE	ΔH(CM)
APRIL 2/77	9.4
APRIL 22/77	7.1
MAY 4/77	9.8
JUNE 4/77	7.0

GWW - STREAM

DATE	ΔH(CM)
APRIL 2/77	8.9
APRIL 6/77	12.3
APRIL 22/77	8.8
MAY 4/77	13.1
JUNE 4/77	10.1

TABLE 4. TEMPORAL AND SPATIAL VARIATIONS IN STREAM OXYGEN-18 DURING SNOWMELT RUNOFF

HILLMAN CREEK - FEBRUARY 22, 1977

LOCATION	TIME	O^{18}(^{O}/oo)
WEIR	11:15	- 8.8
WEIR	17:45	-11.3
VERBEKE'S BRIDGE	15:15	-12.2
VERBEKE'S BRIDGE	16:15	-11.9

TABLE 5. PERCENTAGE OF GROUNDWATER IN SNOWMELT RUNOFF HILLMAN CREEK - FEBRUARY 22/77

LOCATION	TIME	ESTIMATED SNOWMELT O^{18}(^{O}/oo)	PERCENT GROUNDWATER
WEIR	11:15	15.4	100
WEIR	12:45	15.4	62
VERBEKE'S BRIDGE	15:15	15.4	36
VERBEKE'S BRIDGE	16:15	15.4	40

TABLE 6. WATER LEVEL RESPONSE IN GROUNDWATER INSTALLATIONS NEAR H44WT8 AS A FUNCTION OF DISTANCE FROM THE STREAM HILLMAN CREEK - FEBRUARY 22, 1977

SITE	DISTANCE TO STREAM (M)	TIME	WATER LEVEL(M)	WATER LEVEL RISE (M)	RATE OF WATER LEVEL RISE (M/HR)
H38P14	~65	1420	203.552	+.005	.003
		1604	203.557		
H38P20	~65	1420	203.55	0	0
		1605	203.556		
H2AP11	~ 5	1457	203.149	+.050	.048
		1600	203.199		
H44WT8	~3	1445	203.183	+.042	.036
		1555	203.225		
H44P8	~1	1458	203.111		
		1601	203.163	+.052	.050

TABLE 7. TEMPORAL VARIATIONS OF NITRATE CONTENT IN HILLMAN CREEK AT WEIR 2 - MARCH 4-5, 1977

TIME		ACCUMULATED RAINFALL (MM	NO_3^--N (mg/L)	RELATIVE STAGE AT MINISTRY GAUGE (CM)
MAR 4	1150	6	2.8	12
	1350	7	1.4	19
	1550	7	2.5	22
	1750	7	3.9	24
	1950	7	3.3	26
	2150	7	3.3	27
	2350	7	2.4	25
MAR 5	0150	7	4.0	20
	0350	7	3.4	15
	0550	7	3.1	13
	0750	7	2.7	11
	0950	7	3.6	9
	1350	7	2.9	7

TABLE 8. WATER LEVEL RESPONSE IN GROUNDWATER INSTALLATIONS NEAR H44WT8 AS A FUNCTION OF DISTANCE FROM THE STREAM - HILLMAN CREEK - APRIL 13-28, 1977

APRIL	13-21	NO RAIN
APRIL	22	38 mm
APRIL	23	35 mm
APRIL	24	NO RAIN
APRIL	25	31 mm (16 mm to 12:00)
APRIL	26	3 mm
APRIL	27	NO RAIN
APRIL	28	1 mm

SITE	DISTANCE TO STREAM (M)	TIME	WATER LEVEL (M)	RISE (M)	AVERAGE RATE OF RISE (mm/hr)
H38P14	~65	1000 APR13	204.020	+0.085	+0.3
		1120 APR25	204.105	+0.020	+3.6
		1650 APR25	204.125	+0.221	+3.3
		1215 APR28	204.346		
H2AP11	~ 5	1005 APR13	203.177	+0.262	+0.9
		1125 APR25	203.439	+0.022	+4.1
		1647 APR25	203.461	-0.123	-2.8
		1218 APR28	203.271		
H44WT8	~3	0950 APR13	203.235	+0.186	+0.6
		1240 APR25	203.421	-0.123	-1.7
		1125 APR28	203.298		
H44P8	~ 1	1125 APR25	203.358	+0.029	+5.5
		1645 APR25	203.387	-0.162	-2.4
		1220 APR28	203.225		
GWW	0	1015 APR13	203.260	+0.136	+0.3
		1105 APR25	203.396	-0.085	-1.2
		1150 APR28	203.311		

TABLE 9. TEMPORAL AND SPATIAL VARIATIONS OF OXYGEN-18, CONDUCTIVITY, AND NITRATE IN THE STREAM, RAIN, OVERLAND FLOW, AND TILE DRAIN - HILLMAN CREEK - APRIL 25, 1977

TYPE	LOCATION	TIME	O^{18} (°/oo)	COND. (µS)	NO_3^-N (mg/L)
RAIN	VERBEKE'S BRIDGE	TO 1030	-17.4	22	-
		TO 1230	-19.4	45	-
		TO 1545	-19.0	21	-
	WHITTLE FARM	TO 0830	-16.5	41	-
		TO 1205	-18.6	38	-
		TO 1522	-19.2	82	-
	VERBEKE HOUSE	TO 0950	-17.2	-	0.6
		TO 1230	-19.8	-	0.5
		TO 1535	-18.8	-	-
	VERBEKE HOUSE	AT 0915	-19.3	28	-
		AT 1225	-20.0	12	-
TILE DRAIN	WHITTLE'S	1525	- 9.5	826	62.7
OVERLAND FLOW	WHITTLE'S	0915	-16.7	67	
		1200	-18.1	40	2.9
		1515	-17.6	89	-
		1700	-16.8	122	-
	NORTH WHITTLE'S	0910	-16.4	136	-
		1205	-17.1	110	5.3
		1520	-17.5	54	5.8
	VERBEKE BRIDGE	1030	-11.8	615	7.7
		1115	-12.3	569	7.9
		1140	-12.6	528	9.6
		1230	-12.7	483	6.2
		1545	-10.9	638	8.5
		1630	-10.3	664	8.0
STREAM AT	VERBEKE BRIDGE	0125	-8.5	722	8.1
		0900	-7.8	736	8.0
		0940	- 8.2	738	-
		1100	- 8.2	726	8.7
		1115	- 8.4	732	-
		1140	- 8.5	735	5.9
		1230	- 8.5	721	-
		1300	- 8.5	710	8.2
		1500	- 8.9	694	8.4
		1545	- 8.4	693	6.0
		1630	- 8.8	695	8.3
		2100	- 8.0	744	6.6

TABLE 10. TEMPORAL VARIATIONS IN OXYGEN-18, CONDUCTIVITY, AND NITRATE IN EAST CANAGAGIGUE CREEK, MARCH 7-11, 1977

TIME	DATE	δO^{18} (^{O}/oo)	COND. (µS)	NO_3^-N (mg/L)
1245	MAR 7	-11.2		1.5
2045		-10.9		2.6
2245		-10.8		1.8
0045	MAR 8	-11.2		1.8
0445		-11.3	624	2.7
0845		-11.1		2.6
1445		-11.1		2.8
1645		-11.2		3.1
1845		-11.3		2.7
2045		-11.2		2.3
2245		-11.3		2.5
0845	MAR 9	-11.6		2.9
1100		-11.6		2.6
1320		-11.8		2.3
1520		-11.9		2.8
1620		-12.8		2.9
1720		-12.5		2.7
1920		-11.9		2.8
2120		-12.3		3.1
2320		-12.5		3.3
0120	MAR 10	-12.3	555	2.9
0320		-12.6		3.7
0520		-12.3	530	3.8
0720		-12.1	534	4.0
0920		-12.2	539	3.9
1320		-12.4	516	4.3
1520		-12.6	476	4.6
1710		-13.2	432	5.1
1750		-13.3	424	4.7
1950		-14.0	406	5.9
2150		-14.0	412	5.4
0800	MAR 11	-14.1	468	6.0
0900		-13.8		6.1

TABLE 11. TEMPORAL AND SPATIAL VARIATIONS IN SNOW AND SNOWMELT Oxygen-18 EAST CANAGAGIGUE BASIN MARCH 8-10, 1977

SITE	TYPE	TIME	δO^{18} (^{O}/oo)	COND (µS)	NITRATE (mg/L)
B	SNOW	1430 MAR 8	-18.8		
		1445 MAR 9	-19.4		
		1535 MAR 10	-17.8	103	
		1435 MAR 8	-11.7		
	SNOWMELT	1445 MAR 9	-13.4		
		1205 MAR 10	-15.9		
C	SNOW	1445 MAR 8	-16.1		
		1450 MAR 9	-16.9		
		1540 MAR 10	-17.5	147	
	SNOWMELT	1600 MAR 8	-14.2		1.4
D	SNOW	1445 MAR 8	-19.6		
		1500 MAR 9	-19.8		
		1545 MAR 10	-19.0		
E	SNOW	1505 MAR 8	-17.9		
		1505 MAR 9	-18.0		
		1550 MAR 10	-19.2		
	SNOWMELT	1510 MAR 8	-14.6		
		1115 MAR 9	-14.4		
		1505 MAR 9	-14.7		
		1620 MAR 9	-13.9		
		1400 MAR 10	-13.6	907	
F	SNOW	1515 MAR 8	-18.7		
		1510 MAR 9	-20.1		
		1600 MAR 10	-18.3	255	
	SNOWMELT	1570 MAR 9	-14.6		
		1625 MAR 9	-14.1		
		0920 MAR 10	-14.6	228	
		1215 MAR 10	-14.1	274	
		1410 MAR 10	-14.9	269	
		1555 MAR 10	-14.9	240	
G	SNOWMELT	1605 NAR 8	-14.7		0.2
	SNOW	1420 MAR 9	-16.8		
	SNOWMELT	1515 MAR 10	-14.5	291	
H	SNOW	1535 MAR 8	-20.6		
		1425 MAR 9	-20.2		
		1525 MAR 10	-18.6		

TABLE 11 (CONTINUED)

SITE	TYPE	TIME	δO^{18} (°/oo)	COND (µS)	NITRATE (mg/L)
GAUGE SITE	SNOW	FEB 21/77	- 22.2		
		1400 MAR 8	- 23.6		
		1405 MAR 9	-18.7		
	SNOWMELT	1700 MAR 8	-14.6		
		0900	-13.9	449	4.4
		1140	-13.5		4.1
		1310	-14.1	424	
		1505	-13.7	414	
		1715	--	300	
S.E.OF GAUGE	SNOWMELT	1150 MAR 10	-11.9	360	8.8

TABLE 12. CALCULATION OF NITRATE EXPORT FROM EAST CANAGAGIGUE CREEK MARCH 10, 11, 1977.

TIME	δO^{18} (^{O}/oo)	Q_t (m/s)	Q_P (m/s)	Qe (m/s)	N_t (mg/L)	N_e (mg/L)	C_t µS	C_e µS
MARCH 10								
0120	-12.3	0.42	.27	.16	2.9	3.2	555	---
0520	-12.3	0.41	.26	.15	3.8	5.7	530	488
0720	-12.1	0.44	.31	.14	4.0	6.9	534	488
0920	-12.2	0.48	.32	.16	4.0	6.6	539	506
1320	-12.4	0.71	.40	.29	4.3	6.5	516	461
1520	-12.6	1.13	.57	.57	4.6	6.5	476	397
1710	-13.2	1.75	.50	1.26	5.1	6.0	432	384
1750	-13.3	1.84	.47	1.37	4.7	5.4	424	379
1950	-14.0	2.24	--	2.24	6.0	6.0	406	406
2150	-14.0	2.55	--	2.55	5.4	5.4	412	412
MARCH 11								
0800	-14.1	1.02	--	1.02	6.1	6.1	468	468

ASSUMING
δO^{18}_{P} = -11.3 ^{O}/oo
δO^{18}_{e} = -14.0 ^{O}/oo
N_P = 2.7 mg/L
C_P = 555 µS

TABLE 13. RESPONSE OF NEAR-STREAM GROUNDWATER AT EAST CANAGAGIGUE GAUGE, MARCH 28-29, 1977

LOCATION	APPROXIMATE DISTANCE TO STREAM (m)	TIME	RELATIVE WATER LEVEL (m)	RISE (m)	AVERAGE RATE OF RISE (mm/hr)
C1P10	~2 m	1130 MAR 28	48.333		
		0725 MAR 29	48.478	+0.145	7.3
		1625 MAR 29	48.509	+0.029	3.2
C1P15	~2 m	1130 MAR 28	48.342		
		0725 MAR 29	48.472	+.130	6.5
		1625 MAR 29	48.514	+.042	4.7
C3PA	7 m	1130 MAR 28	48.774		
		0725 MAR 29	48.962	+ .188	9.4
		1625 MAR 29	48.967	+.005	0.6
C3P10	7 m	1130 MAR 28	48.481		
		0725 MAR 29	48.617	+.136	6.8
		1625 MAR 29	48.640	+.023	2.6
C3P24	7 m	1130 MAR 28	49.662		
		0725 MAR 29	49.761	+.099	5.0
		1625 MAR 29	49.777	+.016	1.8
C4P8	50 m	1130 MAR 28	49.315		
		0725 MAR 29	49.494	+.170	8.5
		1625 MAR 29	49.484	+.010	1.1
C4P22	50 m	1130 MAR 28	49.633		
		0725 MAR 29	49.745	+ .112	5.6
		1625 MAR 29	49.747	+.002	0.2
STREAM		1130 MAR 28	48.036		
		0725 MAR 29	48.164	+.128	6.4
		1625 MAR 29	48.238	+ .074	8.2

TABLE 14. CALCULATION OF NITRATE EXPORT FROM WEST CANAGAGIGUE CREEK, MARCH 28-29, 1977

TIME	δO^{18} (^{O}/oo)	Q_t (m^3/s)	Q_P (m^3/s)	Qe (m^3/s)	N_t (mg/L)	N_e (mg/L)
MAR 28						
1050	-13.5	0.54	0.54	0	4.1	---
1150	-13.5	0.58	0.57	.01	4.1	---
1250	-13.4	0.65	0.64	.01	4.1	1.8
1350	-13.4	0.74	0.72	.01	4.0	4.4
1450	-13.3	0.82	0.80	.02	4.1	5.2
1650	-13.1	1.19	1.12	.07	4.2	5.7
1850	-12.8	1.73	1.60	.12	2.9	15.7
1950	-12.4	2.12	1.88	.24	5.1	13.4
2050	-12.3	2.29	2.01	.28	5.1	12.5
2150	-12.2	2.15	1.86	.29	6.2	20.1
2250	-12.2	2.07	1.79	.28	6.2	19.6
2350	-12.4	2.01	1.78	.23	6.1	21.4
MAR 29						
0050	-12.4	1.92	1.71	.22	5.0	12.5
0150	-12.4	1.87	1.66	.21	5.4	15.8
0250	-12.4	1.90	1.68	.22	5.5	16.2
0350	-12.4	1.98	1.76	.22	5.5	16.8
0450	-12.2	2.07	1.79	.28	5.5	14.9
0550	-12.4	2.15	1.91	.24	6.8	27.9
0650	-12.4	2.24	1.98	.25	6.8	27.9
0750	-12.1	2.26	1.94	.33	7.2	27.5
0830	-12.0	2.24	1.89	.35	7.1	25.4
0945	-12.0	2.21	1.86	.34	7.3	23.8
1045	-12.1	2.18	1.86	.31	7.3	25.0
1145	-12.2	2.21	1.91	.30	6.8	26.3
1245	-12.3	2.29			6.5	24.4

ASSUMING $\delta O^{18}p$ = -13.5 ^{O}/oo,
δO^{18}_e = - 6.3 ^{O}/oo to 1750 MAR 28
-3.8 ^{O}/oo after 1750 MAR 28
Np = 4.1 mg/L

TABLE 15. CALCULATION OF NITRATE EXPORT FROM EAST CANAGAGIGUE CREEK MARCH 28-29, 1977

TIME	δO^{18} (^{O}/oo)	Q_t (m^3/s)	Q_P (m^3/s)	Qe (m^3/s)	N_t (mg/L)	N_e (mg/L)
MAR 28						
1025	-12.4	0.22	0.22	---	3.9	---
1225	-12.4	0.28	0.28	---	3.9	---
1425	-12.6	0.40	0.40	---	3.8	---
1825	-12.3	0.79	0.78	.01	4.3	32.6
2025	-12.3	1.16	1.15	.01	4.3	38.3
MAR 29						
0025	-12.0	1.70	1.62	.08	5.5	38.8
0225	-12.1	1.36	1.31	.05	5.7	56.4
0425	-12.0	1.08	1.02	.05	6.0	48.6
0625	-11.9	0.91	0.85	.05	6.1	42.1
0825	-12.0	0.68	0.65	.03	6.3	57.5
1025	-12.3	0.85	0.84	.01	5.9	
1225	-13.0	1.08			4.8	
1425	-13.1	1.36			4.4	

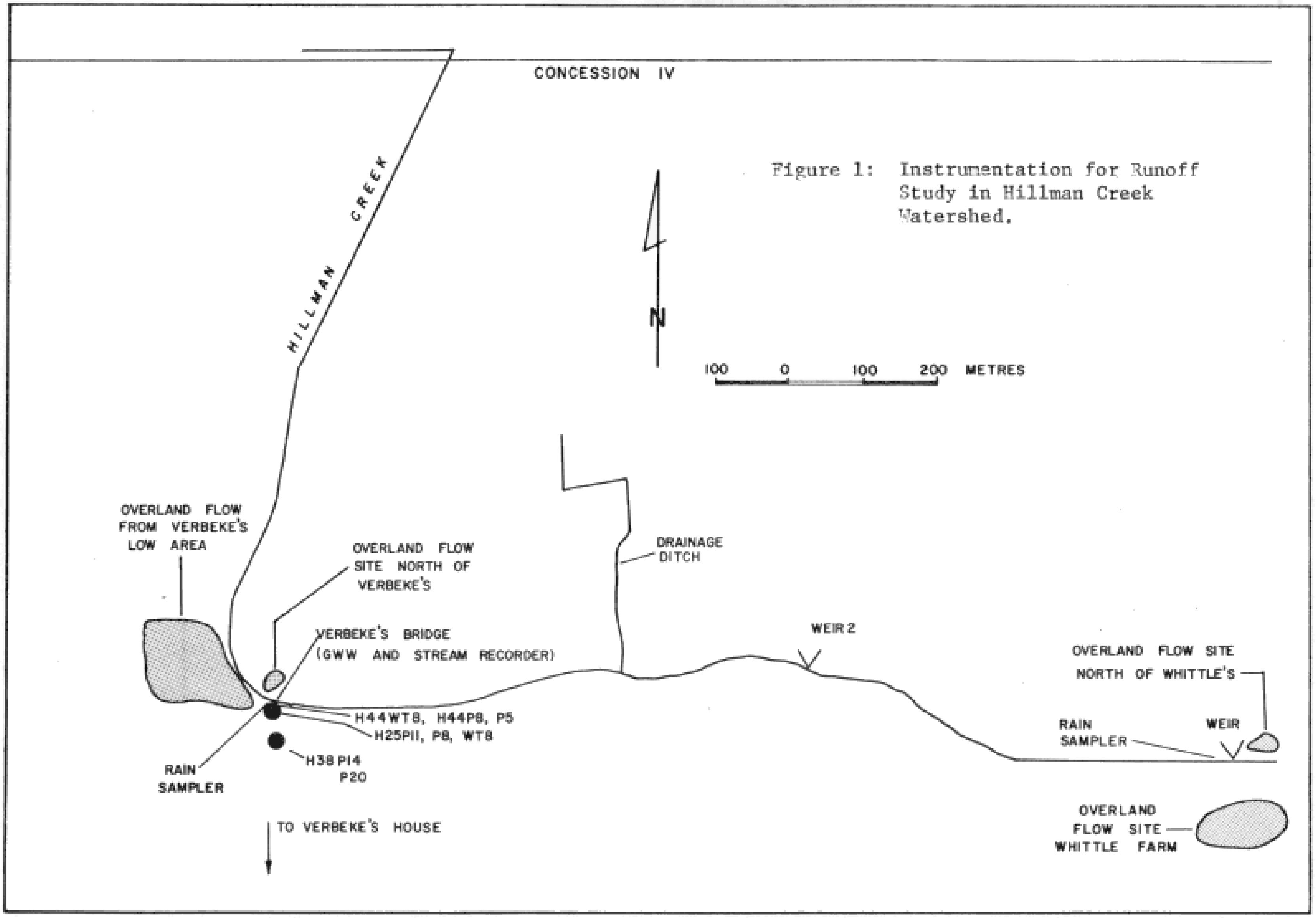

Figure 1: Instrumentation for Runoff Study in Hillman Creek Watershed.

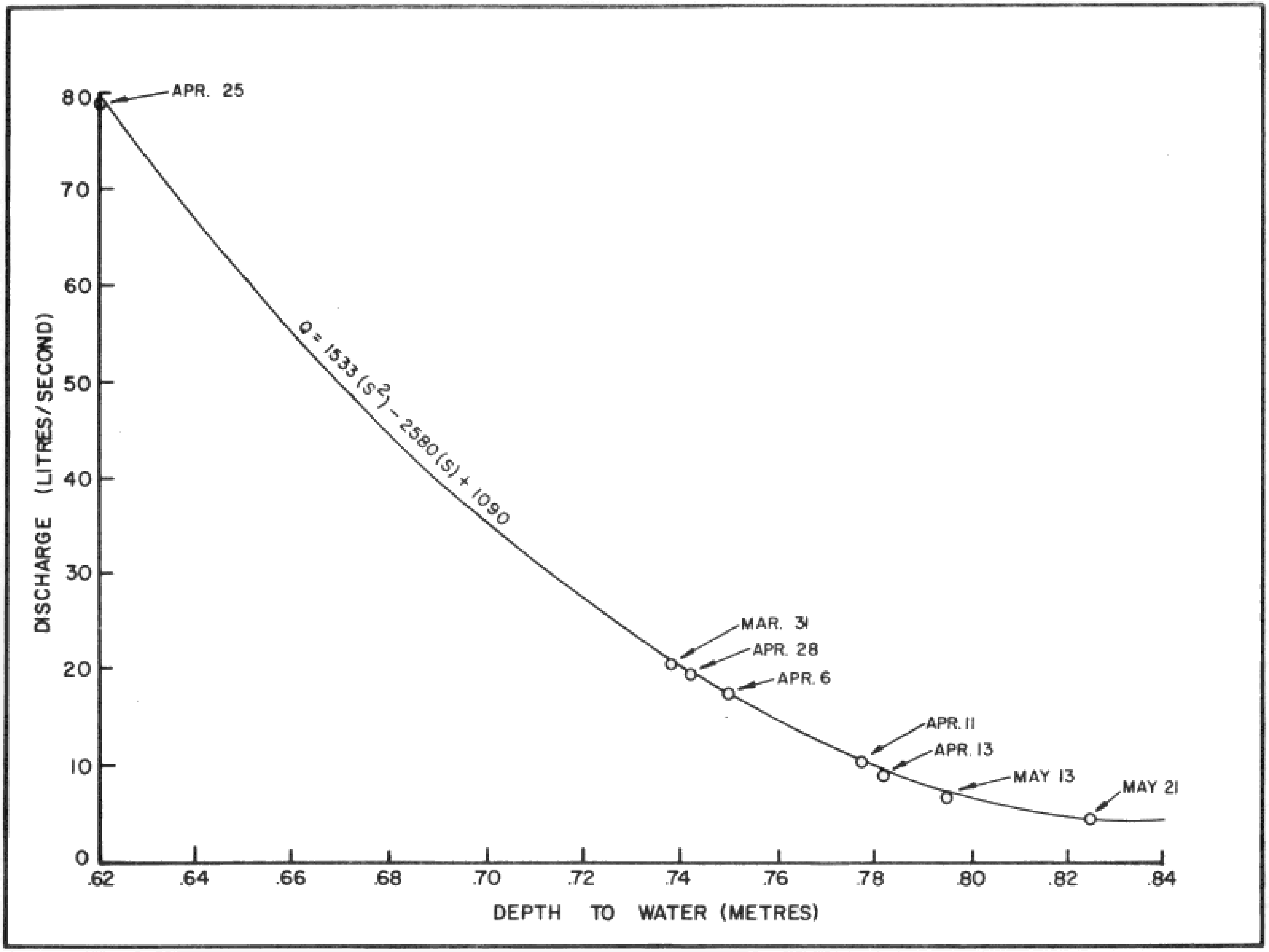

Figure 2a. stage-Discharge Rating Curve for Hillman Creek at Verbeke's Bridge.

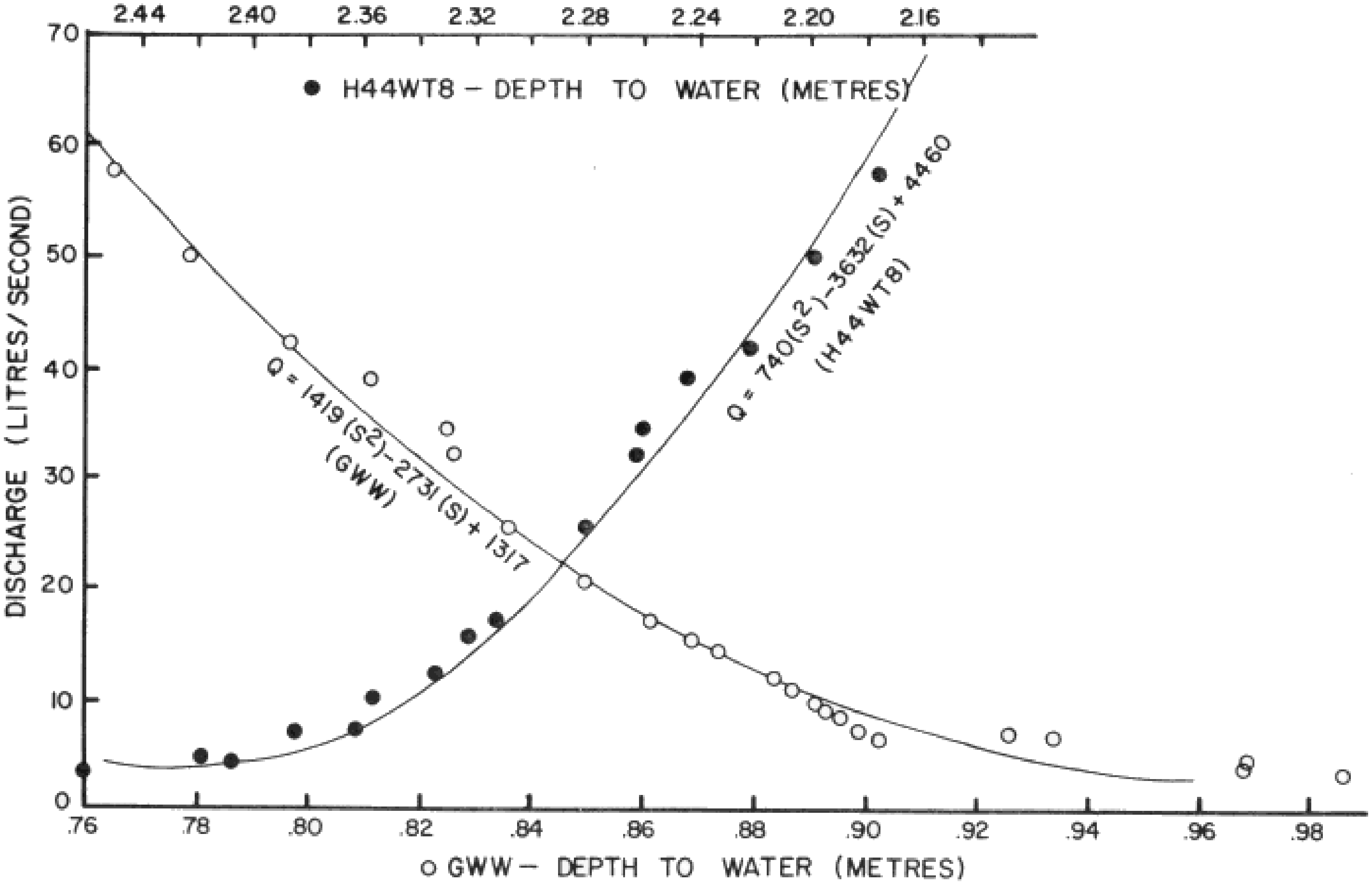

Figure 2b. Groundwater Stage--Groundwater Discharge Rating Curves for GWW and H44WT8

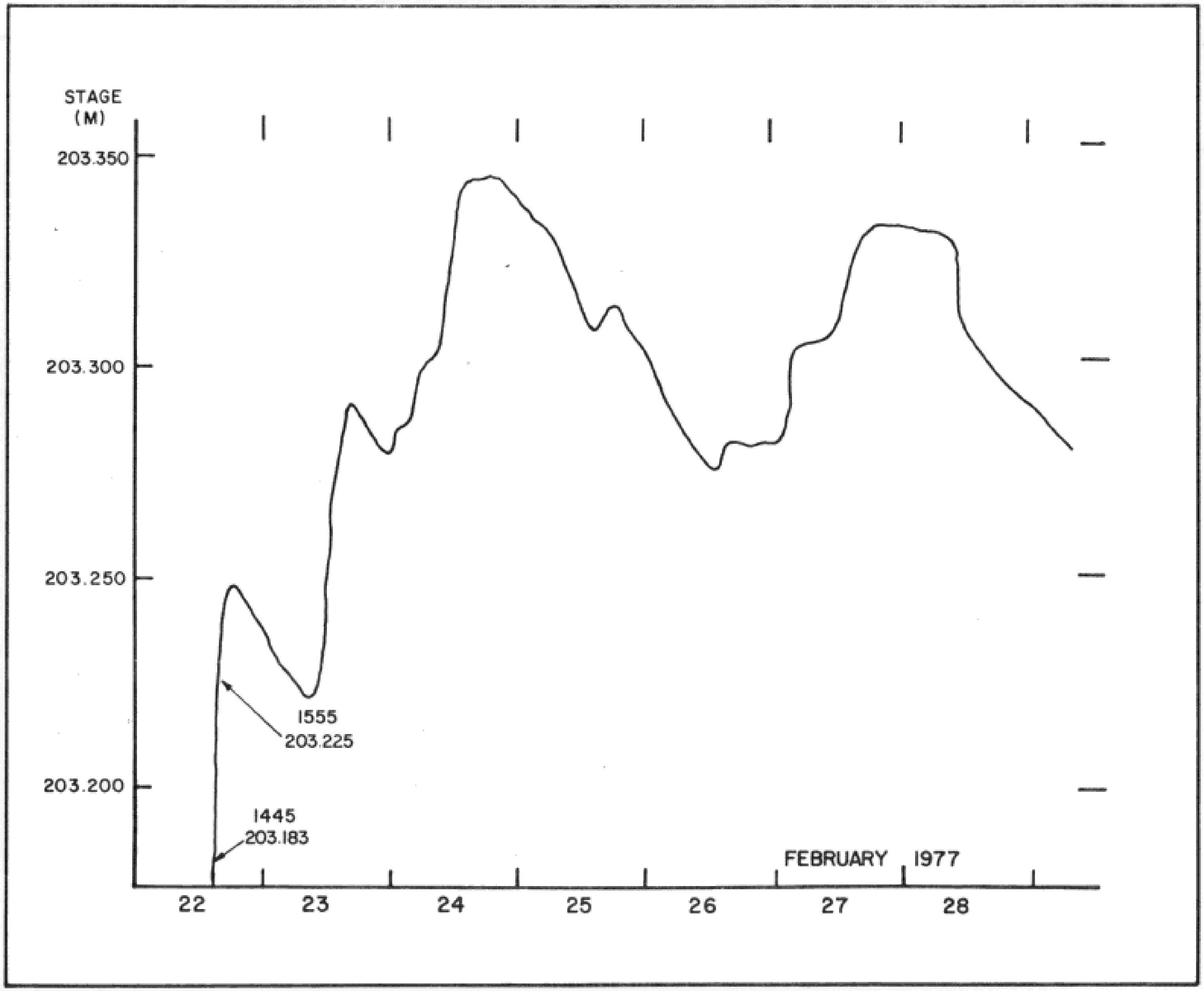

Figure 3. Hydrograph for H44WT8 during snowmelt event, February 22-28, 1977.

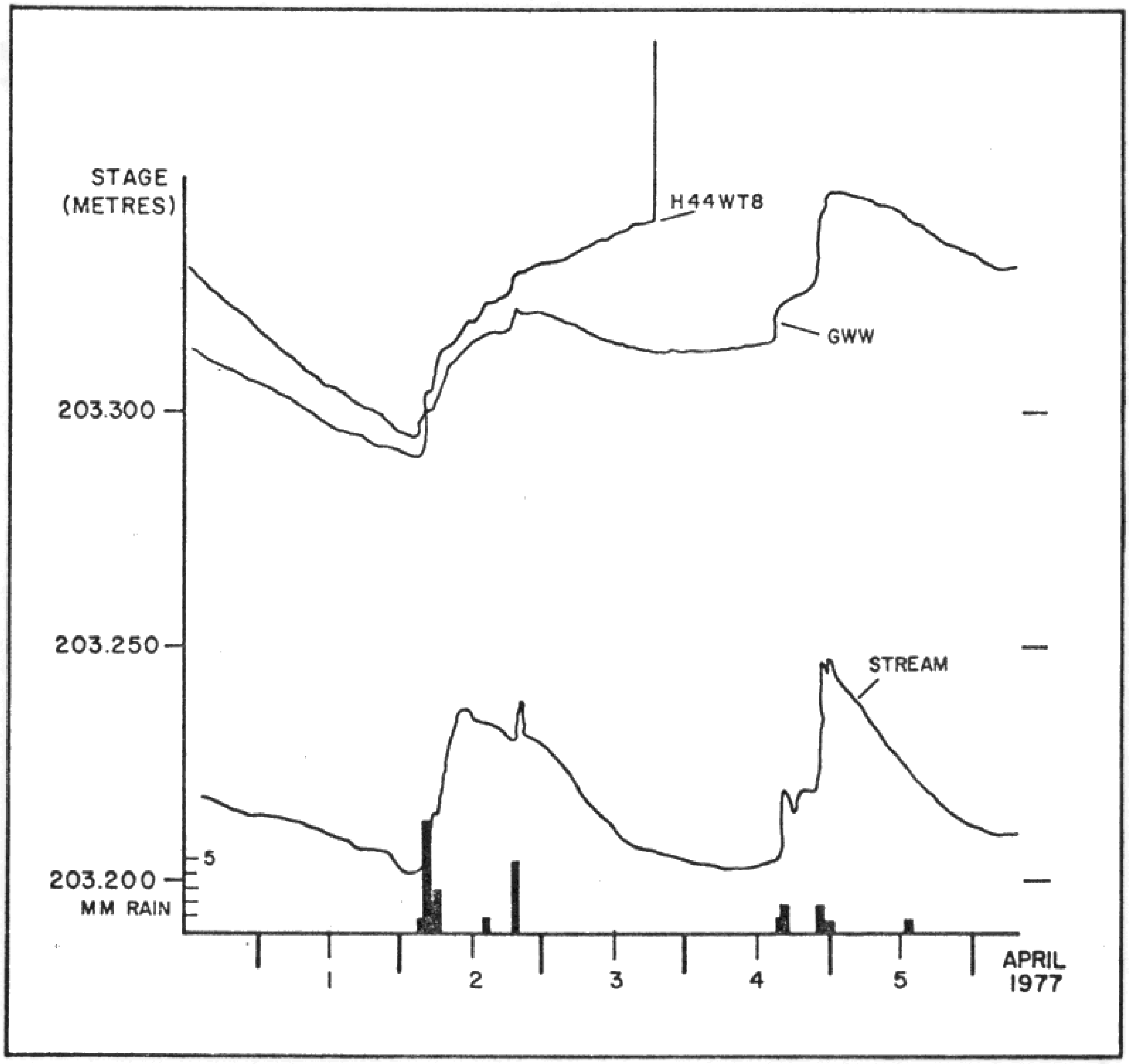

Figure 4. Stream and groundwater hydrographs and rating curve hydrograph separations for Hillman Creek at Verbeke's Bridge, April 1-5,1977.

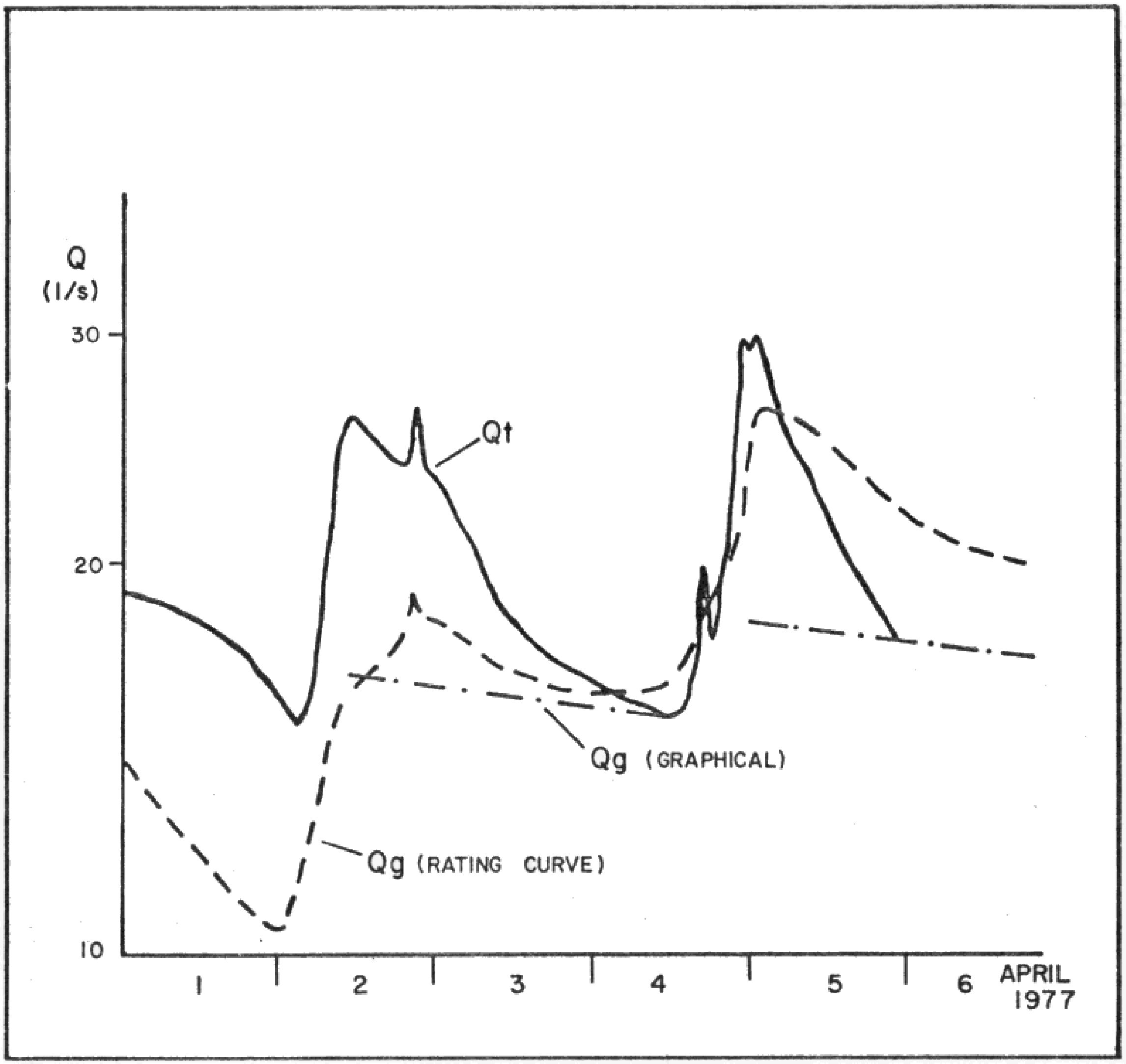

Figure 5. Hydrograph separations of storm runoff on Hillman Creek at Verbeke's Bridge by the graphical rating curve techniques, April 1-6, 1977.

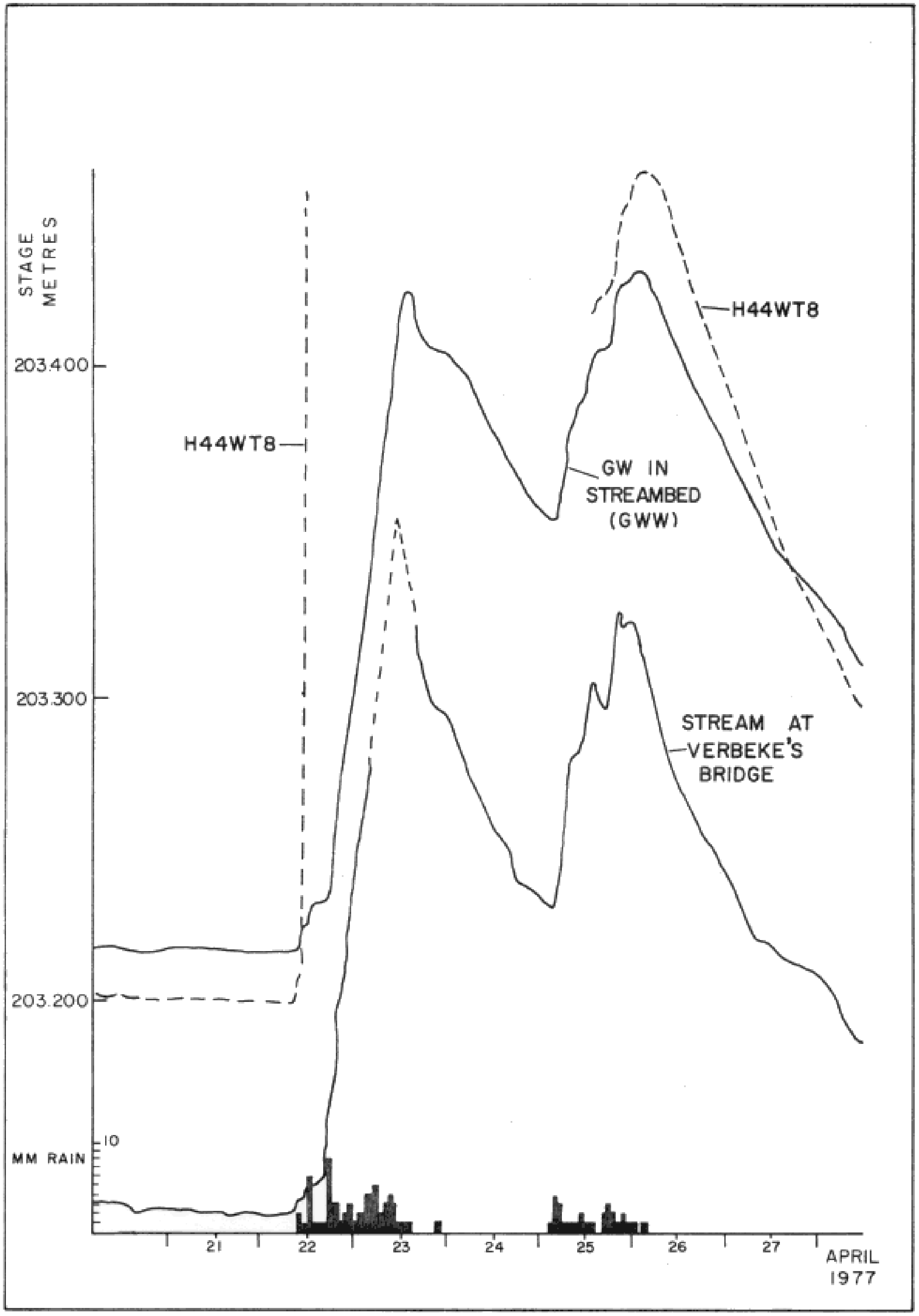

Figure 6. Stream and groundwater hydrographs, Hillman Creek at Verbeke's Bridge, April 21-27, 1977.

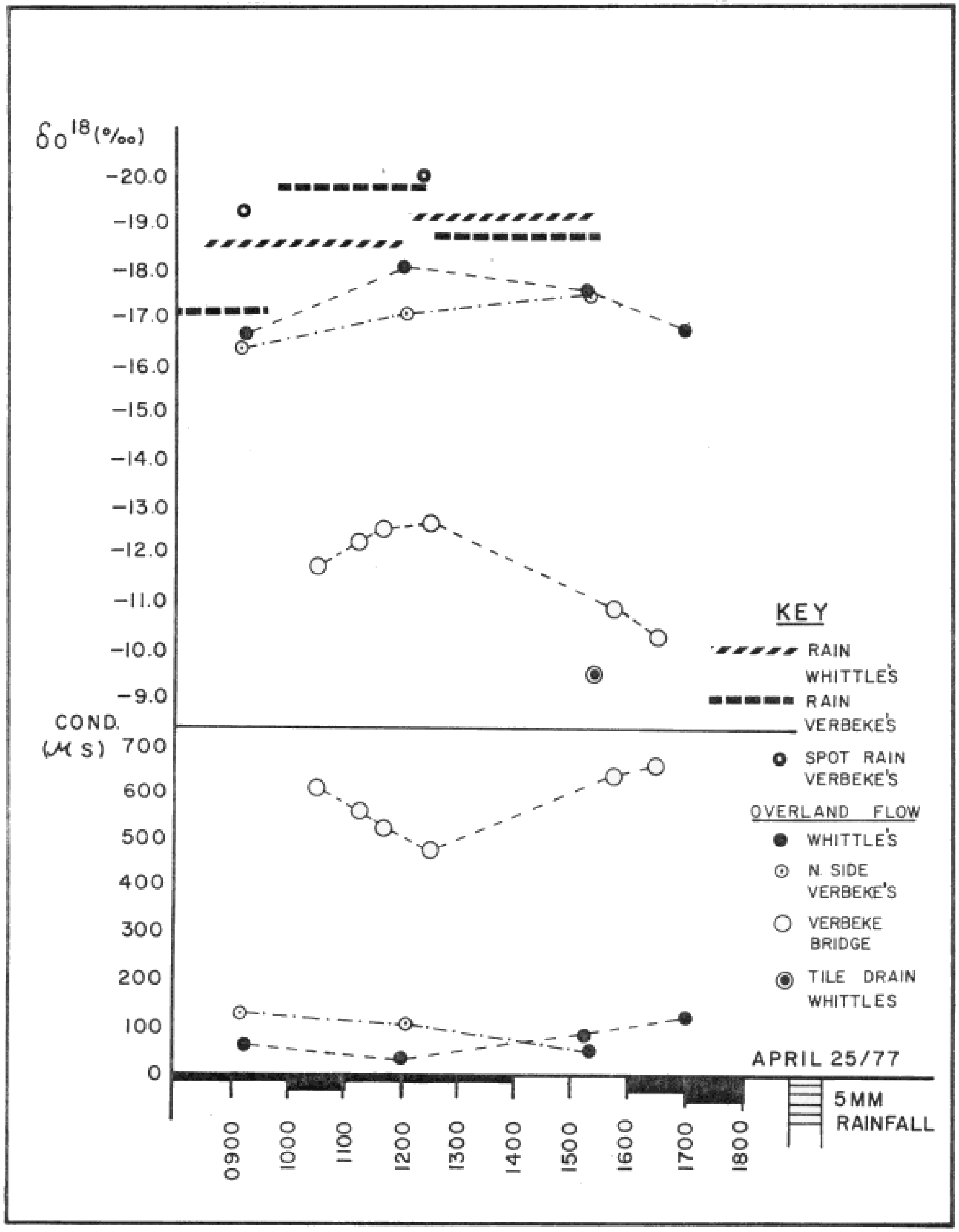

Figure 7. Temporal variations in oxygen-18 and conductivity of overland flow and rain during storm on April 25, 1977, Hillman Creek.

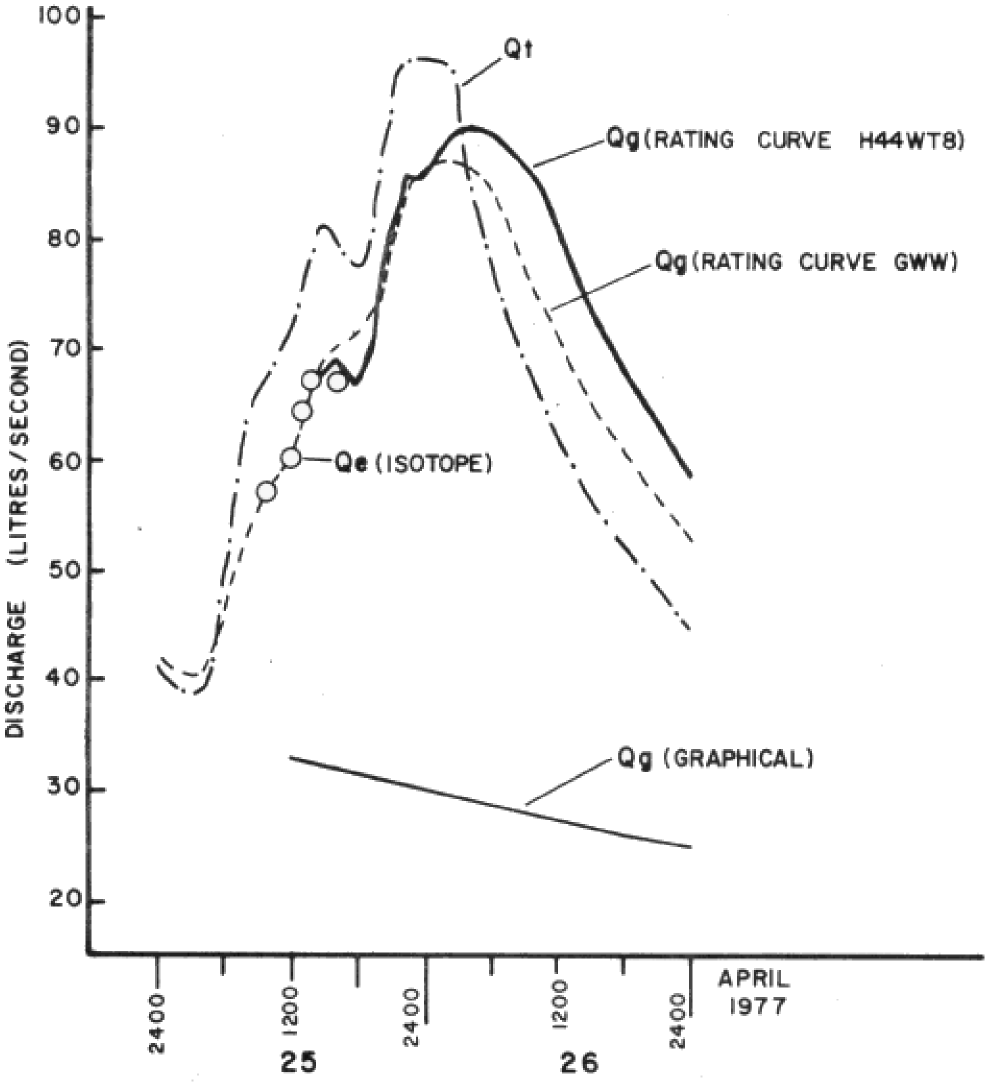

Figure 8. Hydrograph separations by the isotope, rating curve and graphical methods for Hillman Creek, April 25-26, 1977.

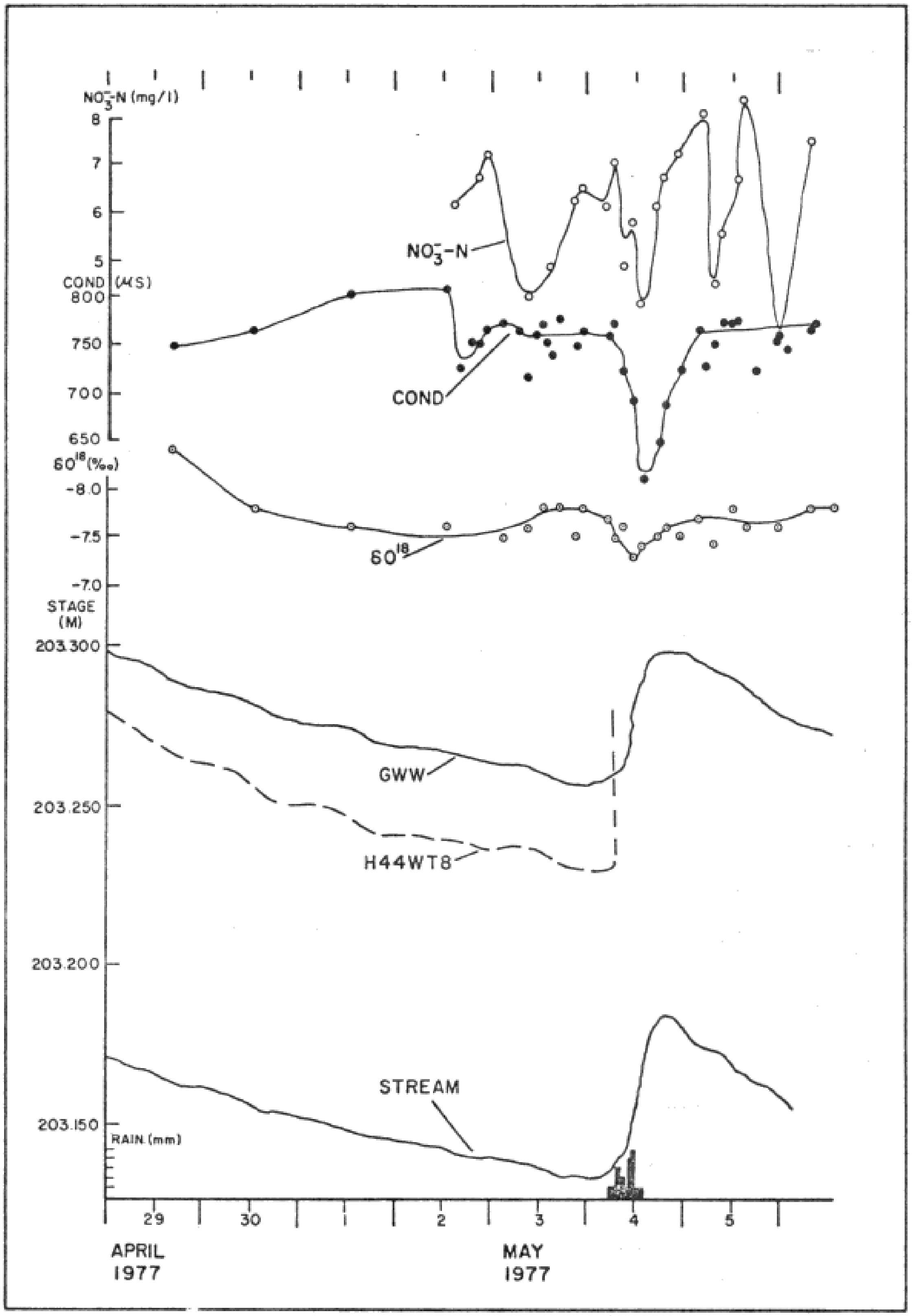

Figure 9. Temporal variations in oxygen-18, conductivity and nitrate in the stream and groundwater hydrographs for Hillman Creek, April 29 - May 5, 1977.

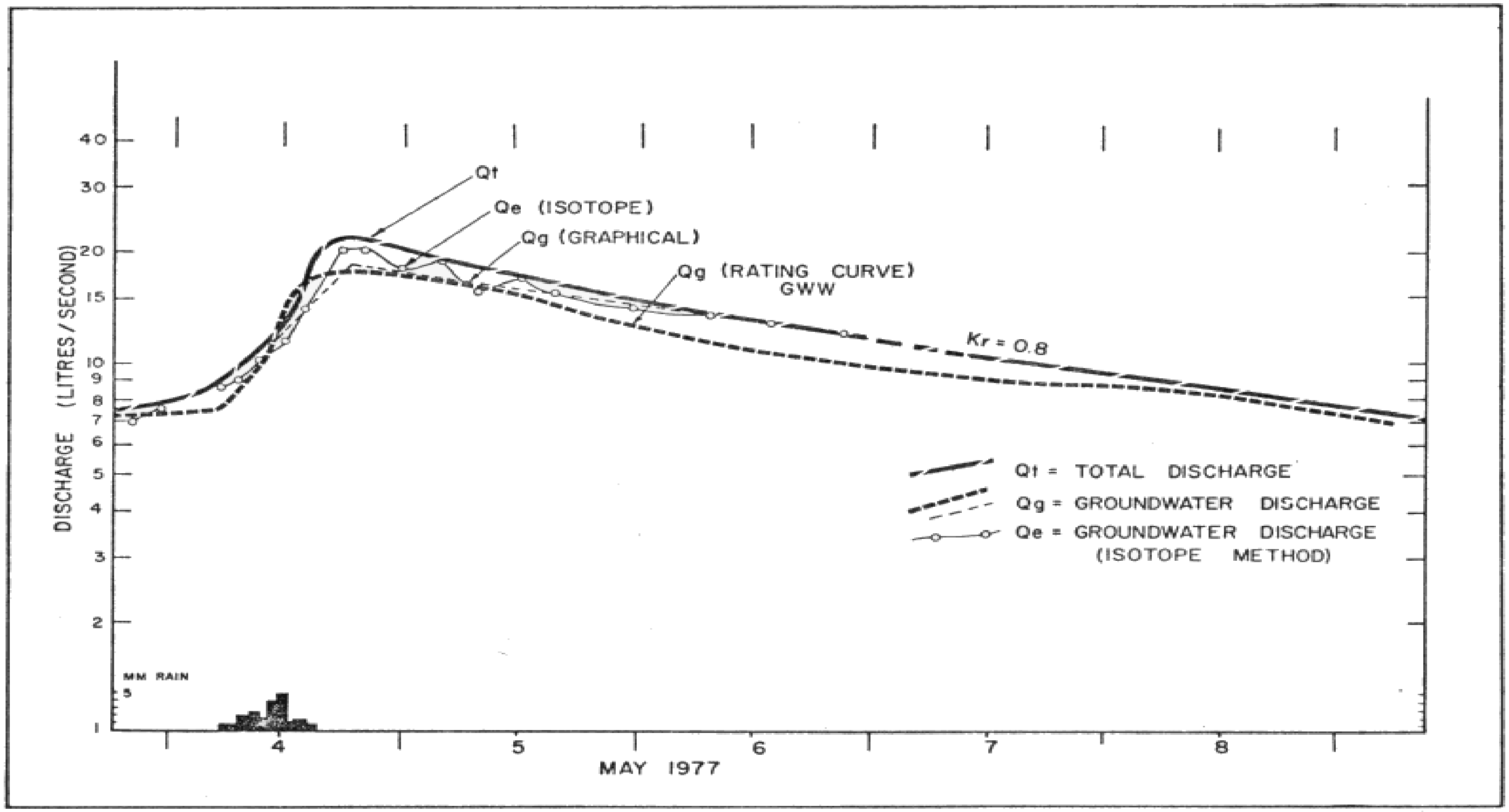

Figure 10. Hydrograph separations by the isotope, rating curve and graphical methods for Hillman Creek, May 4-8, 1977.

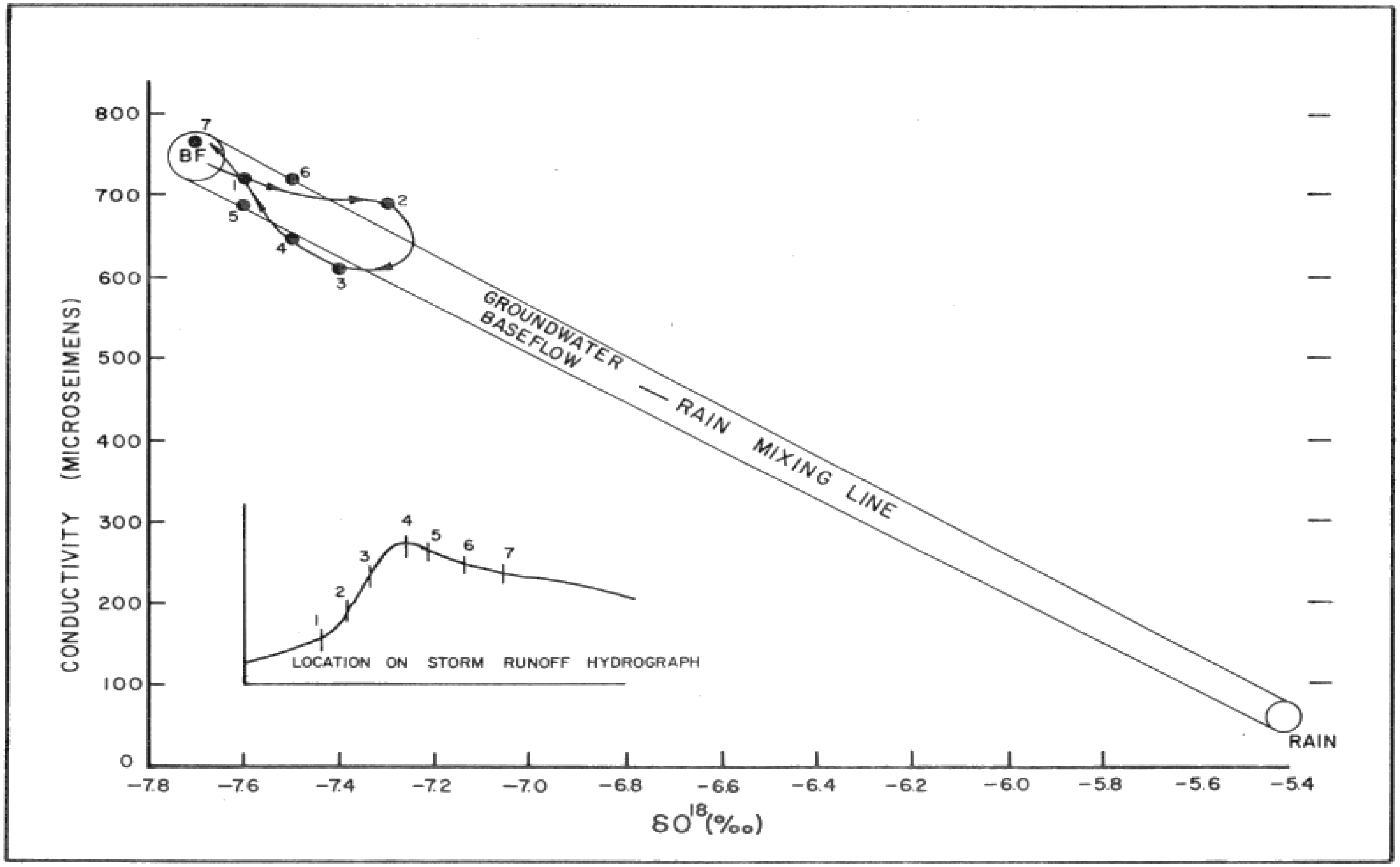

Figure 11. The relationship between oxygen-18 and conductivity in Hillman Creek, May 4-5, 1977.

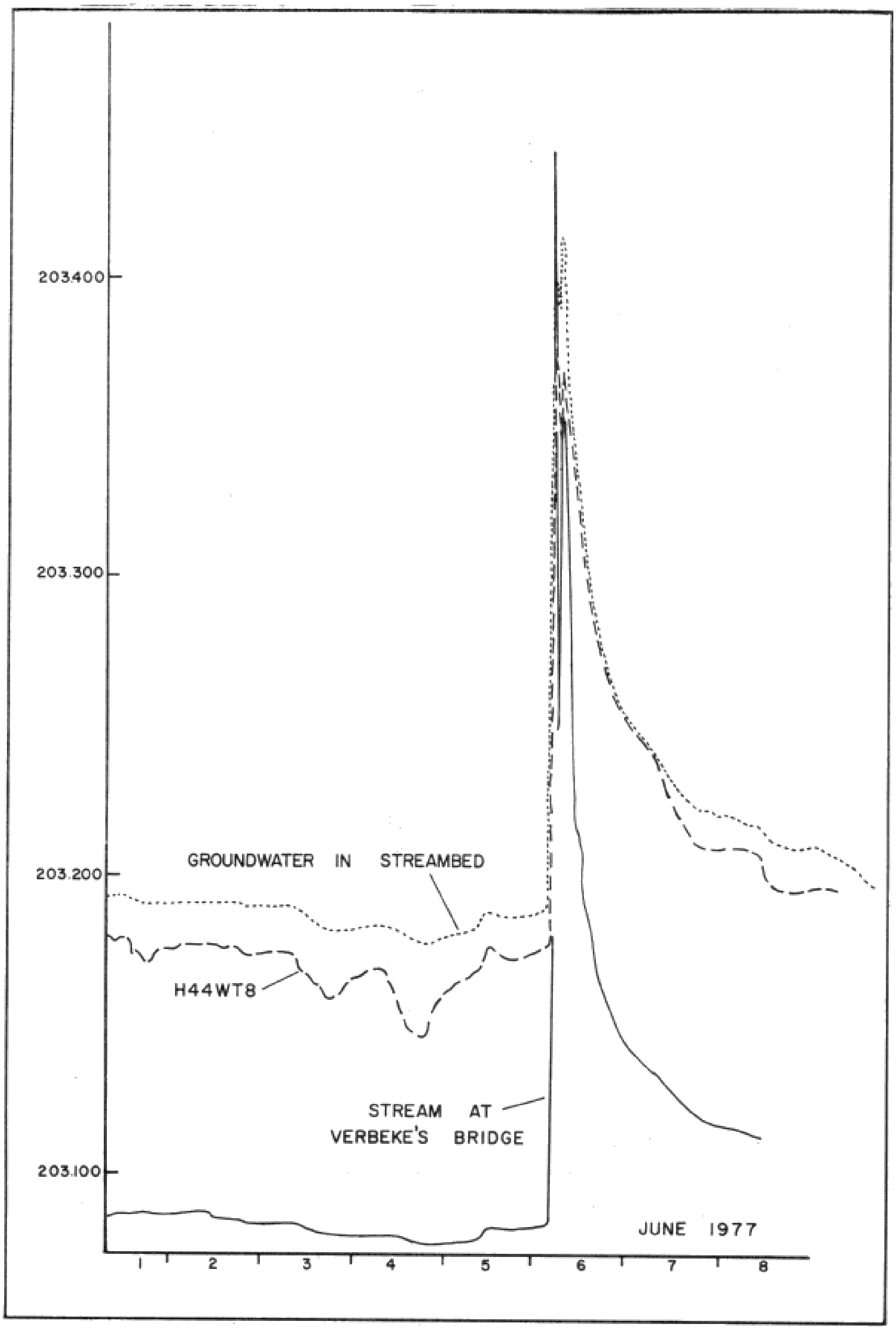

Figure 12. Stream and groundwater hydrographs for Hillman Creek, June 1-8,, 1977.

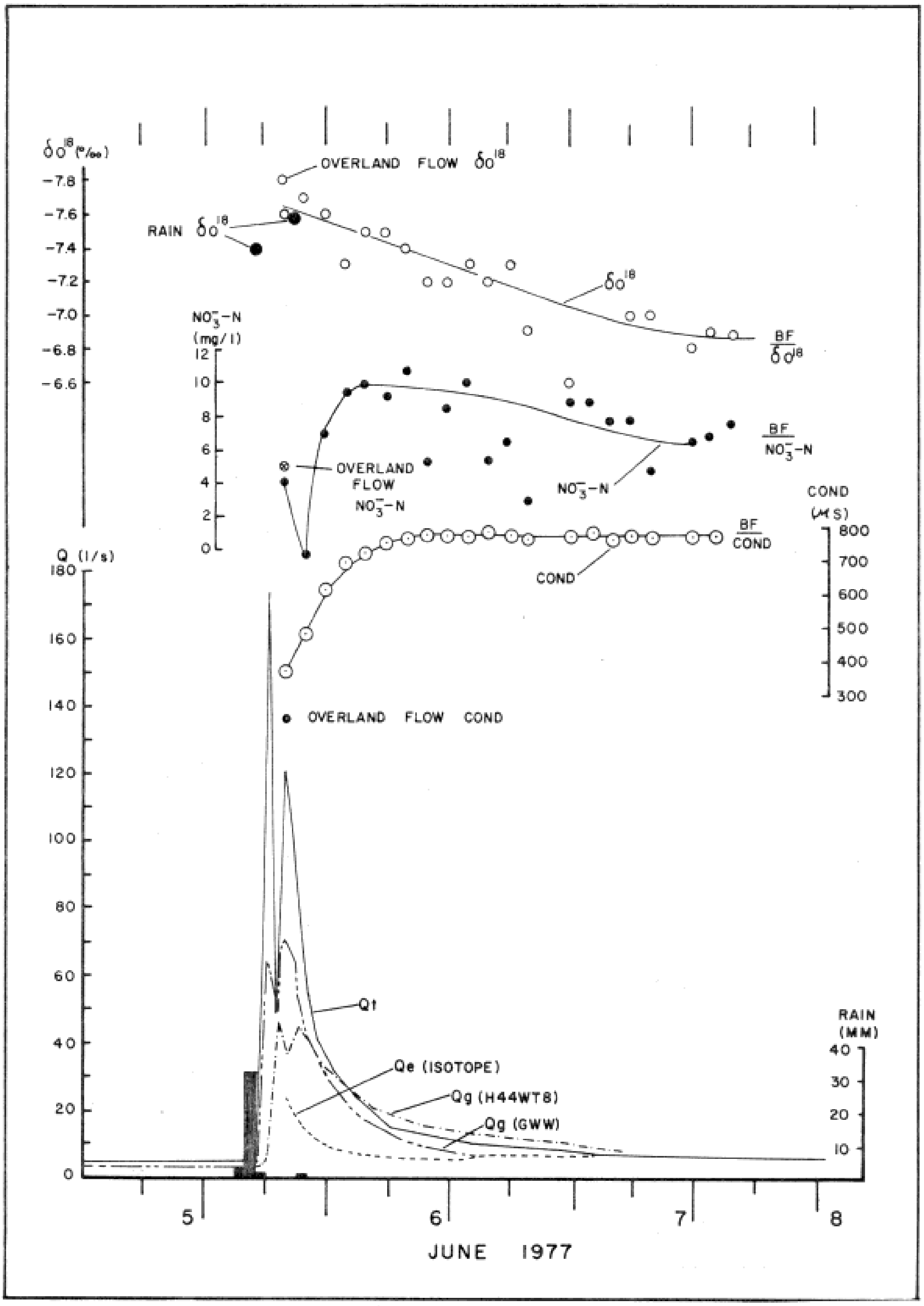

Figure 13. Temporal variations in stream discharge, oxygen-18, and conductivity, Hillman Creek, June 5-8, 1977.

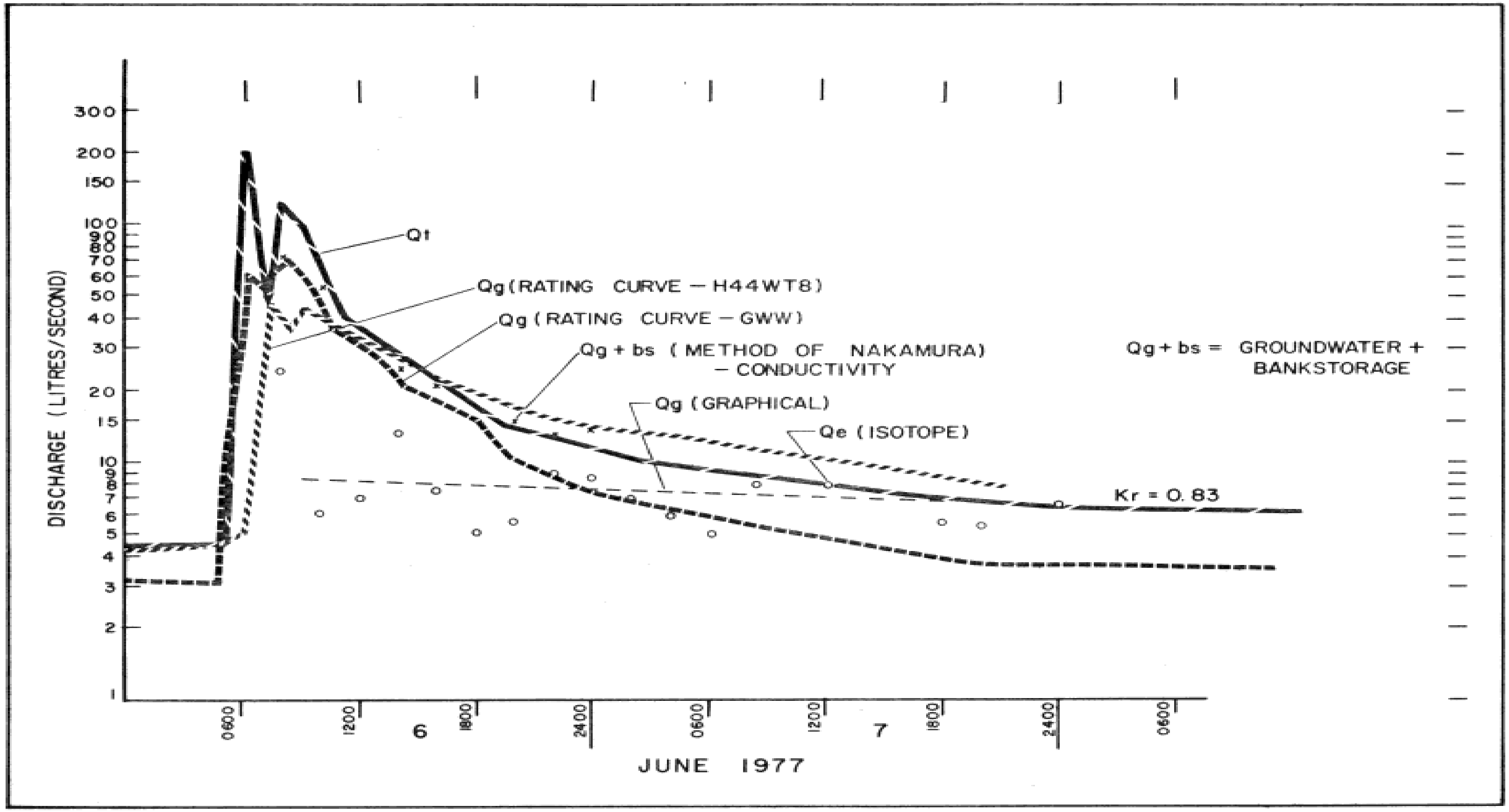

Figure 14. Hydrograph separations by the isotope, rating curve, graphical and Nakamura methods for Hillman Creek, June 6-8, 1977.

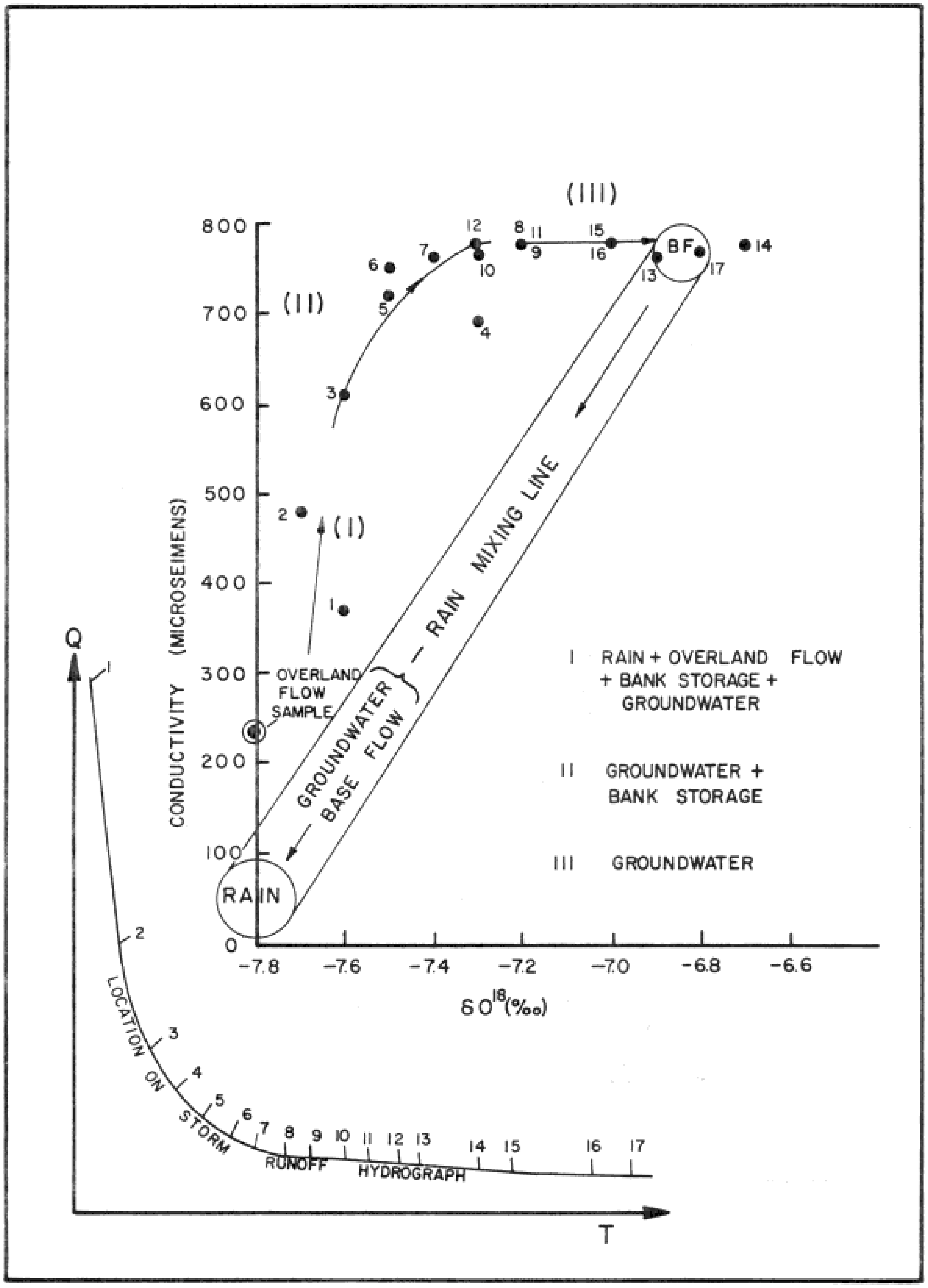

Figure 15. The relationship between oxygen-18 and stream discharge and conductivity and stream discharge in Hillman Creek, June 6-7, 1977.

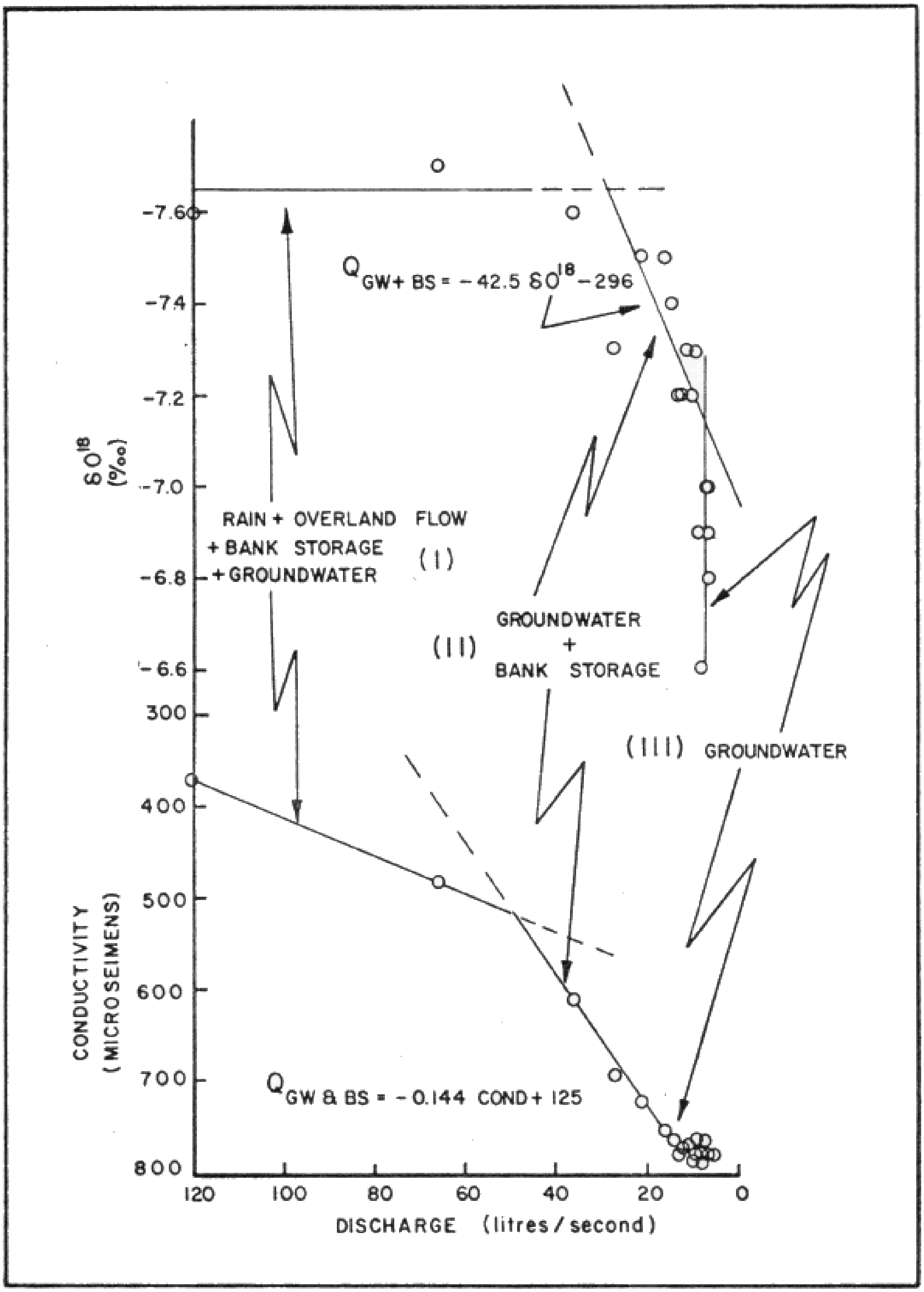

Figure 16. The relationships between oxygen-18 and stream discharge and conductivity and stream discharge in Hillman Creek, June 6-7, 1977.

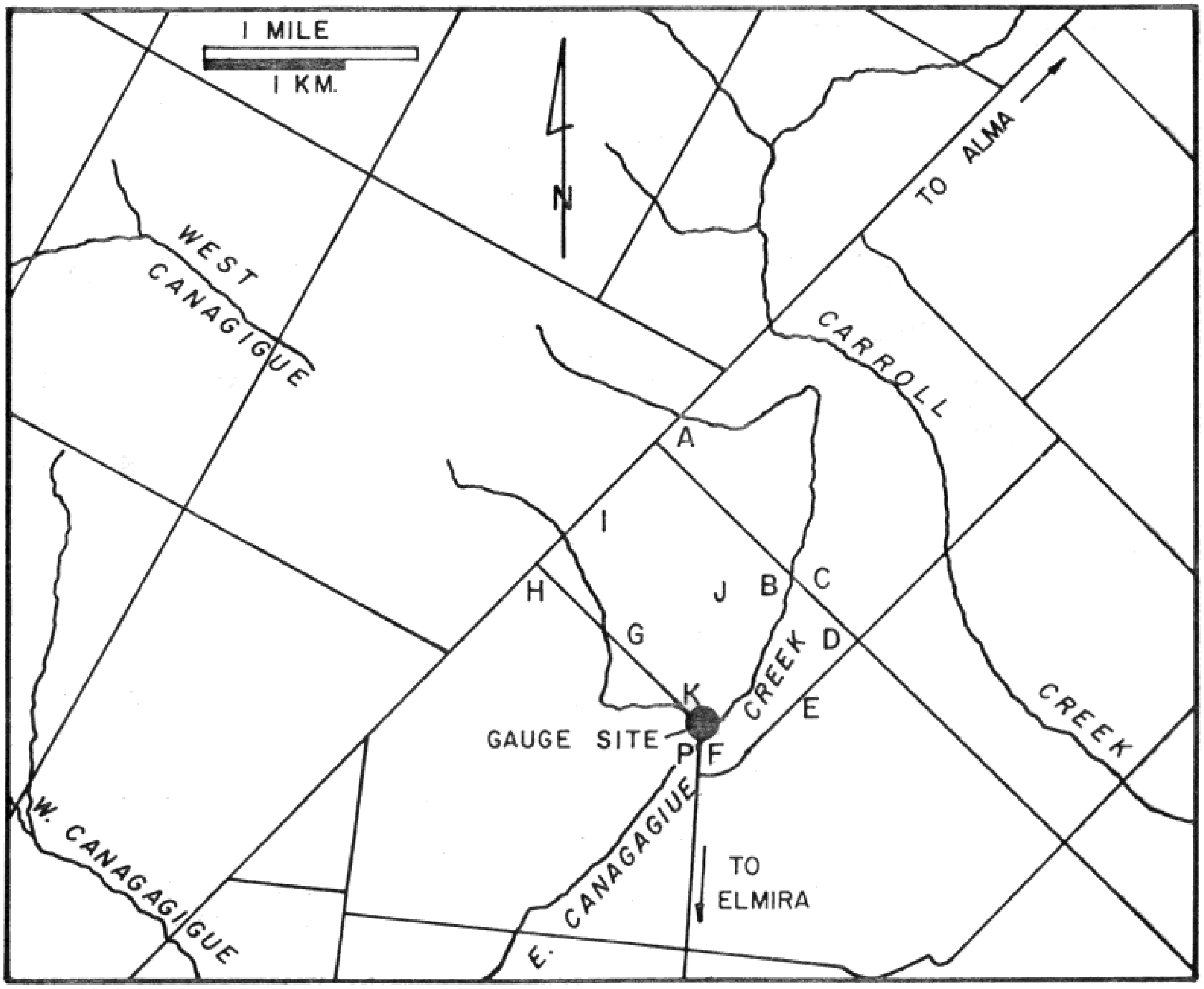

Figure 17. Location of snowmelt and snow sampling sites in the East Canagagigue Creek watershed

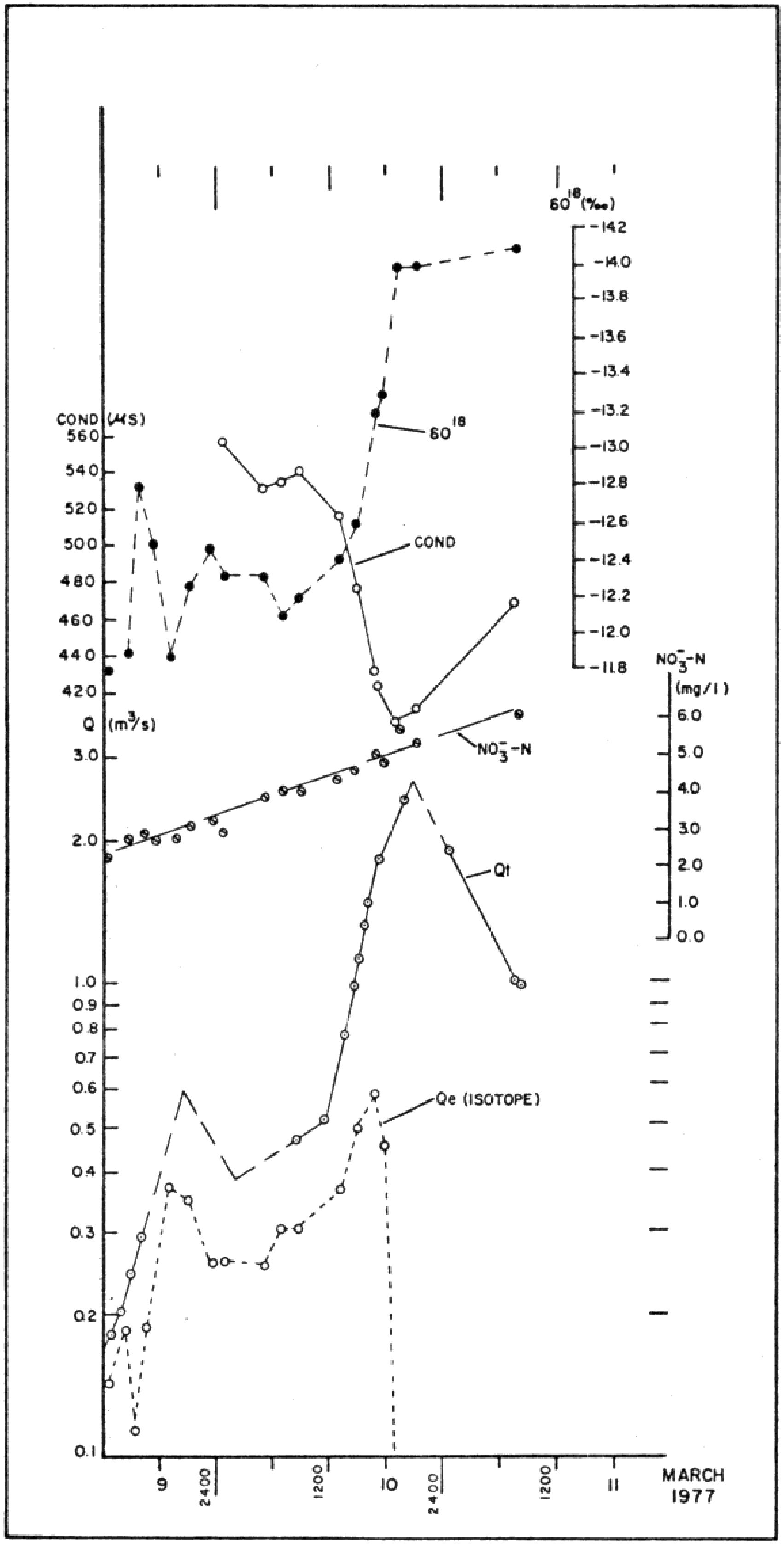

Figure 18. Temporal variations in stream discharge, oxygen-18, conductivity and nitrate in East Canagagigue Creek, March 9-11, 1977.

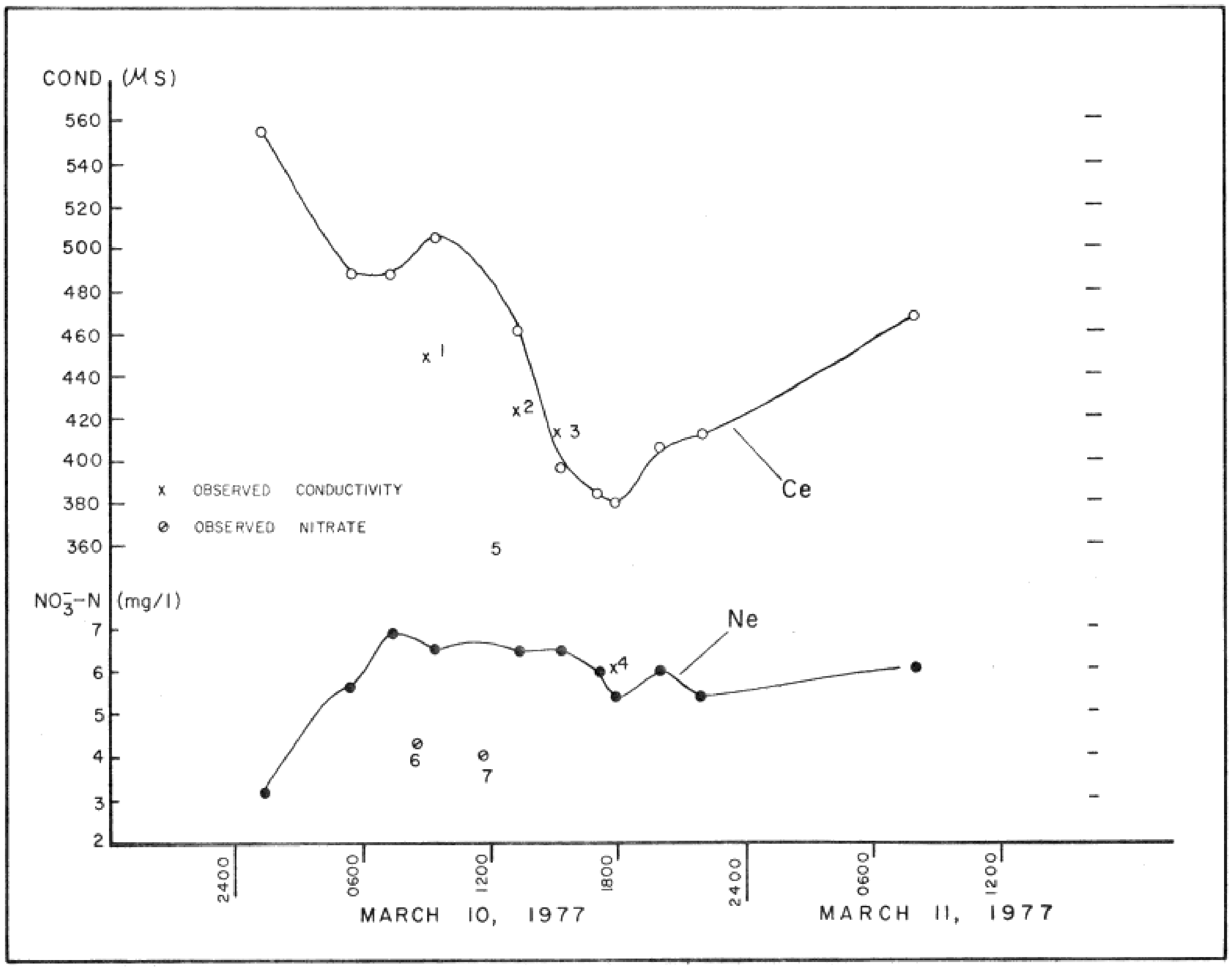

Figure 19. Temporal variations in the calculated basin average nitrate and conductivity of overland flow, East Canagagigue Creek, March 10-ll, 1977.

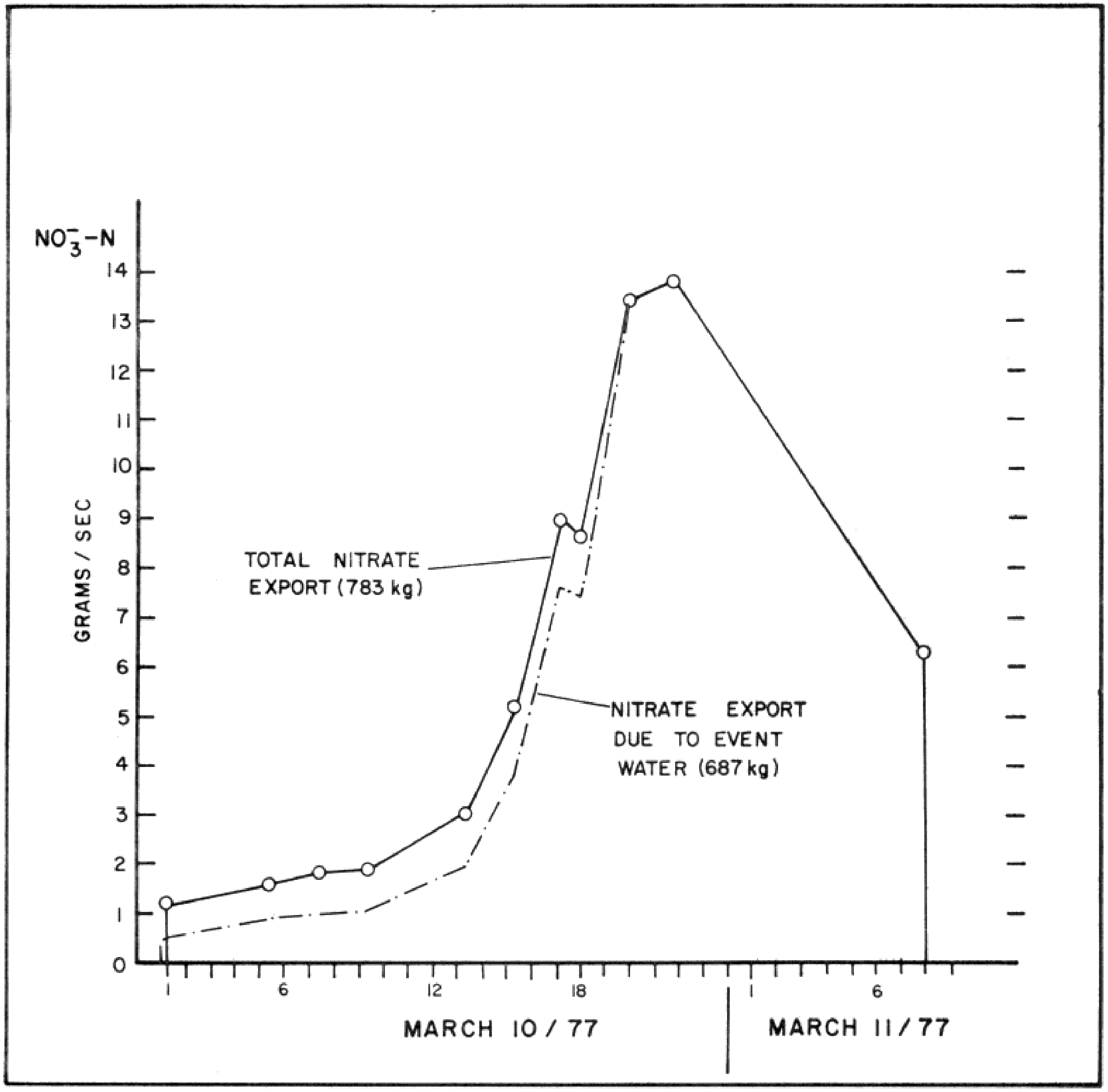

Figure 20. Nitrate export for snowmelt event on East Canagagigue Creek, March 10-11, 1977.

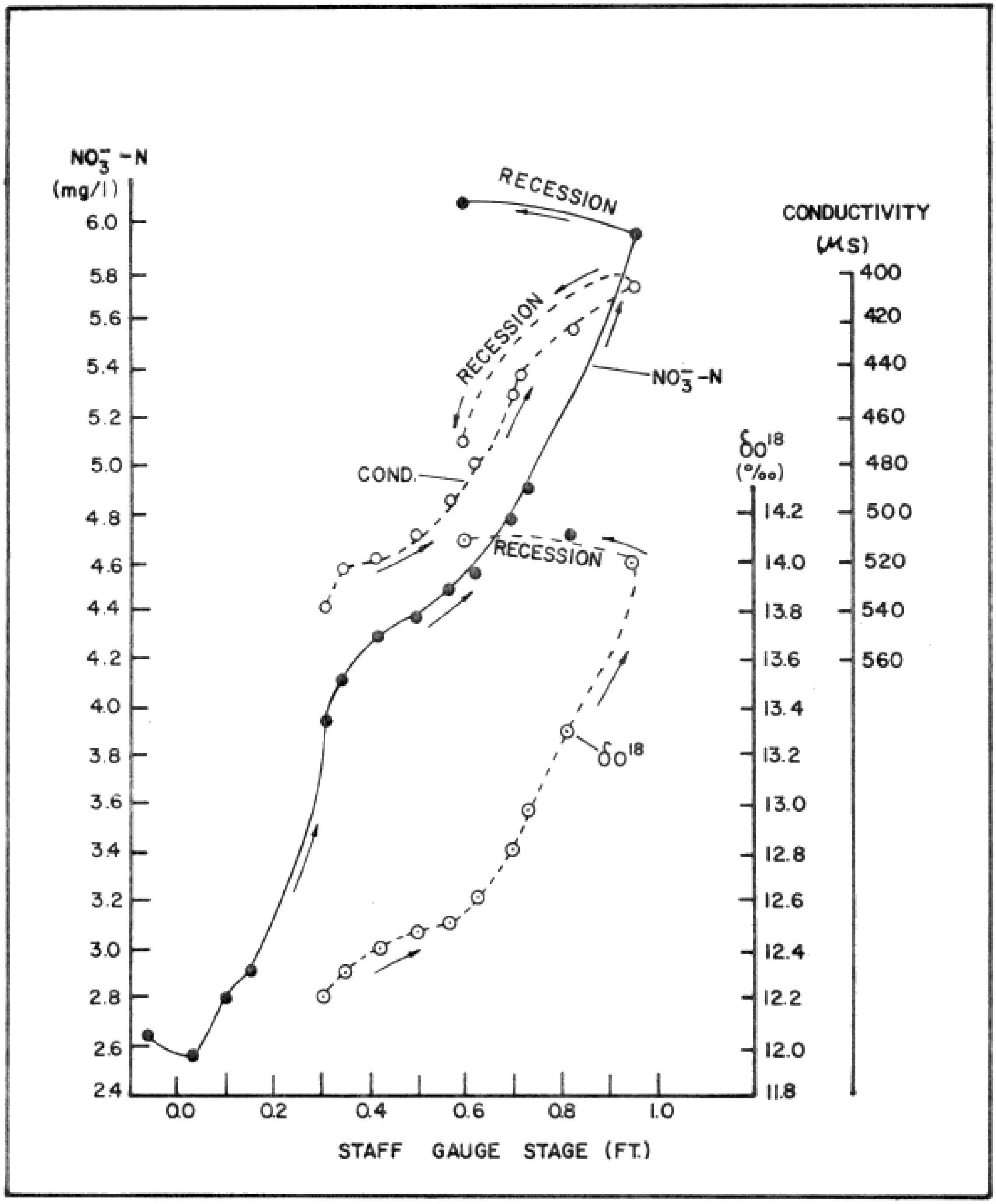

Figure 21. Variations in oxygen-18, conductivity and nitrate in the stream with stream stage, East Canagagigue Creek, March 10-11, 1977.

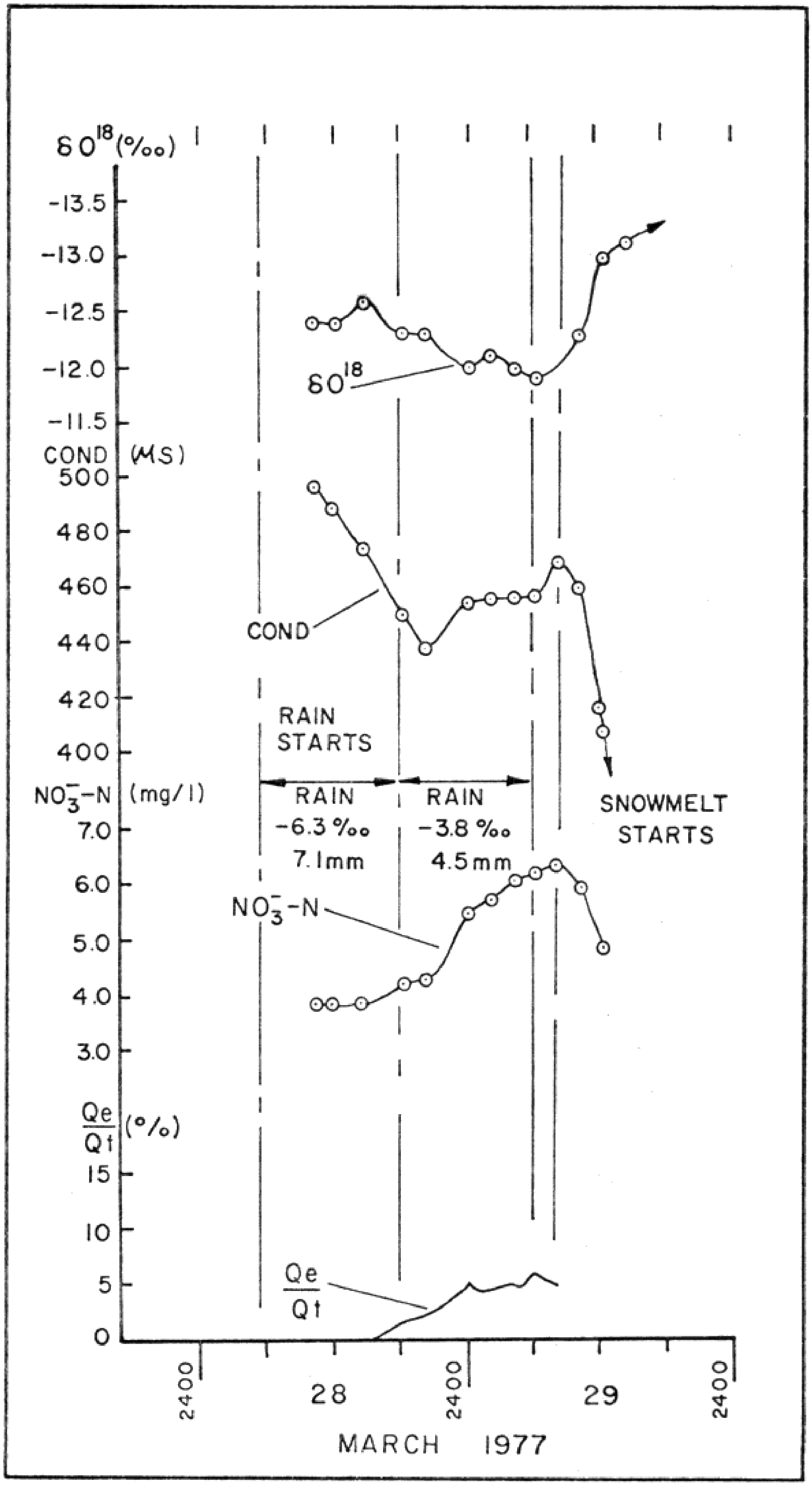

Figure 22. Temporal variations in oxygen-18, conductivity and nitrate in the stream and hydrograph separation (isotope technique) for East Canagagigue Creek, March 28-29, 1977.

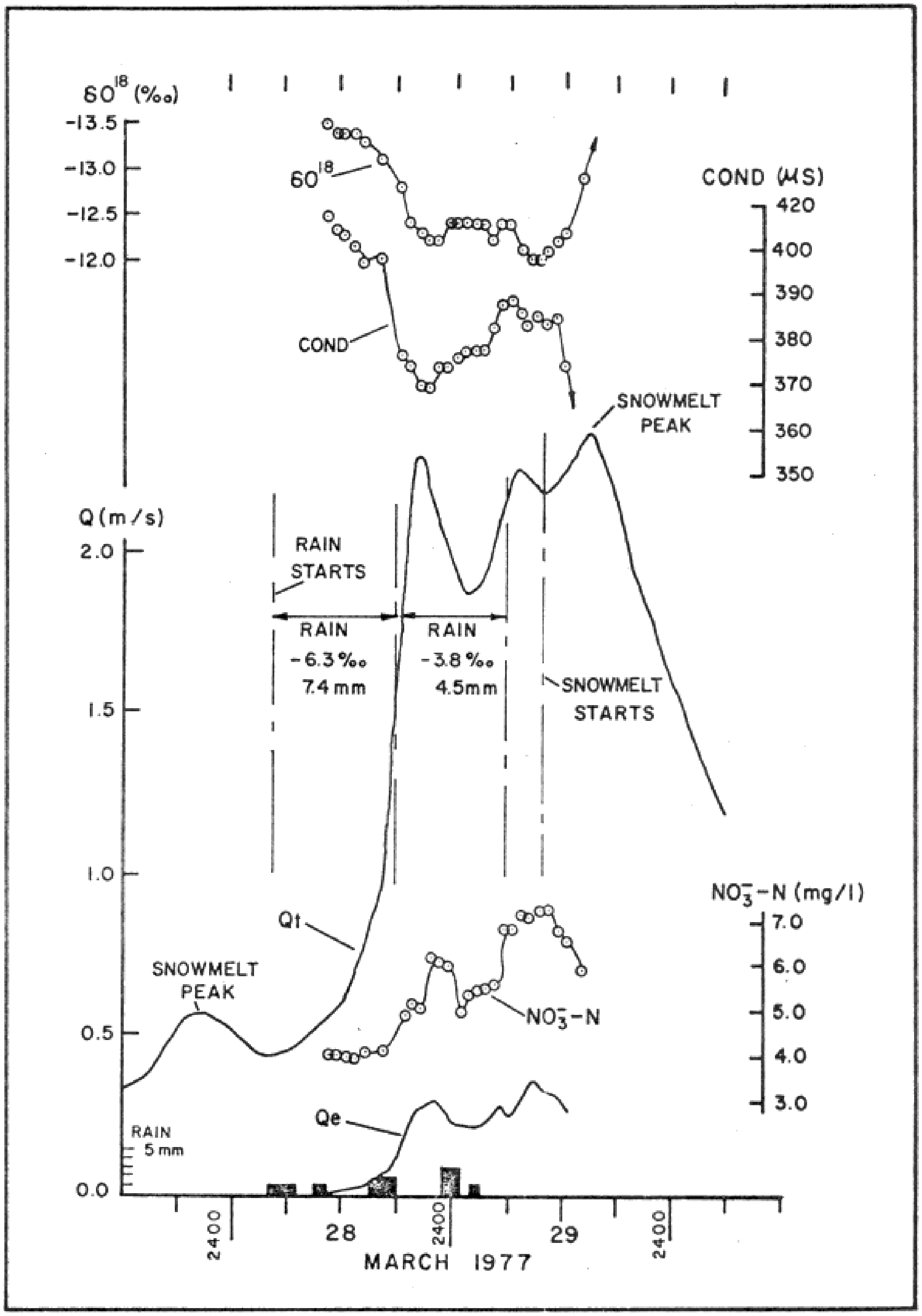

Figure 23. Temporal variations in stream discharge, oxygen-18, conductivity and nitrate and hydrograph separation (isotope technique) for East Canagagigue Creek, March 28-29, 1977.

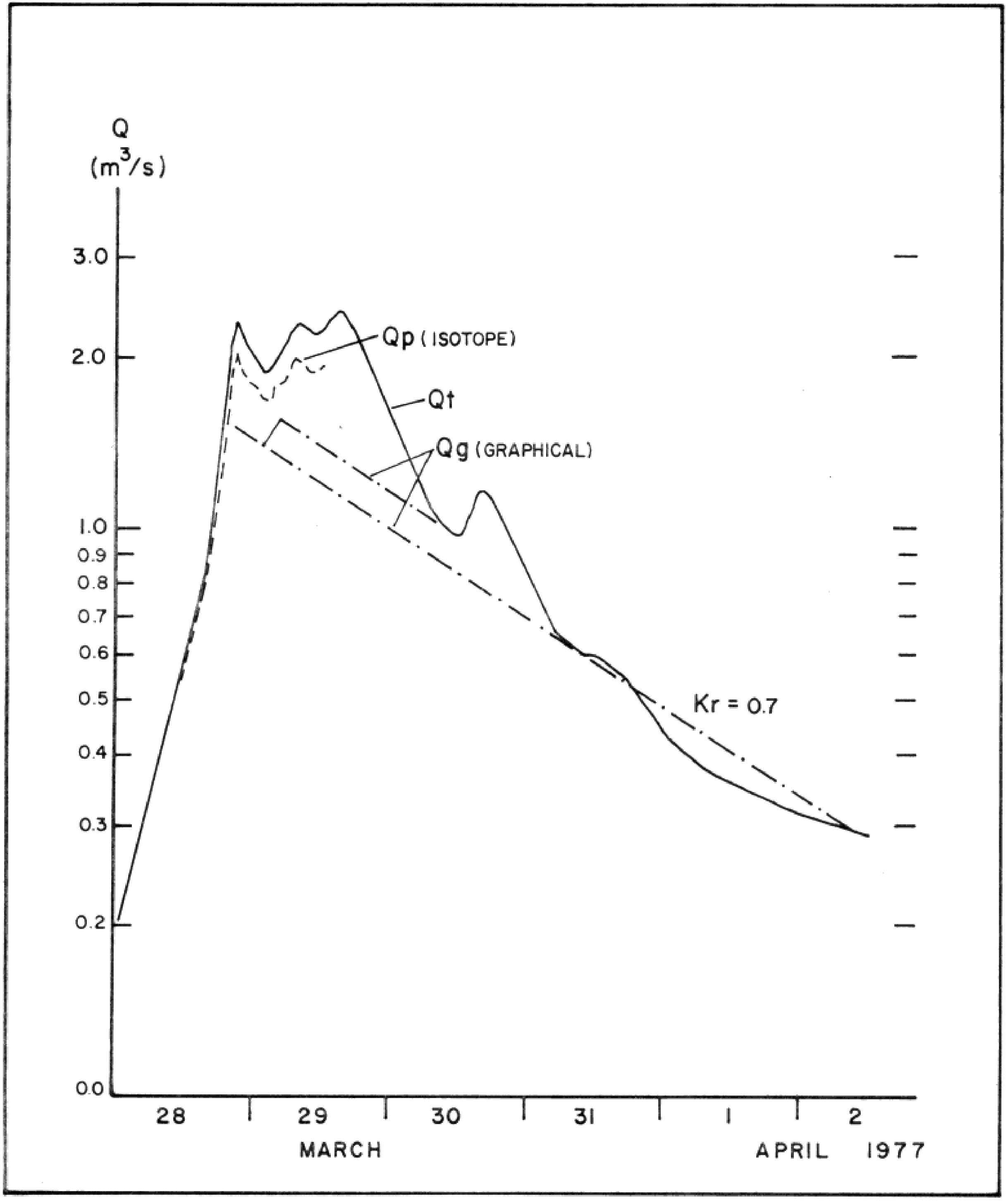

Figure 24. Hydrograph separations by the isotope and graphical techniques for West Canagagigue Creek, March 28-29, 1977.

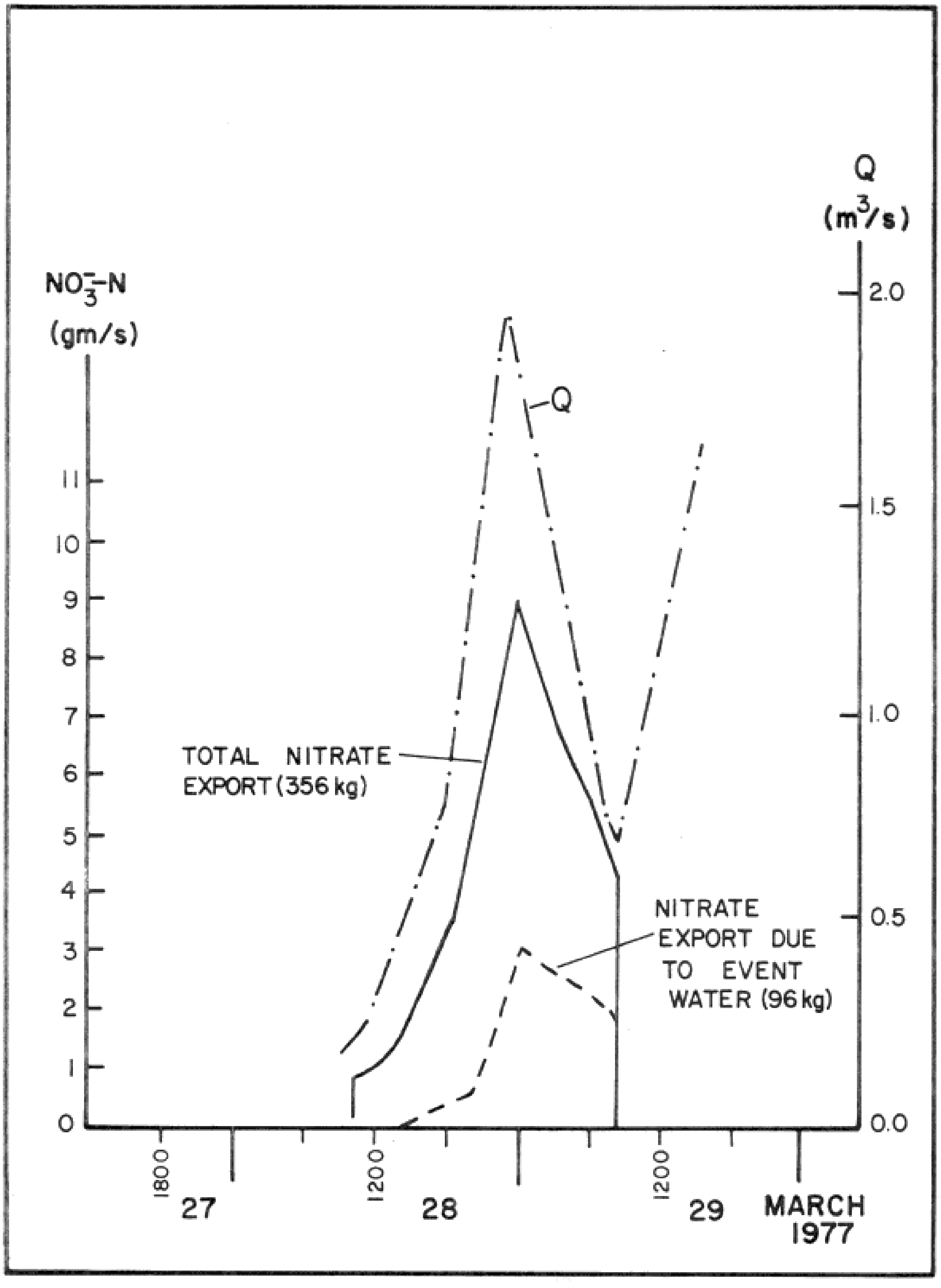

Figure 25. Nitrate export for rain event on East Canagagigue Creek, March 28-29, 1977.

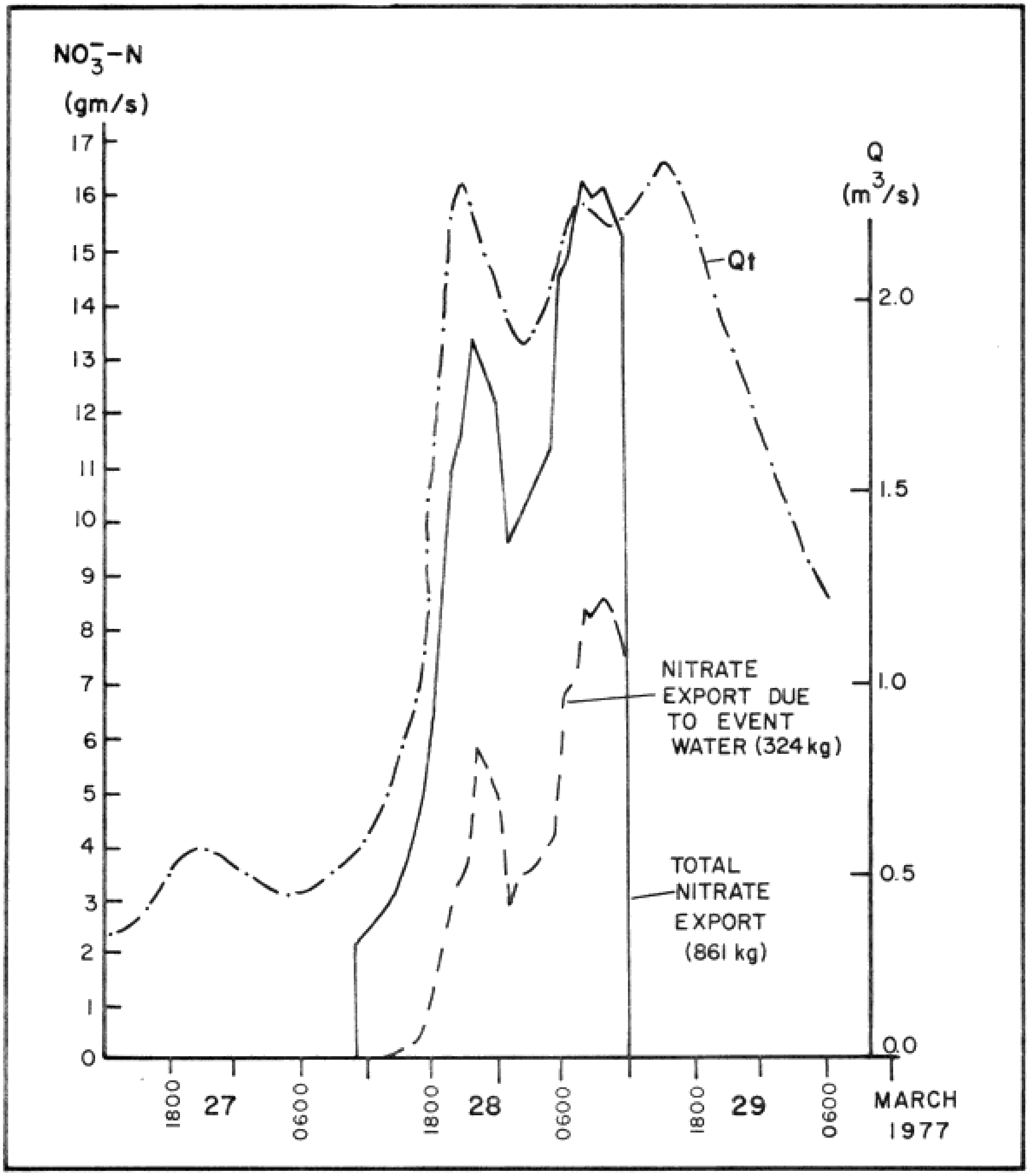

Figure 26. Nitrate export for rain event on West Canagagigue Creek, March 28-29, 1977.

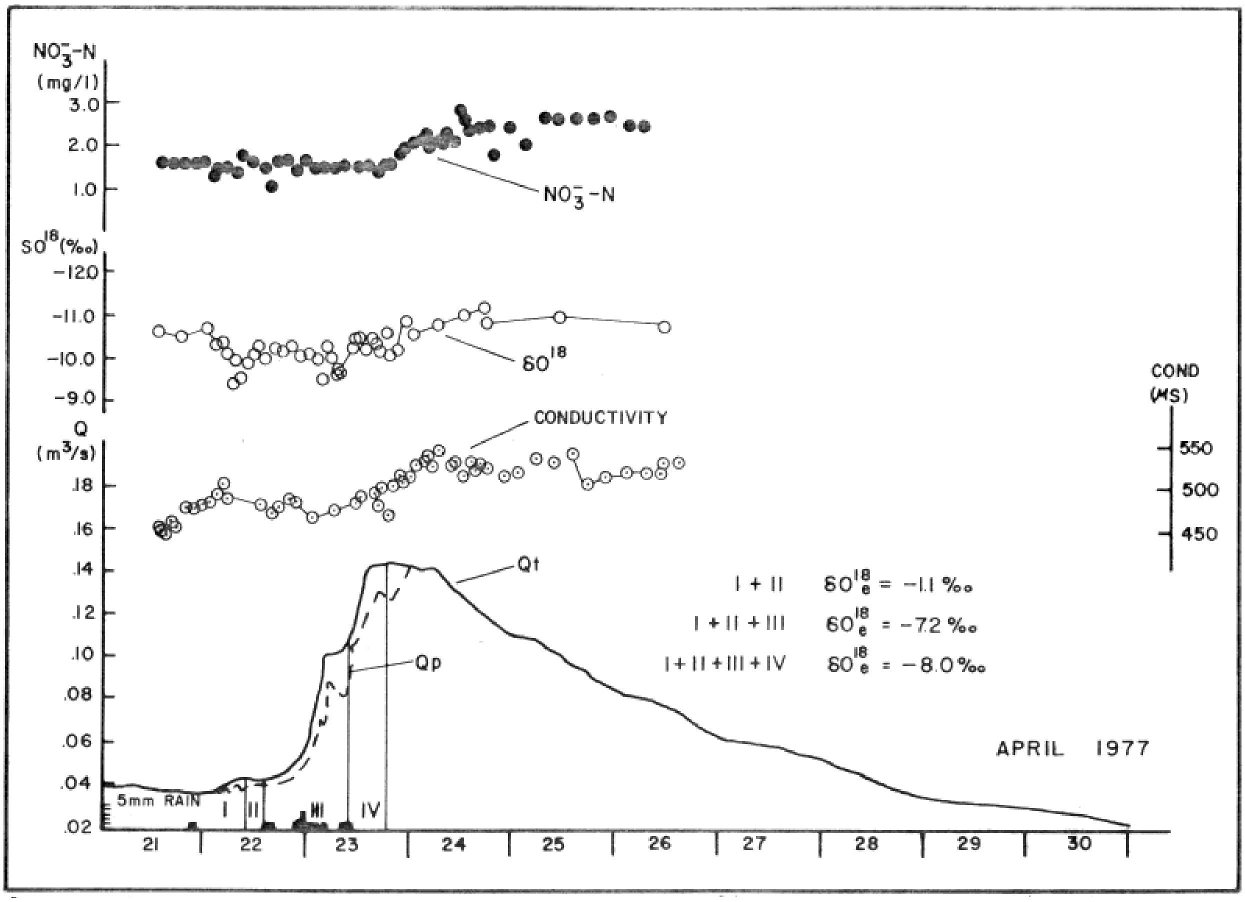

Figure 27. Temporal variations in stream discharge, oxygen-18, conductivity, and nitrate and hydrograph separation (isotope technique), West Canagagigue Creek, April 21-30, 1977.

APPENDIX A - SAMPLE ANALYSES

WATERSHED LOCATION: HILLMAN CREEK, ESSEX COUNTY, ONTARIO

SAMPLE NUMBER	LOCATION AND TYPE	HOUR	DAY	MO	YR	OXYGEN-16 (PARTS/MIL)	CONDUCTIVITY (US)	NITRATE (MG/L)
1	SNOW NEAR WEIR		22	02	77	-24.9		
2	SNOW AT WEIR		22	02	77	-14.7		
3	SNOW AT H44 WT8		22	02	77	-19.6		
4	SNOW NEAR H44WT8		22	02	77	-7.5		
5	H25P11 GROUNDWATER	1500	22	02	77	-9.1		
6	H25WT8 GROUNDWATER	1500	22	02	77	-8.3		
7	H44WT8 GROUNDWATER	1500	22	02	77	-8.9		
8	H38P14 GROUNDWATER	1420	22	02	77	-9.4		
9	H38P20 GROUNDWATER	1420	22	02	77	-8.9		
10	WEIR STREAM	1115	22	02	77	-8.8		
11	STREAM AT H44	1515	22	02	77	-12.2		
12	STREAM AT H44	1615	22	02	77	-11.9		
13	OVERLAND FLOW AT H44	1525	22	02	77	-15.2		
14	OVERLAND FLOW AT WEIR	1750	22	02	77	-15.5		
15	WEIR STREAM	1745	22	02	77	-11.3		
16	TILE DRAIN ATH44	1620	22	02	77	-8.7		
17	WEIR 2 STREAM	1150	04	03	77			2.8
16	WEIR 2 STREAM	1350	04	03	77			1.4
19	WEIR 2 STREAM	1550	04	0.3	77	-9.5		2.5
20	WEIR 2 STREAM	1750	04	03	77			2.9
21	WEIR 2 STREAM	1950	04	03	77			3.3
22	WEIR 2 STREAM	2150	04	03	77			3.3
23	WEIR 2 STREAM	2350	04	03	77			2.4
24	WEIR 2 STREAM	0150	05	03	77	-10.0		4.0
25	WEIR 2 STREAM	0350	05	03	77			3.4
26	WEIR 2 STREAM	0550	05	03	77			3.1
27	WEIR 2 STREAM	0750	05	03	77			2.7
28	WEIR 2 STREAM	0950	05	03	77			3.6
29	WEIR 2 STREAM	1350	05	03	77			2.9
30	WEIR STREAM	1100	04	03	77	-10.9		1.9
31	WEIR STREAM	0925	05	03	77	-9.7		3.1
32	OVERLAND FLOW N OF WHITTLE’S	1100	04	03	77	-10.3		4.1
33	OVERLAND FLOW ON WHITTLE’S	1110	04	03	77	-10.1		3.3
34	OVERLAND FLOW AT H44	1230	04	03	77	-9.1		3.0
35	OVERLAND FLOW N OF H44	1230	04	03	77	-9.3		2.0
36	H25WT8 GROUNDWATER	1240	04	03	77	-8.4		0.2
37	H38P20 GROUNDWATER	1300	04	03	77	-9,2		0.2
38	H44P8 GROUNDWATER	1250	04	03	77	-9.4		0.1
39	H25P8 GROUNDWATER	1240	04	03	77			0,1
40	H44P5 GROUNDWATER	1250	04	03	77	-9.2		0.1

APPENDIX A - SAMPLE ANALYSES

WATERSHED LOCATION. HILLMAN CREEK, ESSEX COUNTY, ONTARIO

SAMPLE NUMBER	LOCATION AND TYPE	HOUR	DAY	MO	YR	OXYGEN-18 (PARTS/MIL)	CONDUCTIVITY (US)	NITRATE (MG/L)
41	H38P14 GROUNDWATER	1300	04	03	77	-9.7		2.0
42	H25P11 GROUNDWATER	1240	04	03	77	-9.1		0.2
43	WEIR STREAM	1200	20	03	77	-8.5		4.8
44	WEIR STREAM	1600	31	03	77	-8.1		5.3
45	TILE DRAIN AT H44	1330	31	03	77	-8.1		9.3
46	WEIR STREAM	1120	14	04	77		694	
47	WEIR STREAM	1200	15	04	77		500	3.9
48	WEIR STREAM	1030	16	04	77	-8.1	697	4.5
48	WEIR STREAM	1050	17	04	77		611	3.1
50	WEIR STREAM	1215	18	04	77		681	
51	WEIR STREAM	1455	20	04	77		558	2.6
52	WEIR STREAM	1625	21	04	77		569	
53	WEIR STREAM	0930	22	04	77		594	
54	WEIR STREAM	1500	23	04	77	-6.0	711	7.6
55	WEIR STREAM	1200	24	04	77		525	9.6
56	WEIR STREAM	0830	25	04	77		669	
57	WEIR STREAM	1205	25	04	77	-9.0	668	
58	WEIR STREAM	1520	25	04	77	-9.2	668	8.3
59	VERBEKE BRIDGE STREAM	1510	11	04	77	-7.2	667	5.5
60	VERBEKE BRIDGE STREAM	1220	15	04	77		763	3.8
61	VERBEKE BRIDGE STREAM	1110	17	04	77	-6.9	558	3.4
62	VERBEKE BRIDGE STREAM	0630	18	04	77	-7.7	805	6.5
63	VERBEKE BRIDGE STREAM	1200	19	04	77	-6.8	764	4.7
64	VERBEKE BRIDGE STREAM	0825	20	04	77	-6.6	444	
65	VERBEKE BRIDGE STREAM	1130	14	04	77	-7.7	784	5.0
66	VER3EKE BRIDGE STREAM	1655	21	04	77	-6.9	668	
67	VERBEKE BRIDGE STREAM	0910	22	04	77	-6.7	679	3.3
68	VERBEKE BRIDGE STREAM	0625	22	04	77		525	2.1
69	VERBEKE BRIDGE STREAM	1100	22	04	77		707	4.4
70	VERBEKE BRIDGE STREAM	0335	23	04	77		660	10.5
71	VERBEKE BRIDGE STREAM	1325	23	04	77		711	2.6
72	VERBEKE BRIDGE STREAM	1125	24	04	77		583	
73	VERBEKE BRIDGE STREAM	0125	25	04	77	-8.5	722	8.1
74	VERBEKE BRIDGE STREAM	0900	25	04	77	-7.8	736	8.0
75	VERBEKE BRIDGE STREAM	0940	25	04	77	-8.2	738	
76	VERBEKE BRIDGE STREAM	1100	25	04	77	-8.2	726	8.7
77	VERBEKE: BRIDGE STREAM	1115	25	04	77	-8.4	732	
78	VERBEKE BRIDGE STREAM	1140	25	04	77	-8.5	735	5.9
79	VERBEKE BRIDGE STREAM	1230	25	04	77	-8.5	721	
80	VERBEKE BRIDGE STREAM	1300	25	04	77	-8.5	710	8.2

APPENDIX A - SAMPLE ANALYSES

WATERSHED LOCATION: HILLMAN CREEK, ESSEX COUNTY, ONTARIO

SAMPLE NUMBER	LOCATION AND TYPE		HOUR	DAY	MO	YR	OXYGEN-18 (PARTS/MIL)	CONDUCTIVITY (US)	NITRATE (MG/L)
81	VERBEKE BRIDGE STREAM		1500	25	04	77	-8.9	694	8.4
82	VERBEKE BRIDGE STREAM		1545	25	C4	77	-8.4	693	6.0
83	VERBEKE BRIDGE STREAM		1630	25	04	77	-8.8	695	8.3
85	RAIN AT VERBEKE'S BRIDGE	TO	1030	25	04	77	-17.4	22	
86	PAINAT VERBEKE'S BRIDGE	TO	1230	25	04	77	-19.4	45	
87	RAIN AT VERBEKE'S BRIDGE	TO	1545	25	04	77	-19.0	21	
88	RAIN AT WHITTLE'S FARM	TO	0830	25	04	77	-16.5	41	
99	RAIN AT WHITTLE'S FARM	TO	1205	25	04	77	-18.6	38	
90	RAIN AT WHITTLE'S FARM	TO	1522	25	04	77	-19.2	82	
91	RAIN AT VERBEKE'S HOUSE	TO	0950	25	04	77	-17.2		0.6
92	RAIN AT VERBEKE'S HOUSE	TO	1230	25	04	77	-19.8		0.5
93	RAIN AT VERBEKE'S HOUSE	TO	1535	25	04	77	-18.8		
94	RAIN FROM VERBEKE'S EAVES	AT	1225	25	04	77	-20.0	12	
95	TILE DRAIN ATWHITTLE'S		1525	25	04	77	-9.5	626	62.7
96	OVERLAND FLOW - WHITTLE'S		0915	25	04	77	-16.7	67	
97	OVERLAND FLOW- WHITTLE'S		120G	25	04	77	-18.1	40	2.9
98	OVERLAND FLOW - WHITTLE'S		1515	25	04	77	-17.6	89	
99	OVERLAND FLOW AT VERBEKE'S BR.		1030	25	04	77	-11.8	615	7.7
100	OVERLAND FLOW AT VERBEKE'S BR.		1115	25	04	77	-12.3	569	7.9
101	OVERLAND FLOW AT VERBEKE'S BR.		1140	25	04	77	-12.6	528	9.6
102	OVERLAND FLOW AT VERBEKE'SBR.		1230	25	04	77	-12.7	483	6.2
103	OVERLAND FLOW AT VERBEKE'S BR.		1545	25	04	77	-10.9	638	8.5
104	OVERLAND FLOW AT VERBEKE'S BR.		1630	25	04	77	-10.3	664	8.0
105	OVERLAND FLOW N. OF WHITTLE'S		0910	25	04	77	-16.4	136	
106	OVERLAND FLOW N. OF WHITTLE'S		1205	25	04	77	-17.1	110	5.3
107	OVERLAND FLOW N. OF WHITTLE'S		1520	25	04	77	-17.5	54	5.8
111	RAIN FROM VERBBKE EAVES	AT	0915	25	04	77	-19.3	28	
112	OVERLAND FLOW WHITTLE’S FARM		1700	25	04	77	-16.8	122	
113	WEIR STREAM		1700	25	04	77	-9.5	654	
114	VERBEKE BRIDGE STREAM		0900	25	04	77	-7.8	753	
116	VERBEKE BRIDGE STREAM		2100	25	04	77	-8.0	744	6.6
117	VERBEKE BRIDGE STREAM		0300	26	04	77		750	
118	VERBEKE BRIDGE STREAM		0900	26	04	77		751	2.2
119	VERBEKE BRIDGE STREAM		1500	26	04	77		753	5.8
120	VERBEKE BRIDGE STREAM		2100	26	04	77		751	6.0
121	VERBEKE BRIDGE STREAM		0300	27	04	77		757	5.4
122	VERBEKE BRIDGE STREAM		0700	27	04	77		761	7.3
123	VERBEKE BRIDGE STREAM		1300	28	04	77		778	5.6
124	WEIR STREAM		1100	28	04	77		708	
125	WEIR STREAM		1550	29	04	77		708	6.4

APPENDIX A - SAMPLE ANALYSES

WATERSHED LOCATION: HILLMAN CREEK, ESSEX COUNTY, ONTARIO

SAMPLE NUMBER	LOCATION AND TYPE		HOUR	DAY	MD	YR	OXYGEN-18 (PARTS/MIL)	CONDUCTIVITY (US)	NITRATE (MG/L)
126	WEIR STREAM		1150	30	04	77		708	6.3
127	WEIR STREAM		1120	01	05	77		704	6.4
128	WEIR STREAM		1335	02	05	77		699	
129	WEIR STREAM		1235	03	05	77		696	5.5
130	WEIR STREAM		0900	04	05	77		683	6.2
131	WEIR STREAM		1120	05	05	77		691	7.0
132	WEIR STREAM		0935	06	05	77		704	6.5
133	WEIR STREAM		1015	07	05	77		688	4.6
134	RAIN AT VERBEKE HOUSE	TO	0900	04	05	77	-5.3	69	
135	RAIN FROM VERBEKE EAVES	AT	0850	04	05	77	-5.9	44	0.5
136	RAIN AT WEIR	TO	0900	04	05	77	-5.8	75	
137	VERBEKE BRIDGE STREAM		0915	05	05	77		784	
138	RAIN AT VERBEKE BRIDGE			04	05	77	-5.2		
139	VERBEKE BRIDGE STREAM								
139	VERBEKE BRIDGE STREAM		1620	29	04	77	-8.4	749	6.5
140	VERBEKE BRIDGE STREAM		1205	30	04	77	-7.6	765	
141	VERBEKE BRIDGE STREAM		1240	01	05	77	-7.6	801	
142	VERBEKE BRIDGE STREAM		1300	02	05	77	-7.6	813	
143	VERBEKE BRIDGE STREAM		1500	02	05	77		722	6.2
144	VERBEKE BRIDGE STREAM		1900	02	05	77		761	
145	VERBEKE BRIDGE STREAM		2100	02	05	77		750	6.8
146	VERBEKE BRIDGE STREAM		2300	02	05	77		764	7.2
147	VERBEKE BRIDGE STREAM		0300	03	05	77	-7.5	771	
148	VERBEKE BRIDGE STREAM		0700	03	05	77		764	
149	VERBEKE BRIDGE STREAM		0900	03	05	77	-7.6	713	4.2
150	VERBEKE BRIDGE STREAM		1100	03	05	77		760	
151	VERBEKE BRIDGE STREAM		1205	03	05	77		771	
152	VERBEKE BRIDGE STREAM		1300	03	05	77	-7.8	750	
153	VERBEKE BRIDGE STREAM		1500	03	05	77		736	4.9
154	VERBEKE BRIDGE STREAM		1700	03	05	77	-7.8	778	
155	VERBEKE BRIDGE STREAM		2100	03	05	77	-7.5	749	6.2
156	VERBEKE BRIDGE STREAM		2300	03	05	77	-7.8	753	6.5
158	VERBEKE BRIDGE STREAM		0500	04	05	77	-7.7	760	6.2
159	VERBEKE BRIDGE STREAM		0700	04	05	77	-7.5	771	7.1
160	VERBEKE BRIDGE STREAM		0900	04	05	77	-7.6	722	4.9
161	VERBEKE BRIDGE STREAM		1140	04	05	77	-7.3	693	5.9
162	VERBEKE BRIDGE STREAM		1340	04	05	77	-7.4	610	4.3
163	VERBEKE BRIDGE STREAM		1740	04	05	77	-7.5	647	6.1
164	VERBEKE BRIDGE STREAM		1940	04	05	77	-7.6	688	6.8
165	VERBEKE BRIDGE STREAM		2340	04	05	77	-7.5	722	7.2

APPENDIX A - SAMPLE ANALYSES

WATERSHED LOCATION: HILLMAN CREEK, ESSEX COUNTY, ONTARIO

SAMPLE LOCATION NUMBER AND TYPE		HOUR	DAY	MO	YR	OXYGEN-18 (PARTS/MIL)	CUNDUCTIVITY (US)	NITRATE (MG/L)
166	VERBEKE BRIDGE STREAM	0340	05	05	77	-7.7	765	
167	VERBEKE BRIDGE STREAM	0540	05	05	77		725	8.1
168	VERBEKE BRIDGE STREAM	0740	05	05	77	-7.4	750	4.5
169	VERBEKE BRIDGE STREAM	0940	05	05	77		771	5.6
170	VERBEKE BRIDGE STREAM	1200	05	05	77	-7.8	771	
171	VERBEKE BRIDGE STREAM	1340	05	05	77		771	6.7
172	VERBEKE BRIDGE STREAM	1540	05	05	77	-7.6	721	8.4
173	VERBEKE BRIDGE STREAM	2340	05	05	77	- 7.0	751	3.3
174	VERBEKE BRIDGE STREAM	0140	06	05	77		743	
175	VERBEKE BRIDGE STREAM	0740	06	05	77	-7.8	764	7.5
176	VERBEKE BRIDGE STREAM	0900	06	05	77		771	
177	VERBEKE BRIDGE STREAM	1300	06	05	77	-7.8	725	4.7
178	VERBEKE BRIDGE STREAM	1500	06	05	77		721	5.0
179	VERBEKE BRIDGE STREAM	1700	06	05	77	-7.5	711	
180	VERBEKE BRIDGE STREAM	1900	06	05	77		701	6.3
181	VERBEKE BRIDGE STREAM	2100	06	05	77	-7.7	722	5.5
183	VERBEKE BRIDGE STREAM	0107	06	05	77		771	4.5
184	VERBEKE BRIDGE STREAM	0507	06	05	77		778	4.5
185	VERBEKE BRIDGE STREAM	0707	06	05	77		771	5.8
186	VERBEKE BRIDGE STREAM	0907	06	05	77		729	6.2
187	TILL DRAIN ATH44	1345	13	05	77	-7.4	1021	
188	PIEZ A AT H44	1345	13	05	77	-9.5	618	
189	PIEZ E AT H44	1345	13	05	77	-10.7	653	
190	PIEZ C AT H44	1345	13	05	77	-9.9	667	
191	GW IN STREAMBED NEAR RECORDER	1325	13	05	77		646	
192	VERBEKE BRIDGE STREAM	1200	07	05	77	-7.3	882	5.6
193	VERBEKE BRIDGE STREAM	1200	08	05	77	-7.3	819	
194	VERBEKE BRIDGE STREAM	1330	08	05	77		819	11.2
195	VERBEKE BRIDGE STREAM	1215	09	05	77	-7.1		
196	VERBEKE BRIDGE STREAM	1715	09	05	77		833	6.6
197	VERBEKE BRIDGE STREAM	1200	11	05	77	-7.4	889	
198	VERBEKE BRIDGE STREAM	1210	12	05	77	-7.4	833	6.3
199	VERBEKE BRIDGE STREAM	1150	13	05	77		889	10.1
200	WEIR STREAM	0930	08	05	77		785	4.5
201	WEIR STREAM	1320	08	05	77		764	5.6
202	WEIR STREAM	1630	09	05	77		764	5.3
203	WEIR STREAM	1130	10	05	77		778	5.4
204	WEIR STREAM	1205	11	05	77	-7.4	778	5.5
205	WEIR STREAM	1240	12	05	77		771	5.0
206	WEIR STREAM	1100	13	05	77		771	

APPENDIX A - SAMPLE ANALYSES

WATERSHED LOCATION: HILLMAN CREEK, ESSEX COUNTY, ONTARIO

SAMPLE LOCATION NUMBER AND TYPE			HOUR	DAY	MO	YR	OXYGEN-18 (PARTS/MIL)	CONDUCTIVITY (US)	NITRATE (MG/L)
207	VERBEKE BRIDGE STREAM		1600	31	05	77	-6.3	754	0.9
208	VERBEKE BRIDGE STREAM		1700	31	05	77	-6.4	751	0.0
209	VERBEKE BRIDGE STREAM		1900	31	05	77	-6.3	705	3.0
210	VERBEKE BRIDGE STREAM		2100	31	05	77	-6.3	724	2.7
211	VERBEKE BRIDGE STREAM		0100	01	06	77	-6.6	749	0.0
212	VERBEKE BRIDGE STREAM		0300	01	06	77	-6.6	751	0.0
213	VERBEKE BRIDGE STREAM		0700	01	06	77	-6.7	753	0.0
214	VERBEKE BRIDGE STREAM		0900	01	06	77	-6.6	763	0.0
215	VERBEKE BRIDGE STREAM		1100	01	06	77	-6.7	743	0.0
216	PIEZ A		0900	01	06	77	-8.3	710	0.0
217	PIEZ B		0900	01	06	77	-8.8	757	0.0
218	PIEZ C		0900	01	06	77	-8.9	771	0.0
219	VERBEKE BRIDGE STREAM		1240	28	05	77	-6.7	708	4.3
220	VERBEKE BRIDGE STREAM		1240	29	05	77	-6.9	778	5.1
221	VERBEKE BRIDGE STREAM		1205	31	05	77	-6.7	747	5.1
222	WEIR STREAM		1155	26	05	77	-8.2	646	3.1
223	WEIR STREAM		1200	30	05	77	-8.2	679	2.9
224	WEIR STREAM		1215	31	05	77	-8.3	654	3.1
225	WEIR STREAM		1030	02	06	77	-8.1	674	0.0
226	RAIN VERBEKE HOUSE	AT	1700	31	05	77	-2.3		
227	RAIN VERBEKE SOUSE	AT	1800	31	05	77	-4.8	82	0.0
228	RAIN VERBEKE HOUSE	AT	1840	31	05	77	-6.4	110	
229	RAIN VERBEKE HOUSE	TO	0700	01	06	77	-5.0	119	
230	RAIN VERBEKE BRIDGE	TO	0730	01	06	77	-5.0		
231	RAIN AT WEIR	TO	1030	01	06	77	-3.5		
232	RAIN AT VERBEKE HOUSE	TO	0500	06	06	77	-7.4	49	
233	RAIN VERBEKE EAVES	AT	0855	06	06	77	-7.6	169	0.0
234	RAIN VERBEKE EAVES	AT	1030	06	06	77	-9.7	72	0.0
235	OVERLAND FLOW AT VERBEKE BR.		0600	06	06	77	-7.8	238	4.5
236	VERBEKE BRIDGE STREAM		1220	02	06	77	-6.8	778	0.0
237	VERBEKE BRIDGE STREAM		0800	06	06	77	-7.6	371	4.2
238	VERBEKE BRIDGE STREAM		1000	06	06	77	-7.7	482	0.0
239	VERBEKE BRIDGE STREAM		1200	06	06	77	-7.6	611	7.1
240	VERBEKE BRIDGE STREAM		1400	06	06	77	-7.3	694	9.5
241	VERBEKE BRIDGE STREAM		1600	06	06	77	-7.5	722	10.0
242	VERBEKE BRIDGE STREAM		1800	06	06	77	-7.5	753	9.2
243	VERBEKE BRIDGE STREAM		2000	06	06	77	-7.4	764	10.8
244	VERBEKE BRIDGE STREAM		2200	06	06	77	-7.2	778	5.3
245	VERBEKE BRIDGE STREAM		2400	06	06	77	-7.2	771	8.5
246	VERBEKE BRIDGE STREAM		0200	07	06	77	-7.3	767	10.0

APPENDIX A - SAMPLE ANALYSES

WATERSHED LOCATION: HILLMAN CREEK, ESSEX COUNTY, ONTARIO

SAMPLE LOCATION NUMBER AND TYPE		HOUR	DAY	MO	YR	OXYGEN-18 (PARTS/MIL)	CONDUCTIVITY (US)	NITRATE (MG/L)
247	VERBEKE BRIDGE STREAM	0400	07	06	77	-7.2	785	5.4
248	VERBEKE BRIDGE STREAM	0600	07	06	77	-7.3	778	6.6
249	VERBEKE BRIDGE STREAM	0800	07	06	77	-6.9	763	3.0
250	VERBEKE BRIDGE STREAM	1200	07	06	77	-6.6	778	8.9
251	VERBEKE BRIDGE STREAM	1400	07	06	77		785	9.0
252	VERBEKE BRIDGE STREAM	1600	07	06	77		761	7.7
253	VERBEKE BRIDGE STREAM	1800	07	06	77	-7.0	778	7.8
254	VERBEKE BRIDGE STREAM	2000	07	06	77	-7.0	771	4.8
255	VERBEKE BRIDGE STREAM	2400	07	06	77	-6.8	771	6.5
256	VERBEKE BRIDGE STREAM	0200	08	06	77	-6.9	771	6.8
257	VERBEKE BRIDGE STREAM	0400	08	06	77	-6.9	778	7.6
258	VERBEKE BRIDGE STREAM	0900	06	06	77	-1.3	626	2.6
259	VERBEKE BRIDGE STREAM	1300	08	06	77	-7.3	511	4.5
260	VERBEKE BRIDGE STREAM	1500	08	06	77	-7.0		
261	VERBEKE BRIDGE STREAM	1700	08	06	77	-7.0	792	
262	VERBEKE BRIDGE STREAM	1900	08	06	77	-6.9	725	
263	VERBEKE BRIDGE STREAM	1100	09	06	77	-6.8	792	
264	VERBEKE BRIDGE STREAM	1 700	09	06	77	-7.1	668	
265	VERBEKE BRIDGE STREAM	0830	10	06	77	-6.9	722	
266	VERBEKE BRIDGE STREAM	2030	10	06	77	-6.6		
267	PIEZ B	1200	11	06	77	-8.2	819	
268	PIEZ A	1200	11	06	77	-8.1	619	
273	WEIR STREAM	1200	08	06	77			4.1
274	WEIR STREAM	1150	07	06	77			4.4

APPENDIX A - SAMPLE ANALYSES

WATERSHED LOCATION: CANAGAGIGUE CREEK, TRIBUTARY OF GRAND R., ONTARIO

SAMPLE NUMBER	LOCATION AND TYPE		HOUR	DAY	MO	YR	OXYGEN-18 (PARTS/MIL)	CONDUCTIVITY (US)	NITRATE (MG/L)
1	E. CAN AT GAUGE	SNOW		21	02	77	-22.2		
3	E. CAN	STREAM	1020	21	02	77	-11.1		2.7
6	E. CAN	STREAM	1245	07	03	77	-11.2		1.5
8	E. CAN	STREAM	2045	07	03	77	-10.9		2.6
9	E. CAN	STREAM	2245	07	03	77	-10.8		1.8
10	E. CAN	STREAM	0045	08	03	77	-11.2		1.8
11	E. CAN	STREAM	0245	08	03	77			2.5
12	E. CAN	STREAM	0445	08	03	77	-11.3	624	2.7
13	E. CAN	STREAM	0645	08	03	77			2.5
14	E. CAN	STREAM	0845	08	03	77	-11.1		2.6
15	E. CAN	STREAM	1245	08	03	77			2.7
16	E. CAN	STREAM	1445	08	03	77	-11.1		2.8
17	E. CAN	STREAM	1645	08	03	77	-11.2		3.1
18	E. CAN	STREAM	1845	08	03	77	-11.3		2.7
19	E. CAN	STREAM	2045	08	03	77	-11.2		2.3
20	E. CAN	STREAM	2245	08	03	77	-11.3		2.5
21	E. CAN AT GAUGE	SNOW	1400	08	03	77	-23.6		
22	SITE B	SNOW	1430	08	03	77	-18.8		
23	SITE C	SNOW	1445	08	03	77	-16.1		
24	SITE D	SNOW	1455	08	03	77	-19.6		
25	SITE E	SNOW	1505	08	03	77	-17.9		
26	SITE F	SNOW	1515	08	03	77	-18.7		
28	SITE H	SNOW	1535	08	03	77	-20.6		
31	SITE B	SNOWMELT	1435	08	03	77	-11.7		
32	SITE E	SNOWMELT	1510	08	03	77	-14.6		
33	SITE C OVERLAND FLOW		1600	08	03	77	-14.2		1.5
34	SITE G SNOWMELT		1605	08	03	77	-14.7		0.2
35	SITE K SNOWMELT								0.5
36	E. CAN STREAM		0045	09	03	77			2.7
37	E. CAN STREAM		0245	09	03	77			2.6
38	E. CAN STREAM		0445	09	03	77			2.2
39	E. CAN STREAM		0645	09	03	77			2.7
40	E. CAN STREAM		0845	09	03	77	-11.6		2.9
41	E. CAN STREAM		1100	09	03	77	-11.6		2.6
42	E. CAN STREAM		1320	09	03	77	-11.8		2.3
43	E. CAN STREAM		1520	09	03	77	-11.9		2.8
44	E. CAN STREAM		1620	09	03	77	-12.8		2.9
45	E. CAN STREAM		1720	09	03	77	-12.5		2.7
46	E. CAN STREAM		1920	09	03	77	-11.9		2.8
47	E. CAN STREAM		2120	09	03	77	-12.3		3.1

APPENDIX A - SAMPLE ANALYSES

WATERSHED LOCATION: CANAGAGIGUE CREEK, TRIBUTARY OF GRAND R.. ONTARIO

SAMPLE NUMBER	LOCATION AND TYPE	HOUR	DAY	MO	YR	OXYGEN-18 (PARTS/MIL)	CONDUCTIVITY (US)	NITRATE (MG/L)
48	E. CAN STREAM	2320	09	03	77	-12.5		3.3
49	E. CAN GAUGE SNOW	1405	09	03	77	-13.7		
50	SITE A SNOW	1435	09	03	77	-15.2		
51	SITE B SNOW	1445	09	03	77	-19.4		
52	SITE C SNOW	1450	09	03	77	-16.9		
53	SITE D SNOW	1500	09	03	77	-19.8		
54	SITE E SNOW	1505	09	03	77	-18.0		
55	SITE F SNOW	1510	09	03	77	-20.1		
56	SITE G SNOW	1420	09	03	77	-16.8		
57	SITE H SNOW	1425	09	03	77	-20.2		
60	SITE B SNOWMELT	1445	09	03	77	-13.4		
61	SITE E SNOWMELT	1115	09	03	77	-14.4		
62	SITE E SNOWMELT	1505	09	03	77	-14.7		
63	SITE E SNOWMELT	1620	09	0.3	77	-13.9		
64	SITE F SNOWMELT	1520	09	03	77	-14.6		
65	SITE F SNOWMELT	1625	09	03	77	-14.1		
66	SITE 9 SNOWMELT	1415	09	03	77	-16.5		
67	E. CAN STREAM	0120	10	03	77	-12.3	555	2.9
68	E. CAN STREAM	0320	10	03	77	-12.6		3.7
69	E. CAN STREAM	0620	10	03	77	-12.3	530	3.6
70	E. CAN STREAM	0720	10	03	77	-12.1	534	4.0
71	E. CAN STREAM	0920	10	03	77	-12.2	539	4.0
72	E. CAN STREAM	1120	10	03	77			4.1
73	E. CAN STREAM	1320	10	03	77	-12.4	516	4.3
74	E. CAN STREAM	1520	10	03	77	-12.6	476	4.6
75	E. CAN STREAM	1710	10	03	77	-13.2	432	5.1
76	E. CAN STREAM	1750	10	03	77	-13.3	424	4.7
77	E. CAN STREAM	1950	10	03	77	-14.0	406	6.0
78	E. CAN STREAM	2150	10	03	77	-14.0	412	5.4
79	SITE A SNOW	1535	10	03	77	-17.5	47	
80	SITE 8 SNOW	1535	10	03	77	-17.8	103	
81	SITE C SNOW	1540	10	03	77	-17.5	147	
82	SITE D SNOW	1545	10	03	77	-19.0		
83	SITE E SNOW	1550	10	03	77	-19.2		
84	SITE F SNOW	1600	10	03	77	-18.3	255	
85	SITE H SNOW	1525	10	03	77	-18.6		
86	E. CAN GAUGE OVERLAND FLOW	0900	10	03	77	-13.9	449	4.4
87	E. CAN GAUGE OVERLAND FLOW	1140	10	03	77	-13.5		4.1
88	E. CAN GAUGE OVERLAND FLOW	1310	10	03	77	-14.1	424	
89	E. CAN GAUGE OVERLAND FLOW	1505	10	03	77	-13.7	414	

APPENDIX A - SAMPLE ANALYSES

WATERSHED LOCATION: CANAGAGIGUE CREEK, TRIBUTARY OF GRAND R.. ONTARIO

SAMPLE LOCATION NUMBER AND TYPE		HOUR	DAY	MO	YR	OXYGEN-18 (PARTS/MIL)	CONDUCTIVITY (US	NITRATE (MG/L)
90	E. CAN GAUGE OVERLAND FLOW	1715	10	03	77		300	
91	S. E. OF GAUGE OVERLAND FLOW	1150	10	03	77	-11.9	360	8.8
92	SITE B SNOWMELT	1205	10	03	77	-15.9		
93	SITE E SNOWMELT	1400	10	03	77	-13.6	907	
94	SITE F SNOWMELT	0920	10	03	77	-14.6	228	
95	SITE F SNOWMELT	1215	10	03	77	-14.1	274	
96	SITE F SNOWMELT	1410	10	03	77	-14.9	269	
97	SITE F SNOWMELT	1555	10	03	77	-14.9	240	
98	SITE G SNOWMELT	1515	10	03	77	-14.5	291	
99	E. CAN STREAM	0800	11	03	77	-14.1	468	6.0
100	E. CAN STREAM	0900	11	03	77	-13.8		6.1
101	E. CAN GAUGE SNOWMELT	1700	08	03	77	-14.6		
102	E. CAN STREAM	1025	28	03	77	-12.4	496	3.9
103	E. CAN STREAM	1225-	28	03	77	-12.4	488	3.9
104	E. CAN STREAM	1425	28	03	77	-12.6	473	3.8
105	E. CAN STREAM	1825	28	03	77	-12.3	449	4.3
106	E. CAN STREAM	2025	28	03	77	-12.3	438	4.3
107	E. CAN STREAM	0025	29	03	77	-12.0	454	5.5
108	E. CAN STREAM	0225	29	03	77	-12.1	457	5.7
109	E. CAN STREAM	0425	29	03	77	-12.0	456	6.0
110	E. CAN STREAM	0625	29	03	77	-11.9	458	6.1
111	E. CAN STREAM	0825	29	03	77	-12.0	469	6.3
112	E. CAN STREAM	1025	29	03	77	-12.3	460	5.9
113	E. CAN STREAM	1225	29	03	77	-13.0	408	4.8
114	E. CAN STREAM	1425	29	03	77	-13,1	361	4.4
115	W. CAN STREAM	1050	28	03	77	-13.5	407	4.1
116	W. CAN STREAM	1150	28	03	77	-13.4	404	4.1
117	W. CAN STREAM	1250	28	03	77	-13.4	403	4.0
118	W. CAN STREAM	1350	28	03	77	-13.4	400	4.0
119	W. CAN STREAM	1450	28	03	77	-13.3	397	4.1
120	W. CAN STREAM	1650	28	03	77	-13.1	399	4.2
121	W. CAN STREAM	1850	28	03	77	-12.8	376	4.9
122	W. CAN STREAM	1950	28	03	77	-12.4	374	5,1
123	W. CAN STREAM	2050	28	03	77	-12.3	369	5.1
124	W. CAN STREAM	2150	28	03	77	-12.2	369	6.2
125	W. CAN STREAM	2250	23	03	77	-12.2	374	6.2
126	W. CAN STREAM	2350	28	03	77	-12.4	374	6.1
127	W. CAN STREAM	0050	28	03	77	-12.4	376	5.0
128	W. CAN STREAM	0150	28	03	77	-12.4	378	5.4
129	W. CAN STREAM	0250	28	03	77	-12.4	378	5.5

APPENDIX A - SAMPLE ANALYSES

WATERSHED LOCATION: CANAGAGIGUE CREEK, TRIBUTARY OF GRAND R., ONTARIO

SAMPLE LOCATION NUMBER AND TYPE			HOUR	DAY	MO	YR	OXYGEN-18 (PARTS/MIL)	CONDUCTIVITY (US)	NITRATE (MG/L)
130	W. CAN STREAM		0350	28	03	77	-12.4	.378	5.5
131	W. CAN STREAM		0450	28	03	77	-12.2	383	5.5
132	W. CAN STREAM		0550	28	03	77	-12.4	388	6.8
133	W. CAN STREAM		0650	28	03	77	-12.4	389	6.6
134	W. CAN STREAM		0750	28	03	77	--12.1	386	7.2
135	W. CAN STREAM		0830	28	03	77	-12.0	383	7.1
136	W. CAN STREAM		0945	28	03	77	-12.0	386	7.3
137	W. CAN STREAM		1045	28	03	77	-12.1	363	7.3
138	W. CAN STREAM		1145	28	03	77	-12.2	385	6.8
139	W. CAN STREAM		1245	28	03	77	-12.3	374	6.5
140	W. CAN STREAM		1430	28	03	77	-12.9	353	5.9
141	SITE G AND H SNOWMELT		1640	28	03	77	-16.8		
142	E. CAN STREAM		1010	28	03	77	-12.1		
143	RAIN MARTIN FARM 5.7 MM		1800	28	03	77	-6.3	69	
144	RAIN MARTIN FARM 3.6 MM		0640	29	03	77	-3.3	51	
145	RAIN HORST FARM 7.5 MM		1745	28	03	77	-6.3	40	
146	RAIN HORST FARM 7.1 MM		0600	29	03	77	-4.3	64	
147	RAIN GINGRICH FARM 7.9 MM		1810	28	03	77	-6.4	44	
147	RAIN GINGRICH FARM 4.7 MM		0600	29	03	77	-3.7		
149	GINGRICH FARM PUDDLE		1055	28	03	77	-12.1		
150	GINGRICH FARM PUDDLE		1815	28	03	77	-11.1		
151	RAIN MARTIN FARM 3.3 MM	TO	0900	22	04	77	-0.4		2.6
152	RAIN MARTIN FARM 6.1 MM	TO	1435	22	04	77	-1.3		1.8
153	RAIN MARTIN FARM 8.8 MM	TO	0815	23	04	77	-7.6		0.7
154	RAIN MARTIN FARM 4.2 MM	TO	1755	23	04	77	-14.1		0.6
155	RAIN GINGRICH FARM 2.3 MM	TO	0950	22	04	77	-1.0		
156	RAIN GINGRICH FARM 0.5 MM	TO	1420	22	04	77	-1.4		
157	RAIN GINGRICH FARM 11.2 MM	TO	0945	23	04	77	-8.7		
158	RAIN GINGRICH FARM 2.32 MM	TO	1825	23	04	77	-13.1		
159	RAIN GINGRICH FARM EAVES TROUGH		1425	22	04	77	-2.3		
160	RAIN GINGRICH FARM EAVES TROUGH		0945	23	04	77	-12.2		
161	W. CAN STREAM		2020	19	04	77	-11.0	478	2.2
162	W. CAN STREAM		0820	20	04	77	-10.4	486	2.3
164	W. CAN STREAM		1345	21	04	77	-10.6	451	1.6
165	W. CAN STREAM		1320	21	04	77		447	1.7
166	W. CAN STREAM		1645	21	04	77		446	1.6
167	W. CAN STREAM		1745	21	04	77		444	1.6
168	W. CAN STREAM		1845	21	04	77	-10.5	460	1.6
169	W. CAN STREAM		1945	21	04	77		454	1.6
170	W. CAN STREAM		2045	21	04	77		458	1.5

APPENDIX A - SAMPLE ANALYSES

WATERSHED LOCATION: CANAGAGIGUE CREEK, TRIBUTARY OF GRAND R., ONTARIO

SAMPLE LOCATION NUMBER AND TYPE		HOUR	DAY	MU	YR	OXYGEN-18 (PARTS/MIL)	CONDUCTIVITY (US)	NITRATE (MG/L)
171	W. CAN STREAM	2145	21	04	77		472	1.5
172	W. CAN STREAM	2245	21	04	77		458	1.6
173	W. CAN STREAM	2345	21	04	77		472	1.7
174	W. CAN STREAM	0045	22	04	77	-10.7		1.5
175	W. CAN STREAM	0145	22	04	77		479	1.3
176	W. CAN STREAM	0245	22	04	77	-10.3		1.2
177	W. CAN STREAM	0345	22	04	77		481	1.5
176	W. CAN STREAM	0445	22	04	77	-10.4		1.5
179	W. CAN STREAM	0545	22	04	77	-10.1	487	1.5
180	W. CAN STREAM	0645	22	04	77	-9.4	504	1.3
181	W. CAN- STREAM	0745	22	04	77	-10.0	486	1.4
182	W. CAN STREAM	0645	22	04	77	-9.5		1.8
183	W. CAN STREAM	0945	22	04	77			1.7
184	W. CAN STREAM	1045	22	04	77	-9.9		1.6
185	W. CAN STREAM	1135	22	04	77	10.1		1.6
186	W. CAN STREAM	1235	22	04	77	-10.3		1.4
187	W. CAN STREAM	1335	22	04	77		479	1.5
168	W. CAN STREAM	1435	22	04	77	-10.0		1.4
169	W. CAN STREAM	1535	22	04	77		467	1.7
190	W. CAN STREAM	1635	22	04	77	-10.3		1.6
191	W. CAN STREAM	1735	22	04	77		475	1.7
192	W. CAN STREAM	1835	22	04	77	-10.2		1.6
193	W. CAN STREAM	1935	22	04	77		483	1.7
194	W. CAN STREAM	2035	22	04	77	-10.3		1.4
195	W. CAN STREAM	2135	22	04	77		481	1.4
196	W. CAN STREAM	2235	22	04	77	-10.0		1.6
197	W. CAN STREAM	2335	22	04	77			1.7
198	W. CAN STREAM	0035	23	04	77	-10.1		1.6
199	W. CAN STREAM	0135	23	04	77		465	1.4
200	W. CAN STREAM	0235	23	04	77	-10.0		1.5
201	W. CAN STREAM	0335	23	04	77	-9.5		1.5
202	W. CAN STREAM	0435	23	04	77	-10.3		1.4
203	W. CAN STREAM	0535	23	04	77	-10.0		1.4
204	W. CAN STREAM	0635	23	04	77	-9.6	471	1.5
205	W. CAN STREAM	0735	23	04	77	-9.8		1.6
206	W. CAN STREAM	0835	23	04	77	-9.7		1.5
207	W. CAN STREAM	1030	23	04	77	-10.3		1.5
208	W. CAN STREAM	1130	23	04	77	-10.5	479	1.5
209	W. CAN STREAM	1230	23	04	77	-10.5		1.5
210	W. CAN STREAM	1330	23	04	77	-10.2	486	1.5

APPENDIX A - SAMPLE ANALYSES

WATERSHED LOCATION: CANAGAGIGUE CREEK, TRIBUTARY UP GRAND R., ONTARIO

SAMPLE LOCATION NUMBER AND TYPE		HOUR	DAY	MO	YR	OXYGEN-18 (PARTS/MIL)	CONDUCTIVITY (US)	NITRATE (MG/L)
211	W. CAN STREAM	1430	23	04	77	-10.4		1.5
212	W. CAN STREAM	1530	23	04	77	-10.5	494	1.4
213	W. CAN STREAM	1630	23	04	77	-10.4	475	1.4
214	W. CAN STREAM	1730	23	04	77	-10.2	500	1.6
215	W. CAN STREAM	1830	23	04	77	-10.7		1.6
216	W. CAN STREAM	1930	23	04	77	-10.1	465	1.6
217	W. CAN STREAM	2030	23	04	77		500	1.8
218	W. CAN STREAM	2130	23	04	77	-10.2	514	1.8
219	W. CAN STREAM	2230	23	04	77		506	2.0
220	W. CAN STREAM	2330	23	04	77	-10.9		2.1
221	W. CAN STREAM	0030	24	04	77	-10.6	513	2.0
222	W. CAN STREAM	0130	24	04	77		529	2.1
223	W. CAN STREAM	0230	24	04	77		514	2.2
224	W. CAN STREAM	0330	24	04	77		531	2.3
225	W. CAN STREAM	0430	24	04	77		540	2.0
226	W. CAN STREAM	0530	24	04	77		522	2.1
228	W. CAN STREAM	0730	24	04	77		543	2.1
229	W. CAN STREAM	0830	24	04	77			2.3
230	W. CAN STREAM	1045	24	04	77		529	2.1
231	W. CAN STREAM	1145	24	04	77		524	2.8
232	W. CAN STREAM	1245	24	04	77	-11.1	533	2.7
233	W. CAN STREAM	1345	24	04	77		514	2.4
235	W. CAN STREAM	1545	24	04	77		531	2.4
236	W. CAN STREAM	1645	24	04	77		521	2.4
237	W. CAN STREAM	1745	24	04	77		525	2.5
238	W. STREAM	1645	24	04	77	-11.3		2.5
277	W. CAN STREAM	1905	24	04	77	-10.8	522	1.8
278	W. CAN STREAM	2305	24	04	77		513	2.5
279	W. CAN STREAM	0305	25	04	77		519	2.1
280	W. CAN STREAM	0705	25	04	77		531	2.7
281	W. CAN STREAM	1105	25	04	77	-11.0	526	2.7
282	W. CAN STREAM	1505	25	04	77		538	2.7
283	W. CAN STREAM	1905	25	04	77		503	2.7
284	W. CAN STREAM	2305	25	04	77		515	2.8
285	W. CAN STREAM	0305	26	04	77		519	2.5
266	W. CAN STREAM	0705	26	04	77		517	2.5
287	W. CAN STREAM	1105	26	04	77	-10.8	528	
288	W. CAN STREAM	1505	26	04	77		530	