The Hydrology and Water Quality of an Intensive Agricultural Watershed in Quebec

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Abstract

**The hydrology and water quality
of an intensive agricultural watershed in Quebec**

A research project was undertaken to study the hydrology and water quality of a 26 km^2 intensive agricultural watershed over an 18 month period. Flow and precipitation data were used to establish hydrologic parameters for the watershed and to empirically model hydrologic processes. Water samples taken from the outlet of the watershed were analyzed for nitrate, phosphate, suspended sediment and atrazine. Water quality data were analyzed to establish temporal trends in pollutant concentration and load in the watercourse.

The measured time of concentration was found to be consistent with a mean of 6.89 hours for the 25 storms profiled. The time to peak was found to vary linearly with storm duration. The event recession constant was measured to be 0.9715. Regression analysis was performed on measured hydrologic properties. The strongest relationship was found between the percentage of rainfall appearing as runoff versus the sum of the 72 hour antecedent rainfall plus the storm rainfall.

Spring snowmelt was identified as a significant period of pollutant material export. All pollutant materials displayed seasonal variability in the export process. Temporal variability accounted for poor correlations between observed hydrologic and water quality parameters in the two seasons for which data were available.

Peak pollutant concentrations were associated with high flow events. Maximum observed concentrations for nitrate, phosphate, suspended sediment and atrazine were 8.6 mg/l, 0.478 mg/l, 0.7 g/l, and 8.06 ug/l respectively.

Résumé

L'hydrologie et la qualité de l'eau d'un bassin versant agricole du Québec

L'hydrologie et la qualité de l'eau d'un bassin versant de 26 km^2 où l'agriculture est pratiquée de façon intensive ont été étudiées durant une période de 18 mois. On a utilisé des données de débit et de précipitation afin d'établir les paramètres hydrologiques du bassin versant et de modéliser de façon empirique les processus hydrologiques. Des échantillons d'eau ont été prélevés à la sortie du bassin versant et analysés pour les paramètres suivants: nitrates, phosphates, matières en suspension, et atrazine. On a essayé, à partir des résultats des analyses, de distinguer les tendances dans les concentrations et les charges d'éléments polluants dans le cours d'eau à l'intérieur des saisons et des épisodes pluvieux.

Le temps de concentration moyen mesuré lors des 25 épisodes pluvieux observés était de 6.89 heures. Le temps de montée variait de façon linéaire avec la durée des épisodes de pluie. La constante de décrue était de 0.9715. Des analyses de régression ont été faites. La meilleure relation établie a été celle entre le pourcentage de ruissellement généré lors d'une pluie et la somme des précipitations de l'épisode étudié et celles des 72 heures précédentes.

Des charges significatives de polluants ont été transportées hors bassin lors de la fonte des neiges. Pour tous les polluants examinés, on a observé que les processus de transports variaient avec les saisons. Les variabilités à l'intérieur des saisons et des épisodes pluvieux expliquent la faiblesse des corrélations entre les paramètres hydrologiques et de qualité d'eau mesurés au cours des deux années qu'ont durés les travaux.

Les concentrations maximales ont été observées lors d'événements ayant générés des débits importants. Les concentrations maximales de nitrates, phosphates, matières en suspension et atrazine mesurées ont été respectivement de 8.6 mg/l, 0.478 mg/l, 0.7 g/l, et 8.06 ug/l.

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Terms and Abbreviations Used

A	-drainage area (ha)
A_m	-drainage area (square miles)
BMP	-best management practice
C	-runoff coefficient
C_1	-hydrograph recession constant
C_2	-hydrograph recession constant
d	-storm duration
D_r	-sediment delivery ratio
ft	-feet
GIS	-geographic information system
g/l	-grams per litre
h, hr	-hour
ha	-hectare
K_1	-hydrograph recession constant
K_2	-hydrograph recession constant
kg	-kilogram
kg/ha	-kilograms per hectare
km	-kilometre
KPa	-kilopascal
l	-litre
L	-flow length (m)
L_f	-flow length (ft)
m	-metre
MEF	-Ministere de l'environment et faune
mg/l	-milligram per litre
mm	-millimetre
N	-nitrogen
NO_3	-nitrate
NPS	-non-point source
P	-phosphorus
PO_4	-phosphate
PT	-pressure transducer
P_{72}	-72 hour antecedant rainfall
P_s	-storm rainfall
q_o	-initial flow
q_1	-final flow
S	-basin gradient (m/m)
SS	-suspended sediment
t_{c1}	-time of concentration
t_{c2}	-time of concentration
t_l	-lag time
t_p	-time to peak
ug/l	-micrograms per litre
Y	-basin slope (%)
°C	-degrees celsius
%	-percent
%Rr	-percent of rainfall as runoff

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1.0 INTRODUCTION

Increasing chemical utilization under intensive agricultural production has been recognized as a serious contributor to the degradation of water resources in Canada and the United States (Castle, 1993). The primary means by which agricultural areas contribute to the degradation of water resources is through non-point source pollution.

A non-point source of pollution as it relates to a watercourse or groundwater can be defined as pollution which does not have an identifiable entry point into the body of water whereas point source pollution does.

The problem of non-point source (NPS) pollution has been recognized in several agricultural regions of North America. Chesters and Schierow (1985) stated that one half of all water pollution is derived from non-point sources with the fraction of that originating from agricultural sources being the most pervasive and important. Angle et. al., (1986, cited by Searing and Shirmohammadi 1993) reported that 67% of the nitrogen and 39% of the phosphorus pollution that reaches Chesapeake Bay is contributed from non-point sources. Castle (1993) reported that a significant portion of excess nutrient loading in the Great Lakes is due to non-point sources of pollution. Giroux (1992) reported that levels of pesticides which exceeded the standards set for aquatic life were measured on many agricultural watersheds in Quebec. The examples given by these studies are certainly not complete in describing the problem but they indicate it's scope, and the interest taken in the problem by researchers and policy makers in North America.

This research project was undertaken as part of a larger pilot project (*Gestion de l'eau par bassin versant de la partie superieur du ruisseau St. Esprit*) initiated under the Canada-

Quebec Green plan by the Ministere de l'agriculture du Quebec and Agriculture and Agri-food Canada to examine the effect of agricultural production on environmental pollution at the watershed scale and to develop strategies for pollution control (Enright et al., 1995).

This dissertation examines the hydrology and water quality of a 26 km^2 agricultural watershed. The watershed is located about 50 km northeast of the city of Montreal between the villages of St. Esprit and St. Jacques. The watershed is part of the L'Assomption River basin and the majority lies within the parish of St. Alexis de Montcalm. Data were collected in 1994 and 1995, prior to the implementation of best-management-practices (BMP's) on the watershed, and hence provides a "snapshot" of initial hydrologic and water quality conditions.

1.1 Objectives

The objectives of this research project were to:

1. Document water quality and quantity at the watershed scale.
2. Assess the hydrology of the watershed in terms of established hydrograph parameters.
3. Assess the trends in the water quality parameters nitrate-nitrogen (NO_3), phosphate-phosphorous (PO_4), suspended sediment, and atrazine, both seasonally and within storms.
4. Relate the observed hydrologic behaviour to the observed water quality trends.

1.2 Scope

This study examines the hydrology and water quality at the watershed scale. Observations of flow and water quality are derived from samples and records taken from a gauging station at the outlet of the watershed. Flow or water quality data are not derived from points within the watershed.

The study was undertaken during the period from April, 1994 to September, 1995 inclusive. However, due to difficulties in monitoring and obtaining water samples, the period from December, 1994 to March, 1995 has been omitted from the study. While this is a short term of record, other students are carrying on with data collection on the watershed.

Data for atrazine are available for the 1994 season only. In the 1995 season, its concentrations were below the detection limit in most samples. This is believed to be due to the predominantly dry conditions which prevailed during 1995.

2.0 LITERATURE REVIEW

There are different pollutant materials which are included in the study of agriculturally derived NPS pollution. They can be generally described as sediment, plant nutrients, and agricultural chemicals (Chesters and Schierow 1985).

The means of reducing agricultural NPS pollution has been envisioned in the following steps by regulatory agencies in Canada and the United States: 1) the identification of areas which have a high potential to contribute to NPS pollution. 2) the implementation of Best Management Practices (BMPs) on those areas and 3) monitoring to assess the implementation and effectiveness of the BMPs on water quality (Castle 1993).

Coote et al., (1982) reported that for the Great Lakes basin, there were no means of estimating pollutant loads from agricultural sources due to a lack of water quality data. The need for such data can be extrapolated to any region in which NPS pollution is a concern. It is generally recognized that any progress in improving water quality requires an extensive data base (Castle 1993). Water quality data are essential to validate and verify models that can be used to assess the effect of current agricultural practices on water quality and the potential benefits of BMP's on water quality.

2.1 Watershed Hydrology

The watershed has generally been recognized as the preferred hydrologic unit for research and policy initiatives in water quality (Chesters and Schierow 1985). This preference was recognized as well by Omernik and Griffith (1991) who advanced the idea of ecoregions as the preferred unit for water quality studies.

Sidle and Hornbeck (1991) emphasized the close relationship between the hydrologic cycle within the watershed and the resulting water quality. The hydrologic cycle can be summarized in the following manner. Vapor from open bodies of water reaches the upper atmosphere and is transported by moving air masses. When the vapor condenses it forms precipitation which falls to the ground. Once the precipitation reaches the ground it can follow several different courses. The principal pathways are interception by the plant canopy, infiltration into the soil profile, surface run-off, deep percolation and evapotranspiration (Linsley et al., 1982).

The principal means of pollutant transport to water courses is recognized as being through surface run-off or groundwater movement after infiltration and/or percolation. Surface run-off is the primary mover of sediment and associated insoluble pollutants such as phosphorus, heavy metals, some pesticides, as well as soluble material such as nitrates and certain pesticides (Wall et al., 1982). Groundwater movement is primarily responsible for the movement of soluble pollutants such as nitrogen and some pesticides (Smith et al., 1993). While it is possible to generalize about transport paths of pollutants, it is recognized that many of these paths are not well understood and that there is a need for further research on the fate and paths of agricultural pollutants (Sidle and Hornbeck 1991; Smith et al., 1993).

Several researchers have indicated the link between flow in the watershed and pollutant loading and concentration. Owens et al., (1991) found for an Ohio watershed that stormflow accounts for less than 25% of the total precipitation but is responsible for 50% - 75% of the nutrient export from the watershed. Kirby and Mehuys (1987) showed that there is a relationship between the hydrology of a basin, the soil type on the basin and the soil loss due to different hydrologic events. Baker (1993) gave the results for studies on several large American watersheds in the Lake Erie drainage basin. He reported that watershed size affects pollution loading. There were lower concentrations of pollutants on the larger watersheds. Smaller watersheds were characterized by high concentrations of pollutants for a relatively short duration. Large watersheds were characterized by lower concentrations of pollutants for a relatively longer duration. He also found that most phosphorus export on these watersheds occurred during winter and spring run-off.

The above studies can be summarized as follows. Since agricultural pollutants are moved primarily through surface run-off or groundwater movement, a necessary condition for pollutant movement is a precipitation or snowmelt event of sufficient magnitude or intensity to promote water movement, by either of these paths, to a water body. Therefore, the prediction of pollutant loading or concentration requires the accurate prediction of flow in the watershed in response to storm or snowmelt events.

The prediction of flow at the outlet of a watershed after a rainfall or snowmelt event over the watershed has received much attention from hydrologic researchers. Textbooks on hydrology give several methods for predicting peak flow (Schwab et al., 1981, Linsley et al., 1982). Commonly used techniques include the Rational Method and the SCS Method.

Further refinement in peak flow prediction is given by the unit or dimensionless hydrograph concept. The dimensions of these hydrographs are based on empirical equations derived from physical data (Sheridan 1994).

A hydrograph has three recognizable phases. These are the rising limb, the crest, and the recession limb . There are four time components which define a hydrograph. These are the time of concentration, T_c, the time to peak, T_p, the time of recession, T_r, and the lag time, T_l (Linsley et al. 1982). Sheridan (1994) gives a review of many of the derived empirical relations used to calculate these hydrograph components. A recognized problem with using empirical relations is the lack of consistency in defining the parameters used to calculate these time components and a lack of consistency in the definition of the components themselves (Sheridan 1994).

Researchers have found that often these empirical methods require modification if they are to be used successfully in locations other than where they were developed.

Madramootoo and Enright (1988) found that the SCS equations for predicting run-off volume and peak flow were not adequate for the Ottawa- St. Lawrence lowlands region. They found that the method did not adequately account for the antecedent rainfall in the area, the soil type in the area or the flat topography of the watershed. The peak flow and runoff volume were under predicted using the AMC 2 condition and over predicted for the AMC 3 condition.

Similar conclusions regarding other empirical methods were reached by Sheridan (1994) after studies on flat watersheds in the coastal regions of the southeastern United States. He concluded that the relative errors in prediction methods increase with increasing area and decreasing slope. The trend found was for under prediction of the hydrograph time parameters. The hydrology of a basin is closely related with the climate, geology, and shape of the basin as well as the activity on the basin. This explains the sometimes poor performance of empirical methods in predicting the flow from a watershed.

An attempt to incorporate the geomorphological characteristics of a basin into a hydrological theory was made by Rodriguez-Iturbe and Valdes (1979) through the use of an instantaneous unit hydrograph. This concept explored the link between the kinetic and potential energy due to a storm event and the basin morphology respectively, and the velocity of flow at peak discharge. The peak discharge could be combined with the storm intensity to develop a hydrograph of the event.

The type of vegetation and types of activities taking place on a watershed have significant impacts on the hydrology of the basin. Kostadinov and Mitrovic (1994) examined these effects on three small watersheds. It was found that forest cover moderated the magnitude of the peak flow due to storms. They also found that there was a more uniform and constant flow throughout the year on a forested watershed. This is as opposed to agricultural watersheds which exhibited sharp peaks in flow after storms. Further, the agricultural watersheds were more subject to the extremes of torrential flow and dry stream beds than was the forested watershed. The forested watershed had forest cover over more than 70% of its area. The agricultural watersheds had forest cover of between 38 and 48% of the watershed area.

The seasons also play a role in the hydrologic response of a watershed. Coote et al., (1982) found that watersheds in the Great Lakes basin received, on average, 32% of their annual precipitation in the months of January-April but these months accounted for 65% of the total stream discharge for the year. These results indicate the effects of the storage capacity of a basin on its response to precipitation.

The effect of storage effects on southern coastal plains watersheds in the U.S. was examined by Shirmohammadi et al., (1986). It was found that the available storage capacity was a function of both the time of year and the antecedent moisture conditions. Lower available storage was observed for late winter and early spring. The available storage increased throughout the growing season until autumn. The effect of antecedent moisture was seen in the response of the basins to storms for different antecedent moisture conditions. Peak flows were higher by an order of magnitude for high antecedent moisture conditions.

2.2 Pollutant Transport

2.2.1 Sediment Transport

The largest mass of material comprising NPS pollution is sediment (Chesters and Schierow 1985). Sediment is a significant pollutant as it is responsible for the destruction of fish spawning areas and sedimentation of waterways, navigation channels and reservoirs. It is also important in the transport of other pollutants bound to the sediment particles such as phosphorus, heavy metals and pesticides (Wall et al 1982).

As stated by Borah (1989), the process of sediment transport involves the detachment of soil particles, their transport downslope, and deposition at some downslope point. A common concept in the study of sediment transport is the delivery ratio D_r, where:

$$D_r = \text{Basin sediment yield / Basin erosion potential}$$

The basin sediment yield is a measured value whereas the basin erosion potential is estimated using an empirical relationship such as the Universal Soil Loss Equation (USLE) (Novotny and Chesters 1989). Typical values of D_r on agricultural watersheds are between 0.1 and 0.4 (Chesters and Schierow 1985).

Novotny and Chesters (1989) reviewed current literature on sediment transport. They found that sediment delivery was not well correlated with actual upstream erosion and that current methods of sediment estimation, such as the delivery ratio, put emphasis on areas with high erosion potential rather than on areas with high pollution potential. The problem is the spatial distribution of erodible areas in a watershed and their proximity to the main channels. As a result, they pointed out several areas in which our current concepts of sediment transport need further research. The first is the effect of sediment storage in the watershed, particularly as it relates to the degradable pollutants bound to the sediment. The second is increased knowledge of the delivery process and all of its components to sediment transport.

2.2.2 Phosphorus Transport

Phosphorus is an element which is necessary for the proper growth and development of all living organisms (Brady 1984). As a nutrient, it can cause pollution problems if excessive amounts are found in water courses due to increased eutrophication (Rousseau et al., 1988). This is because phosphorus is often the limiting growth factor in aquatic phytoplankton communities (CCME 1994).

Phosphorus exists in the soil in many different forms. For the purposes of studying its behaviour with regard to NPS pollution it is often separated into two groups, those being soluble and insoluble forms (Rousseau et al., 1988). The greatest proportion of phosphorus is held in insoluble forms for most soils (Brady 1984). As indicated earlier, the insoluble phosphorus fraction is transported to water courses through the movement of sediment to the water course. The soluble fraction moves in solution with ground water or with surface run-off.

Studies in Pennsylvania have found that soluble phosphorus accounts for no more than 30% of the total phosphorus export from a basin (Pionke and Kunishi, 1992). The same study pointed out that the transport mechanisms and paths of the various forms of phosphorus have not been well explained, especially at the watershed scale.

Studies in Maryland found that particulate associated phosphorus accounted for 94% of the phosphorus export from an agricultural watershed and 77% of the phosphorus export from a forested watershed (Vaithiyanathan and Correll, 1992).

2.2.3 Nitrate-Nitrogen Transport

Nitrogen is an essential element for plant life (Brady 1984). As such, like phosphorus, it has the potential to cause eutrophication of rivers and lakes if it is present in excessive amounts. Nitrogen is generally considered to be in three different forms in soil. These are organic nitrogen, ammonium nitrogen fixed to clay particles and inorganic nitrate and ammonium compounds. The inorganic forms are generally highly soluble and thus move easily through leaching or run-off. In most soils, the soluble forms of nitrogen represent between 1 and 2% of the total nitrogen in the soil. This ratio can change quickly if there is a large application of inorganic fertilizer or manure to a soil (Brady 1984).

The maximum allowable concentration of nitrate in drinking water is 10 mg/L. Concentrations in excess of 5 mg/L in surface waters may indicate unsanitary conditions around the water body (CCME 1994).

In the Great Lakes basins, 75% of the total nitrogen load is in the soluble form (Neilson et al. 1982). In the same study, it was found that high concentrations of nitrate-nitrogen in a receiving watercourse were associated with application of commercial fertilizers. High storm induced concentrations were infrequent.

An agricultural watershed study in Quebec (Boukchina et al., 1992) showed that the highest peak concentrations of nitrate were found in the month of June but that sustained high concentrations of nitrate were found through the winter months from October through to January.

Because nitrate is highly soluble, it is thought to move from farm fields primarily in leachate to groundwater, however a study in Ontario has shown that after fertilizer application, significant concentrations of nitrate have been found in surface runoff (Bowman et al., 1994).

2.2.4 Pesticide Transport

The study of pesticide movement to water courses is a complex subject due to the wide number of materials which are covered. Pesticides are generally found in water courses in much smaller quantities than phosphorus or nitrogen. However they pose a serious threat to human health and the health of aquatic ecosystems. They are often persistent in the environment and thus have the potential to be transported great distances from their point of application (Chesters and Schierow 1985).

In a review of the pesticide content of surface water from agricultural land, Wauchoppe (1978) reported that for most pesticides, the amount lost to watercourses was about 0.5% of the applied total. This depended on the formulation of the pesticide with wettable powders capable of losing 5% of the applied total. It was found that if the solubility of the pesticide was greater than 10ppm than the primary means of movement to the water course was through the water phase of run-off. This level of solubility is exceeded by most currently used pesticides.

Frank et al (1991) in a study of pesticides in the Grand, Saugeen, and Thames river found that atrazine was present in 72% of the samples taken and metolachlor was present in 6.3%. Other pesticides which were identified in lesser amounts included 2,4-D, cyanazine, alachlor, mecoprop, simazine, dicamba, and metribuzin. By their estimates, the atrazine loss at the mouth of the rivers was equal to 1 - 2% of the applied total on the watershed.

A study in Illinois (Felsot et al., 1990) found that pesticide losses from agricultural fields ranged between 1% and 6% for various pesticides and tillage systems. It was found that conservation systems were effective in reducing the concentration of sediment bound pesticides but that the same response was not seen for water soluble pesticides.

2.3 NPS Pollution and Watershed studies in Quebec

The problem of NPS pollution at the field scale has been well documented in Quebec. Wiyo (1991) and Asselin et al., (1992), found high levels of nitrate in subsurface drain water from intensively cropped fields. Giroux (1992) documented the detection of at least 20 different pesticides since 1980 in the principal watercourses draining the agricultural regions of Quebec and at least 15 pesticides in groundwater samples from agricultural regions of Quebec. Kirby and Mehuys (1987) described the mechanism of soil loss and erosion from fields in Southwestern Quebec.

There are few studies available which document water quality and quantity at the watershed scale. This was indicated by Madramootoo (1992) who pointed out that this type of data is essential to test and refine hydrologic and water quality computer models for use in Quebec. Gangbazo et al., (1994) stated that there was a lack of a coordinated, consistent and uniform system to gather water quality and quantity data from representative agricultural watersheds in Quebec. This type of data is essential to assess losses from agricultural areas throughout the province and to develop strategies to minimize NPS pollution.

Boukchina et al., (1992) and Asselin et al., (1992) reported on watershed studies that have been initiated in the province. The first mentioned study involves the monitoring of a 78 ha watershed on the Agriculture Canada research station in Lennoxville, Quebec. The second study involves the monitoring of a 4.5 km^2 watershed in the Duncan river basin in Quebec.

2.4 Effect of BMP's on Water Quality

A best management practice (BMP) is one which reduces the impact of an activity on the environment. As they relate to water-courses and agricultural practice, a BMP is a practice which reduces the load of pollutants due to agricultural activities that reach a water-course. The hydrology and physical characteristics of a watershed play a role in the effectiveness of BMPs.

A study in Delaware (Ritter et al., 1988) found that the implementation of BMPs over a seven-year period on an agricultural watershed produced significant reductions in sediment and sediment bound pollutants such as phosphorus but had no effect on the nitrogen export from the basin.

Clausen and Meals (1989) examined the effect of BMPs related to dairy production on watersheds in Vermont. It was found that while recommended BMPs reduced the pollution load from agricultural practices, it did not reduce it below acceptable standards.

A study in Ohio (Owens et al., 1991) found that there was negligible difference in the quality of water between watersheds that were forested, in unfertilized pasture, or those in which fertilizer is applied over 55% of the area at modest rates. This indicates that on the watershed scale, there is a background level of pollutants which is naturally occurring and cannot be reduced. As well, it indicates the presence of natural processes on the watershed to store and eliminate potential pollutants before they reach the watercourse. Therefore for every watershed, there seems to exist a threshold below which BMPs will have no effect on reducing pollutant levels in the water-course.

This was shown as well in a study involving 7 watersheds in Kentucky over which there was dispersed agricultural production (Thomas et al., 1992). It was found that over an 18 year period, there was no increase in the levels of NO_3-N or P despite a 100% increase in nitrogen usage on the watershed and a slight increase in phosphorus. On these watersheds, there was little change in land-use patterns observed over the 18 year period. It was concluded that the geology and parent materials of the soils played a greater role in nitrogen and phosphorus levels in the watercourses than did the agricultural activities taking place on the watershed.

Baker (1993) found that the implementation of BMPs on the watersheds in the Lake Erie basin resulted in a significant reduction in sediment and phosphorus but an increase in nitrogen levels. It was postulated that the increasing nitrogen levels are a trade-off associated with the reduction of phosphorus and sediment. Practices which reduce surface run-off and erosion are likely to promote increased subsurface water movement which could increase the nitrogen load reaching the water-course.

2.5 Summary

The quality of water in a watercourse is dependant on many factors. These include the hydrology of the watershed, its geology, morphology, climate, and land use. The preceding review has indicated several important points regarding the hydrology and water quality in a water-course.

Watersheds have the ability to naturally absorb and eliminate some pollutant materials before they become pollution problems. It would appear that on some watersheds this threshold may not be insignificant and in fact may allow for moderate agricultural production over at least 50% of the watershed area without producing serious pollution problems. It would also appear that watersheds have a naturally occurring level of pollutant materials which cannot be reduced through interventions such as BMPs.

The morphology of a watershed would appear to be an important factor as it relates to the storage capacity of the watershed. Increased storage capacity on a watershed would appear to affect the hydrology and discharge of a watershed so as to reduce the concentrations of pollutant materials. Three factors appear to increase the relative storage capacity of a watershed. These are increasing size of the watershed, decreased slope of the watershed and increased forested land over the watershed area. These affect the hydrology of the watershed by causing a relative decrease in the peak flow rate at the outlet.

The hydrology of the watershed is an important factor in assessing water quality. The export of pollutant materials in a watercourse varies with time and with the size of the watershed. The variations in time are related to the climate which influences the periods of high discharge.

In the province of Quebec, there is a lack of adequate water quality data from agricultural watersheds in Quebec that can be used to assess the interactions on a watershed and the resulting water quality. Future modelling efforts will require this type of data.

In order to assess the problem of non-point source pollution it is necessary to develop an understanding of the many factors influencing water quality on the watershed and how they interact.

3.0 Materials and Methods

3.1 Site Description

The study watershed, hereafter referred to as the St. Esprit watershed, is located approximately 50 km northeast of the city of Montreal and consists of the upper portion of the St. Esprit river watershed. The majority of the study watershed lies within the parish of St. Alexis de Montcalm between the villages of St. Esprit and St. Jacques. A map showing the location of the watershed with respect to the island of Montreal is given in Figure 3.1. The total population of the watershed is approximately 200 people.

There are approximately 50 farms on the watershed. The area of the watershed is 26.1 km^2. Of this area, approximately 1680 ha or 64% of the total area is in crop production. The non-cropped area (13.5%) occupies approximately 350 ha, and approximately 575 ha or 22% of the watershed is forested. The forested area largely consists of sugar maple bush. The land-use on the cropped portion of the watershed is shown in Tables 3.1. Approximately 50% of the cropped land is tile drained (Enright et al., 1995).

Table 3.1 Agricultural land use on the St. Esprit watershed.

Land-Use	Area (ha)	Area (%)
Corn	604	35.9
Cereals	347	20.6
Soyabeans	82	4.9
Vegetables	236	14.0
Hay	307	18.3
Pasture	106	6.3
Total	1682	100.0

Nineteen of the farms on the watershed are involved with livestock production. Of these,

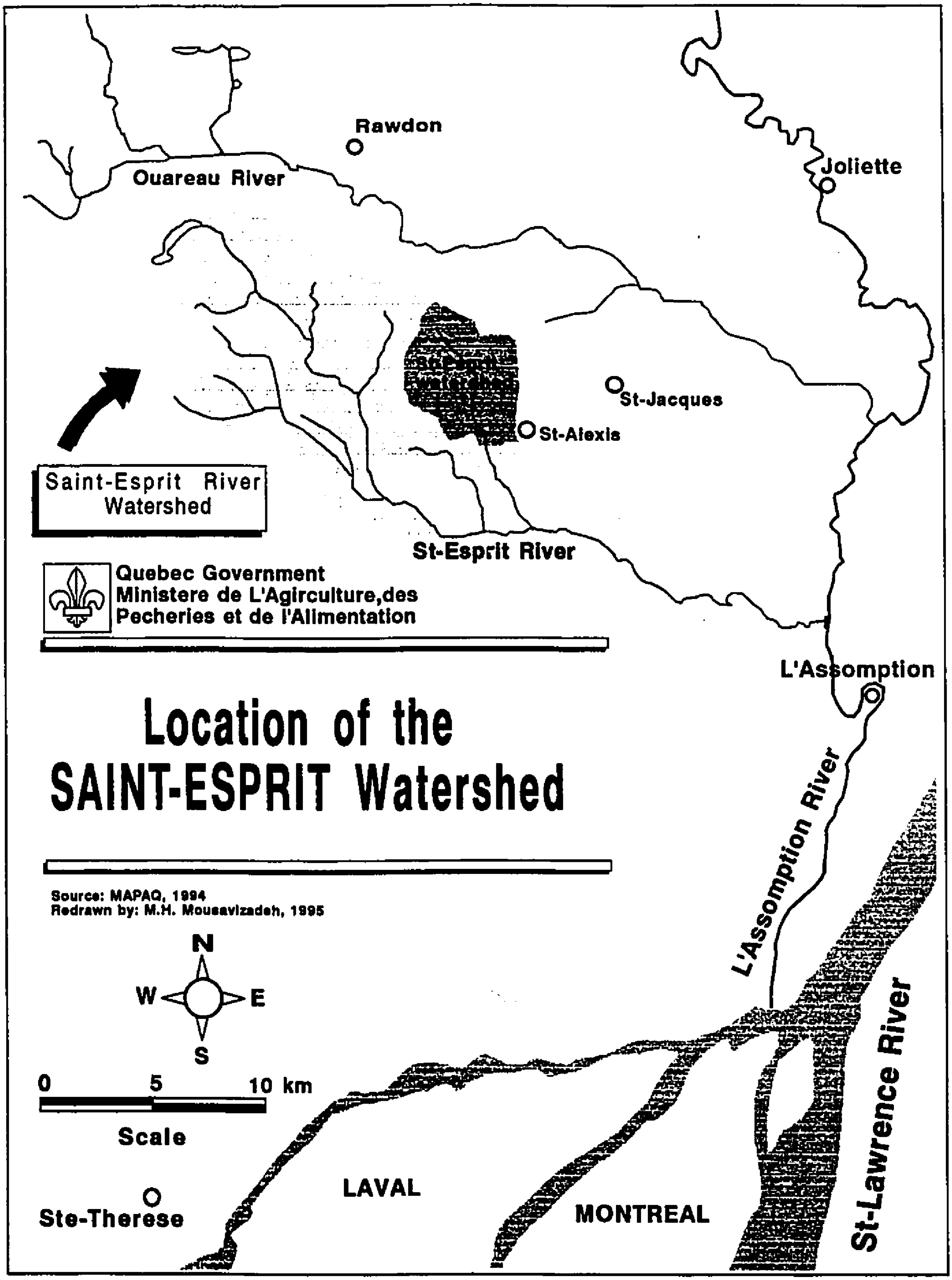
Rawdon
Joliette
Ouareau River
St-Jacques
St-Alexis
Saint-Esprit River
Watershed
St-Esprit River
Quebec Government
Ministere de L'Agirculture,des
Pecheries et de l'Alimentation
L'Assomption
Location of the
SAINT-ESPRIT Watershed
L'Assomption River
Source: MAPAQ, 1994
Redrawn by: M.H. Mousavizadeh, 1995
N
W
E
S
St-Lawrence River
0
5
10 km
Scale
LAVAL
Ste-Therese
MONTREAL

Figure 3.1

nine are dairy farms with the remainder being swine, beef, and poultry operations. The density of animals is 0.8 animal units per hectare.

The soils in the watershed vary from light to heavy with the majority of the crop production taking place on the heavier soils. A summary of the textural classes found on the basin is shown in Table 3.2 (Enright et al., 1995).

Table 3.2 Soil Textural Classes on the St. Esprit watershed

Soil Texture	Area (ha)	% Area
Sand	214	8.2
Loamy sand	147	5.7
Sandy loam	960	36.8
Loam	117	4.5
Silty clay loam	80	3.1
Sandy clay	27	1.0
Clay loam	487	18.6
Clay	576	22.1
Total	2608	100.0

The length of the main channel to the outlet of the watershed is approximately 9km. The topography of the watershed can be described as flat to rolling. The slope of cultivated land generally ranges between 0 and 3%. The drop in elevation from the highest point at the top of the watershed to the outlet is about 40m. The tops of the ridges, land with slopes over 5% and stony areas tend to be left to forest or managed maple sugar bush.

The climate of the watershed is temperate. Average annual precipitation is 1087 mm while the average annual potential evapotranspiration is 572 mm. The average annual temperature is 5.2°C (MEF 1995).

3.2 Instrumentation

The stream gauging station at the outlet of the watershed and the meteorological station on the watershed were established in the winter of 1993-94 by staff and students in the Department of Agricultural and Biosystems Engineering of Macdonald Campus. Figure 3.2 shows the watershed boundaries and main roads as well as the location of the stream gauging station and the weather station.

The control section for the gauging station is located at the upstream side of the bridge where the Rang de Petite Ligne crosses the St. Esprit river. At this point, the river width generally varies within 3 to 7 m depending on the flow conditions, however during flood conditions the river spilled over its banks. The instrumentation for the gauging station is housed in a building (1.8 x 2.4 m) constructed adjacent to the control section. The building is supplied with AC power and is heated.

The water level sensor was a Druck 950 (0 to 34.5 kPa range) submersible pressure transducer buried in the stream bed. As well, a UDG01 ultrasonic level sensor was mounted on the downstream side of the bridge. A Campbell CR10 datalogger installed in the gauging station building was used to collect data from both sensors. The datalogger can be monitored remotely via a modem and telephone connection.

A backup system consisted of a Flowlog datalogger. The probe for the Flowlog system was mounted on a small cement slab which rested on the stream bed. The Flowlog system measured water level and flow velocity, independent of the other systems. However it also relayed data to the Campbell CR10 datalogger.

A rating curve was developed for the river at the control section. An OSS-PC1 propeller

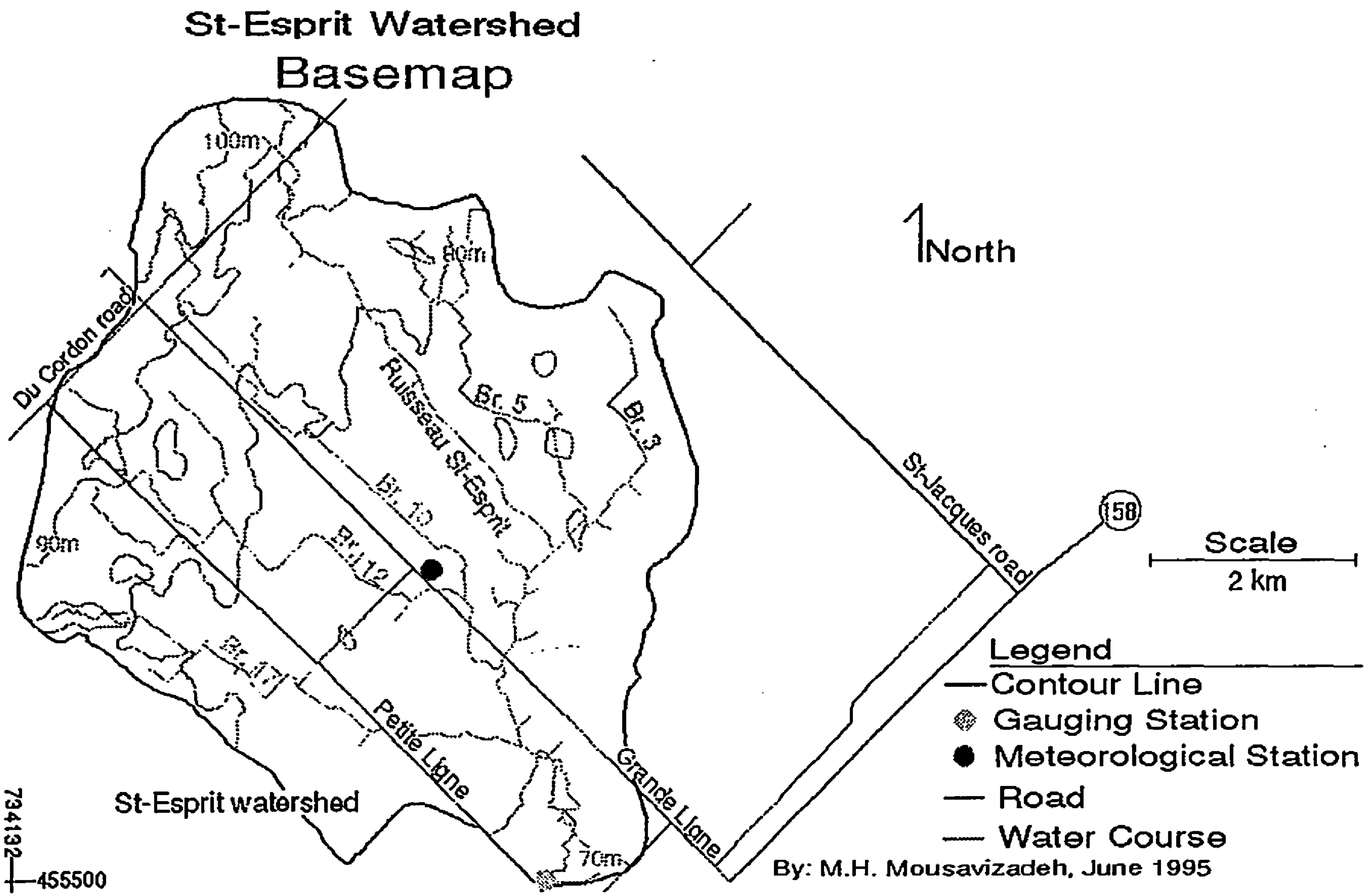
St-Esprit Watershed
Basemap
100m
80m
North
Du Cordon road
Ruisseau St-Esprit
Br. 5
Br. 3
Br. 10
Br. 112
90m
St-Jacques road
158
Scale
2 km
Br. 17
Legend
Contour Line
Gauging Station
Meteorological Station
Road
Water Course
Petite Ligne
Grande Ligne
St-Esprit watershed
734132
455500
70m
By: M.H. Mousavizadeh, June 1995

Figure 3.2

meter was used to take velocity measurements at the control section. A three point method was used, if the depth in the section allowed for it, in 0.5m intervals across the control section. One and two point methods of velocity determination were used during low flow periods. The rating curve is shown in Figure 3.3 (Papineau et al., 1994). The rating curve was programmed into the Campbell datalogger which allowed the datalogger to calculate and store discharge data at 15 minute intervals.

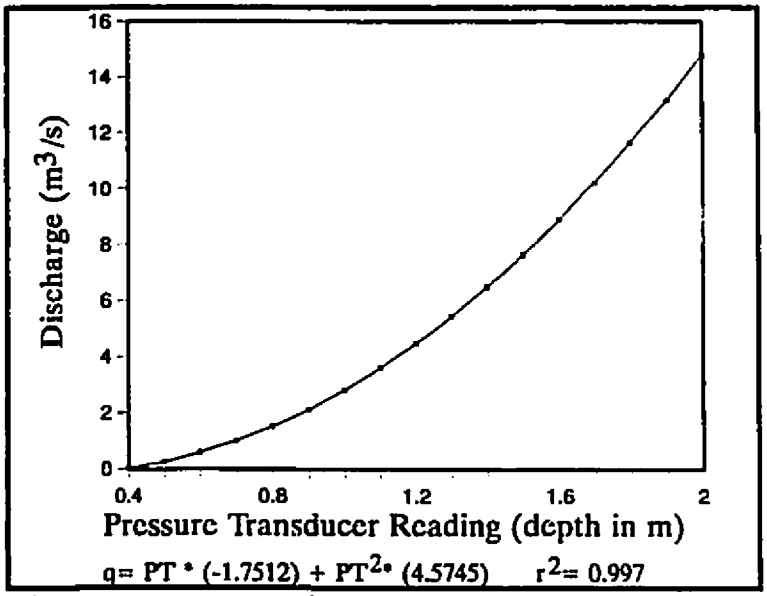

Figure 3.3 Rating curve for the St. Esprit watershed at the control section

An American Sigma 800 SL automatic water sampler was also installed at the gauging station. The intake line for the sampler was suspended from the bridge over the control section. The sampler was refrigerated and contained 24 one-litre bottles in a carousel.

The automatic sampling strategy was based on calculation of the flow volume. Once the accumulated flow exceeded a certain pre-programmed threshold, the datalogger activated the sampler. The threshold value used was variable. It reached a minimum during the summer when it was set to a volume equivalent to 0.5 mm depth of runoff over the watershed. The maximum threshold was 5.0 mm equivalent depth of runoff during the early spring and late fall. This method allowed for more intensive water sampling during runoff events and less intensive sampling during baseflow periods. A sample hydrograph indicating sampling points is shown in

Figure 3.4.

During weekly site visits, a grab sample was taken from the river by hand. The grab sample consisted of two one-litre bottles. During low flow periods, the automatic sampler often did not take a sample between weekly visits, so the grab samples became the only available source of data during these periods.

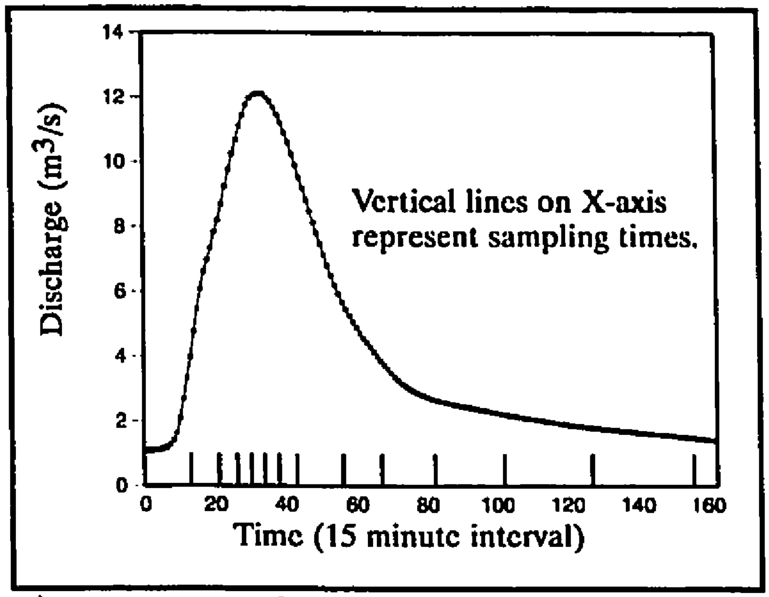

Figure 3.4 Hydrograph of June 27, 1994 event demonstrating increased sampling frequency with increased flow

Besides the stream monitoring sensors, the gauging station was also equipped with a tipping bucket rain gauge, a water temperature sensor, and an air temperature sensor all of which were monitored by the Campbell datalogger.

The meteorological station installed on the basin was also equipped with a Campbell CR10 datalogger. This station was equipped with sensors for air and soil temperature, solar radiation, wind speed and direction, snow accumulation, and a tipping bucket rain gauge.

3.3 Sample Analysis Methods

The water samples were analyzed for three different classes of pollutants: plant nutrients, agricultural chemicals, and sediment. Those pollutants that will be elaborated upon are nitrate nitrogen (NO_3), phosphate phosphorous (PO_4), suspended sediment and atrazine.

Nitrate concentration was determined by the cadmium reduction method (method 4500-NO_3) as outlined by the American Public Health Association (1992). Phosphate concentration was determined by Mehlich III method as outlined by the CPVQ (Agdex 533). The method for determining atrazine concentration involved extraction and analysis procedures which follow the USEPA 625 standard.

Suspended sediment was measured by passing the water sample through a preweighed Whatman 55mm glass microfibre filter paper (0.5 micron) with the aid of vacuum filtration equipment. The filter papers with entrapped sediment were then dried for 24 hours. The final weight of the filter paper was then taken. The measurement of before and after weights of the filter papers as well as the measurements of the initial volumes of the water samples allowed for the computation of the suspended sediment concentration in g/L.

3.4 Data Analysis Methods

3.4.1 Hydrology

There were a number of steps in the hydrologic analysis of the data for this project. The first was to combine the flow records from the gauging station with precipitation records from the weather station. This was done by combining data files with spreadsheet software. The point precipitation measurements taken at the weather station are assumed to be representative of the areal rainfall over the watershed. In practice, point measurements of precipitation should be reduced by a factor depending on storm duration and watershed size. However, as stated by Wenzel (1982), corrections are generally not significant for watershed areas under 26 km^2. This is roughly the area of the study watershed so the point source precipitation measurements were used in an unadjusted form to represent areal precipitation over the basin. Precipitation and flow data were collected at 15 minute intervals.

Monthly graphs of precipitation and flow allowed for the selection of events for further analysis. The criteria used for selection was that the event should be derived from a simple storm pattern and that the event hydrograph should have a smooth recession curve free from the influence of preceding or succeeding storms.

The precipitation and flow for each selected event was then replotted. The objective of this exercise was to derive hydrograph time properties. Those that were examined are the time of concentration (t_c), the lag time (t_l), the time to peak (t_p), the recession constant (K), the peak flow and the volume of surface runoff.

The measured values of t_c and t_l were compared to calculated values determined from commonly used formulae. The lag time was calculated using the SCS nomograph equation (SCS 1972) given as:

$$t_l = \frac{L_f^{0.8}\,(S+1)^{0.7}}{1900Y^{0.5}} \qquad (3.1)$$

where: L_f = maximum length of flow (ft)
Y = basin slope (%)
S = (1000/N) - 10 where N = curve number

The value for the curve number was taken to be 64 based on the soil types and agricultural practices on the watershed. The time of concentration can be determined from the calculated value of t_l as:

$$t_c = t_l/0.6 \qquad (3.2)$$

Two other formulae for determining the time of concentration were tested. These were the Kirpich equation and the Bransby Williams equation (Madramootoo and Enright 1988). The Kirpich equation is given as:

$$t_c = 0.0195\ L^{0.77}\ S^{-0.385} \qquad (3.3)$$

where: L = flow length (m)
S = basin gradient (m/m)

The Bransby Williams formula is given as:

$$t_c = \frac{0.057L}{Y^{0.2}A^{0.5}} \qquad (3.4)$$

where: A = drainage area (ha)
other parameters as previously defined

The time of concentration is defined as the time for all areas of the watershed to contribute to runoff observed at the outlet of the watershed. The lag time is defined as the difference in time between the center of mass of effective rainfall and the center of mass of runoff at the outlet (Viessman et al., 1989). The time of concentration can be considered as a measure of the maximum travel time for runoff on the watershed, whereas the lag time should be regarded as the mean wave travel time for runoff on the watershed. In theory, these two measures are regarded as constants for a given watershed, however in practice it is found that they can be variable depending on season, and storm intensity and duration. The time to peak is defined as the time from the onset of precipitation until peak flow. This quantity is assumed to be most dependant on storm intensity and duration and partially dependant on watershed properties. A schematic diagram showing the definition of these terms is given in Figure 3.5.

The recession constant is the measure of the slope of the line defined by plotting q_o versus q_t for constant time intervals over a recession period. The quantity q_o represents flow at the beginning of each interval and q_i represents the flow at the end of each interval. The interval used was 15 minutes. The recession constant is a measure of the geologic characteristics of the watershed as they relate to groundwater discharge into the surface water course.

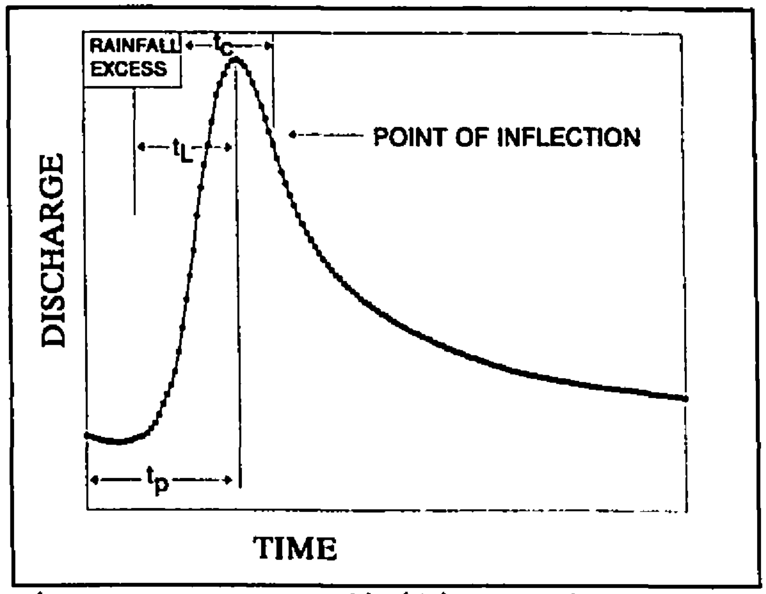

Figure 3.5 Definition Sketch of Hydrologic Parameters

The inflection points on a hydrograph must be identified to determine the time relations of the hydrograph. The inflection points of a curve can be identified as the points where the second derivative of the curve is zero or where the first derivative has a positive or negative peak (Adams 1991). For simplicity of calculation, using the first derivative is the preferable method. The flow data are not a continuous function but rather a series of discrete points in time. Therefore an approximation ($\Delta q/\Delta t$) of the first derivative must be made to identify the inflection points. The approximation for Δq was, for any point, to subtract the average of the values of the two preceding points from the average of the two succeeding points. The average of the values was used as a means of smoothing the data. The value of Δt was taken as unity for each interval.

The positive peak of the $\Delta q/\Delta t$ curve represents the inflection point on the rising limb of the hydrograph. Given a storm of uniform constant intensity over the entire watershed area of a duration exceeding the time of concentration, the inflection point on the rising limb represents the time at which all areas of the watershed are contributing to runoff at the outlet (SCS 1972). Therefore, the time from the start of the event to the inflection point on the rising limb is a measure of the time of concentration. However, if the storm is not of uniform and constant intensity or the duration does not exceed the time of concentration, then this point may not represent the time at which all areas of the watershed are contributing to runoff at the outlet.

The negative peak of the $\Delta q/\Delta t$ curve represents the inflection point on the receding limb of the hydrograph. This point represents the time at which all surface runoff generated by the storm has passed the outlet of the watershed (Viessman et al., 1989). The time from the end of excess rainfall until the inflection point on the receding limb is another measure of the time of concentration. Both means of determining the time of concentration will be used for comparative purposes. It is generally accepted that if the more rigid conditions imposed on the first method of determination are not met, then the second described method is a better measure of this parameter. On large watersheds, few storms exceed the time of concentration in duration.

The lag time can be measured several different ways (Viessman et al., 1989). The method that will be used in this study is to take the interval from the time of peak rainfall rate to the peak flow of the hydrograph.

The volume of surface runoff was determined by using a straight line method of hydrograph separation. The rate of flow at the start of the runoff event is assumed to represent the rate of baseflow discharge for the event. The volume of surface runoff is calculated as the difference between the observed discharge and the baseflow discharge at every interval in the hydrograph from the start of the event until the inflection point on the receding limb.

Empirical relations were tested to assess the relationship between runoff volume versus total precipitation, runoff volume versus antecedent precipitation, and peak flow versus rainfall intensity.

3.4.2 Water quality

Statistical analysis was performed on the measured water quality data. This analysis consisted of finding the mean, variance, and coefficient of skew for nitrate, phosphate, suspended sediment, and atrazine concentrations in each year.

The water quality data were tabulated and the data for each sample were matched to the point in the precipitation/flow data table which represented the time at which the sample was taken. Through the use of spreadsheet software, a linear interpolation was performed between measured water quality data points. Therefore an interpolated concentration was found for each time interval for which no sample was taken. Multiplication of the interpolated concentrations by the measured flow gave an estimate of pollutant loads in the watercourse. This allowed for trend analysis of the various pollutant materials. Comparisons were made between the observed behaviour of each pollutant material on a monthly and daily basis.

An algorithm was developed using spreadsheet software which assigned the observed flow to one of three flow regimes, namely runoff, interflow, and groundwater discharge. The criteria used were as follows. Runoff begins at a time when rainfall occurs and the value of $\Delta q/\Delta t$ is positive. This represents the start of the event. All subsequent intervals were assigned to surface runoff until such time as the negative maxima was reached on the $\Delta q/\Delta t$ curve. This point represents the end of surface runoff. All subsequent intervals were considered to be interflow until such time as the value of $\Delta q/\Delta t$ was greater than -0.01 but less than zero. The value of -

0.01 was selected as the point at which the flow was dominated by groundwater flow. These definitions are shown in Figure 3.6.

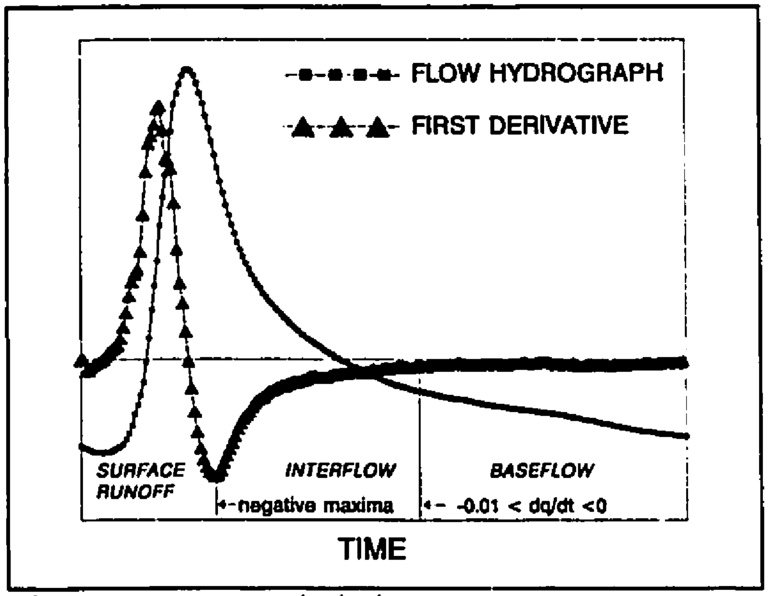

Figure 3.6 Definition Sketch for Flow Separation Algorithm

Baseflow separation techniques are subjective at best. However, an examination of the hydrographs during baseflow indicated that the value of $\Delta q/\Delta t$ approaches a constant value between -0.01 and 0. Other recommended methods for baseflow separation include the straight line method or the use of an empirical formula to determine the point on the hydrograph where baseflow dominates.

The straight line method simply consists of drawing a horizontal line from the point where runoff begins. Where the line intersects the receding limb is where interflow stops and baseflow begins.

A recommended formula for determining the point of baseflow separation is:

$$N = A_m^{0.2} \tag{3.5}$$

where N = the time in days from peak flow until baseflow begins
A_m = the drainage area in square miles

On this watershed, the value of N is 1.58 days.

The straight line method, although simple, would appear to be an oversimplification of the water discharge process on a watershed. The use of the above formula would also appear to be an oversimplification in that it assumes a constant time until baseflow separation for all hydrographs regardless of magnitude. It was found that generally, the two above mentioned methods of baseflow separation were rarely in agreement. On low magnitude events, the time of baseflow separation by the straight line method was considerably less than that predicted by the formula. For large magnitude events, the time predicted by the straight line method was considerably longer.

The use of the value of the first derivative approximation as a measure of the time of baseflow separation has the advantage of being dependant only on flow properties to determine the point of baseflow separation. Therefore on large magnitude events, the identified time was very long, reflecting the increased time required for interflow processes to conclude for a large event. For low magnitude events, the time was often very short. Observations using all three methods indicated that the first derivative produced an estimate of the baseflow separation time which was often intermediate between the other two methods. Using the first derivative approximation has the added advantage of being based on a mathematical property of the flow and thus is easier to identify in a programmed algorithm for separating the different flow stages in a continuous record. The choice of -0.01 as the cutoff was a subjective choice and could no doubt be refined. However, since the process of baseflow separation is a subjective procedure and the use of this estimate produced results which were generally consistent with one of the other two standard methods it would appear to be a valid choice for this purpose.

It will be noted that a straight line method of baseflow separation was used to determine the volume of surface runoff in a previous section. A straight line method of separation is justified under those circumstances since the actual shape of the baseflow curve cannot be determined. The purpose of the above described procedure is to identify the time at which baseflow dominates the flow process on the watershed. Once the algorithm had identified the flow regime for each time interval, it then assigned the calculated pollutant material loading for that time interval. This allowed for analysis of material loading based on flow regime.

Empirical relations were then tested to assess the relationship between total pollutant load versus total runoff, and observed concentration versus discharge for each pollutant material.

A final analysis technique consisted of developing exceedance frequency curves for each pollutant material. These curves were developed by ranking the observed concentrations and then plotting the observed concentration versus the rank expressed as a percentage.

4.0 Results and Discussion

4.1 Rainfall and Discharge

The long term seasonal climatic variation for this basin has been established by the MEF Quebec weather station at St. Jacques, Quebec (station#: 7017380) which lies just outside the study basin. Table 4.1 shows the rainfall and runoff for the months under study in 1994 as well as the long term monthly average taken over 16 years of record. Table 4.2 shows the same information for the months under study in 1995.

Table 4.1 Precipitation and runoff data for 1994.

Month	Precip. (mm) 1994	Long term Average Precip. (mm)	Difference in Precip. (mm)	Runoff (mm)
April	67.8	72.1	-4.3	244.2
May	112.5	93.0	+19.5	78.7
June	175.4	113.6	+61.8	84.4
July	107.8	85.2	+22.6	55.4
August	114.6	102.0	+12.6	33.9
September	37.8	100.4	-62.6	5.6
October	16.4	96.7	-80.3	8.4
November	114.2	87.0	+27.2	25.5

In 1994, the period from May to August was wetter than average while September and October were drier than average. In 1995, May to June and August to September were dryer than average. Only in the month of July was above average precipitation recorded. Discharge records for the growing season indicate that from May through September in 1994, the total discharge was 258 mm, while in 1995 over the same period, the total discharge was only 159 mm.

The precipitation and discharge patterns for the months under study are given in Figures

4.1 to 4.15.

Table 4.2 Precipitation and runoff data for 1995

Month	Precip. 1995 (mm)	Long term Average Precip.(mm)	Difference in Precip. (mm)	Runoff (mm)
March	36.4	61.2	-24.8	111.1
April	81.2	72.1	+9.1	61.9
May	78.2	93.0	-14.8	51.4
June	54.2	113.6	-59.4	18.6
July	131	85.2	+45.8	16
August	84.2	102.0	-17.8	6.4
September	61.2	100.4	-39.2	5.0

The years 1994 and 1995 were very different from a hydrologic standpoint. The winter of 1993-1994 produced deep snowcover over much of this part of Quebec. On this watershed, snowmelt continued until mid-April. Above average precipitation levels were recorded through to August. This was followed by very dry conditions through September and October followed by above average precipitation in November. The winter of 1994-1995 did not produce a deep snow pack as was observed the previous winter. Mild conditions through the early spring resulted in snowmelt being finished by mid-March. This was followed by below average precipitation through most of the growing season with the exception of the month of July.

As will be seen in subsequent sections of this chapter, as a result of the rainfall-discharge pattern of these two years the majority of the data for further study of the watershed characteristics has been taken from the 1994 growing season. The 1994 growing season produced a number of significant runoff events primarily due to the continuous high moisture level of the

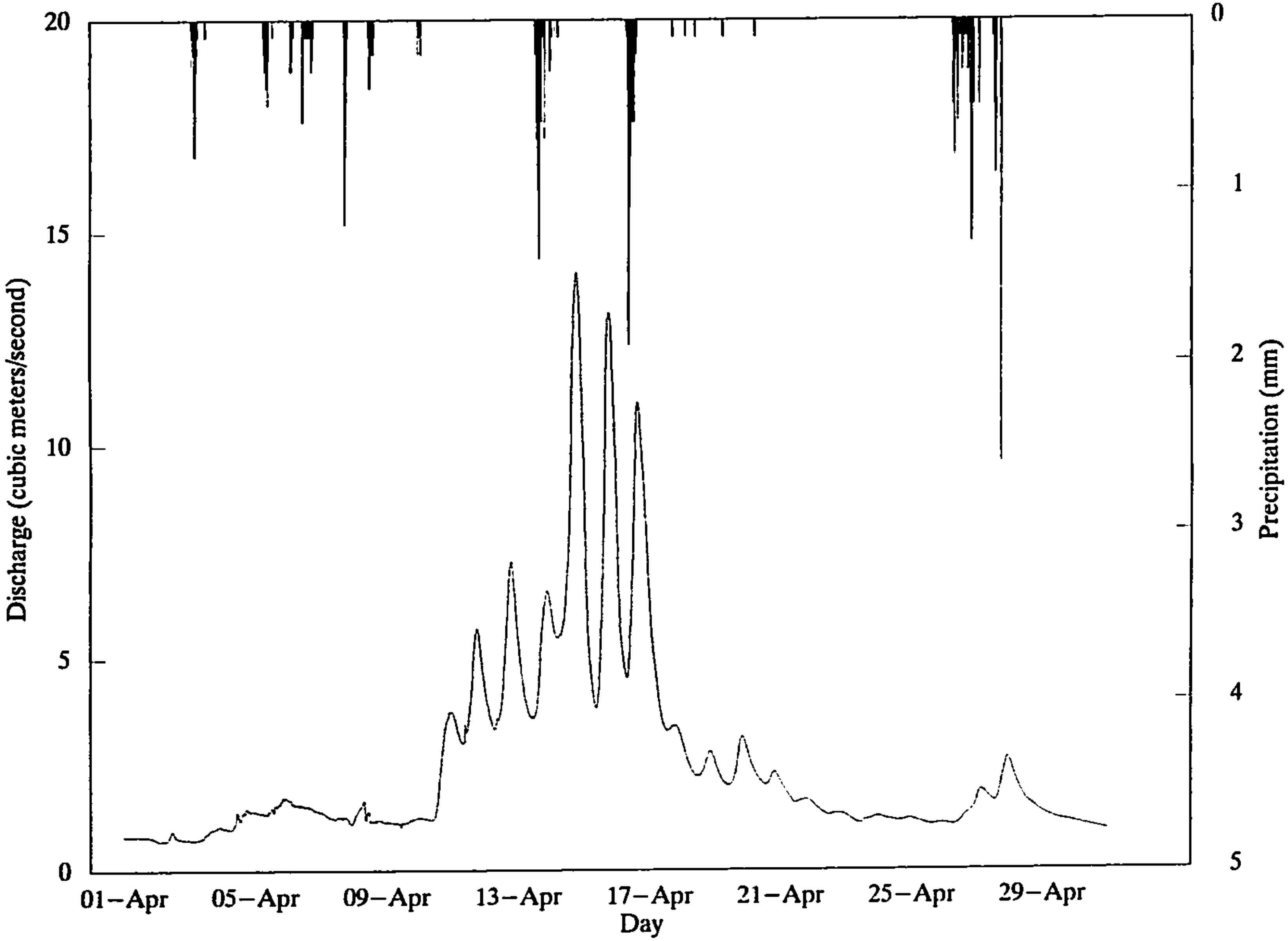

Figure 4.1 Flow and Precipitation – April 1994

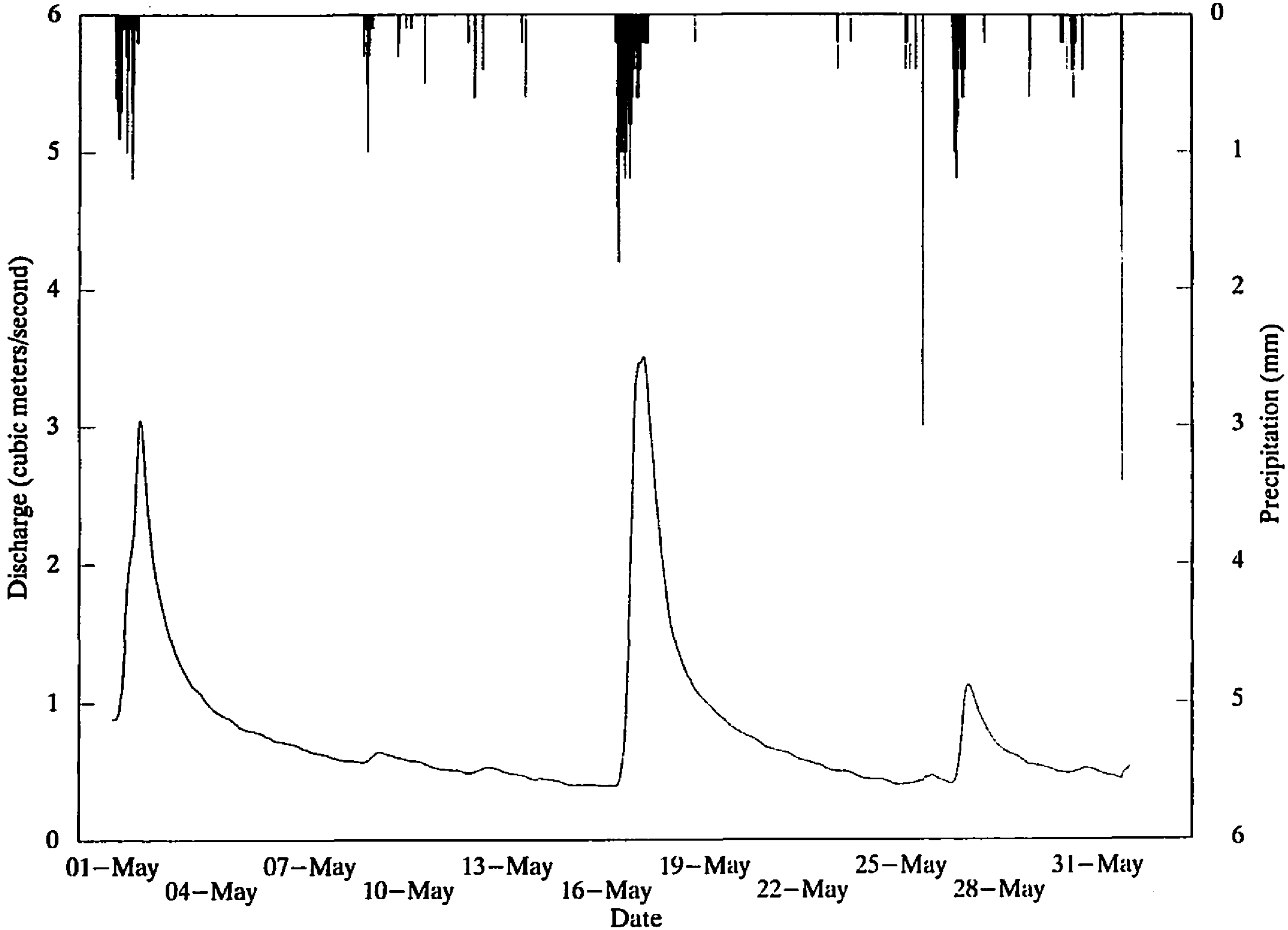

Figure 4.2 Flow and Precipitation – May 1994

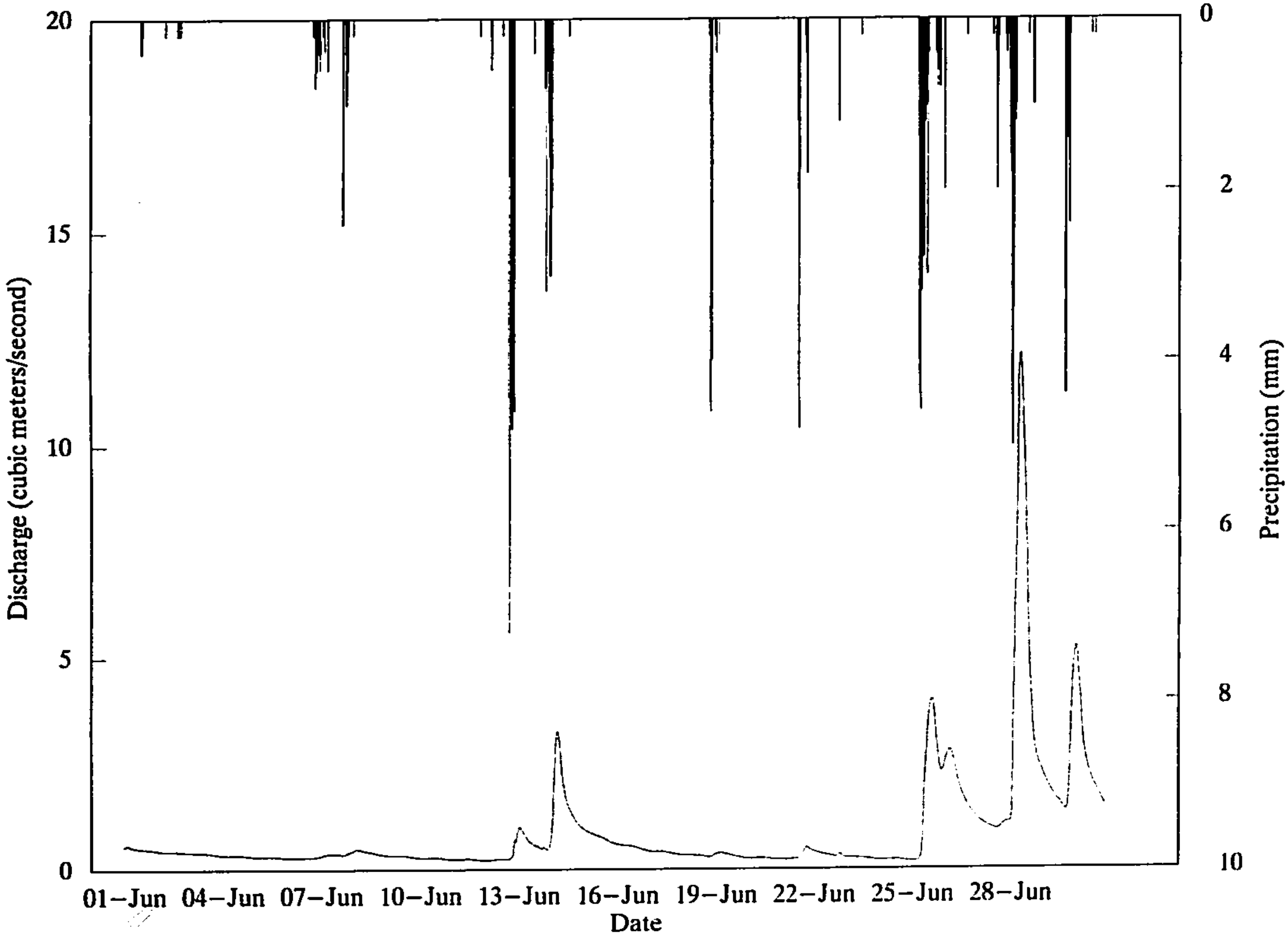

Figure 4.3 Flow and Precipitation – June 1994

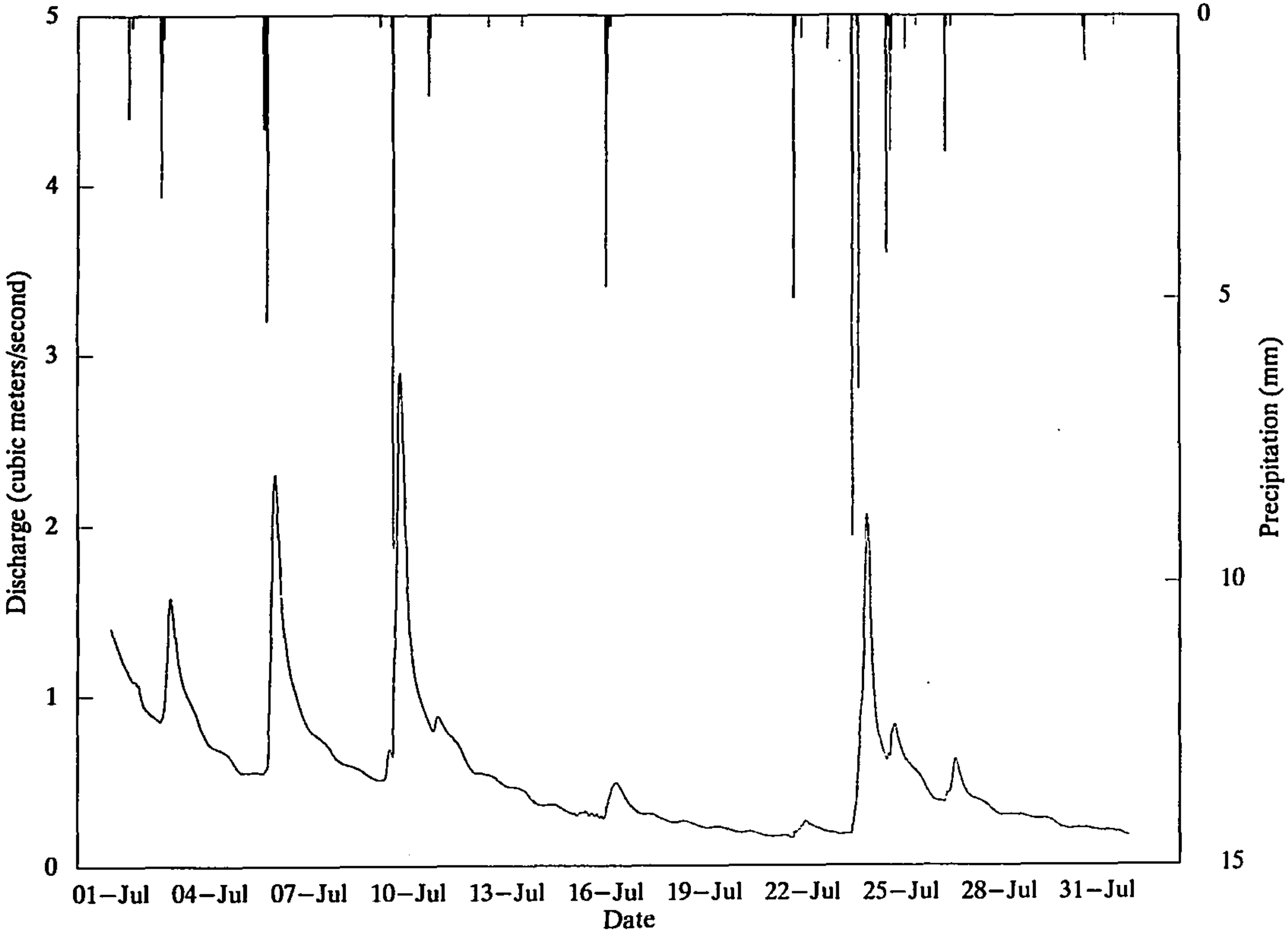

Figure 4.4 Flow and Precipitation – July 1994

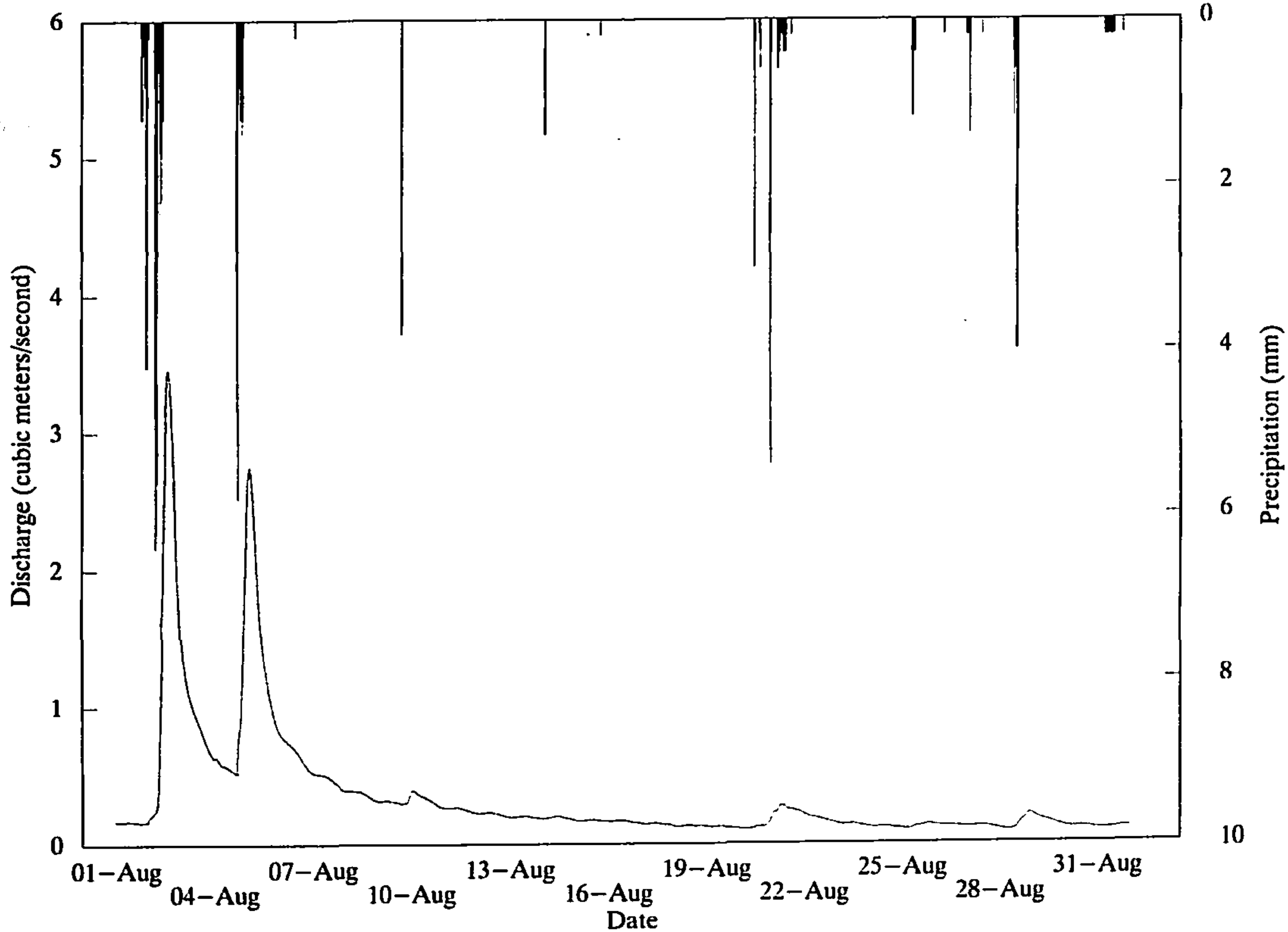

Figure 4.5 Flow and Precipitation – August 1994

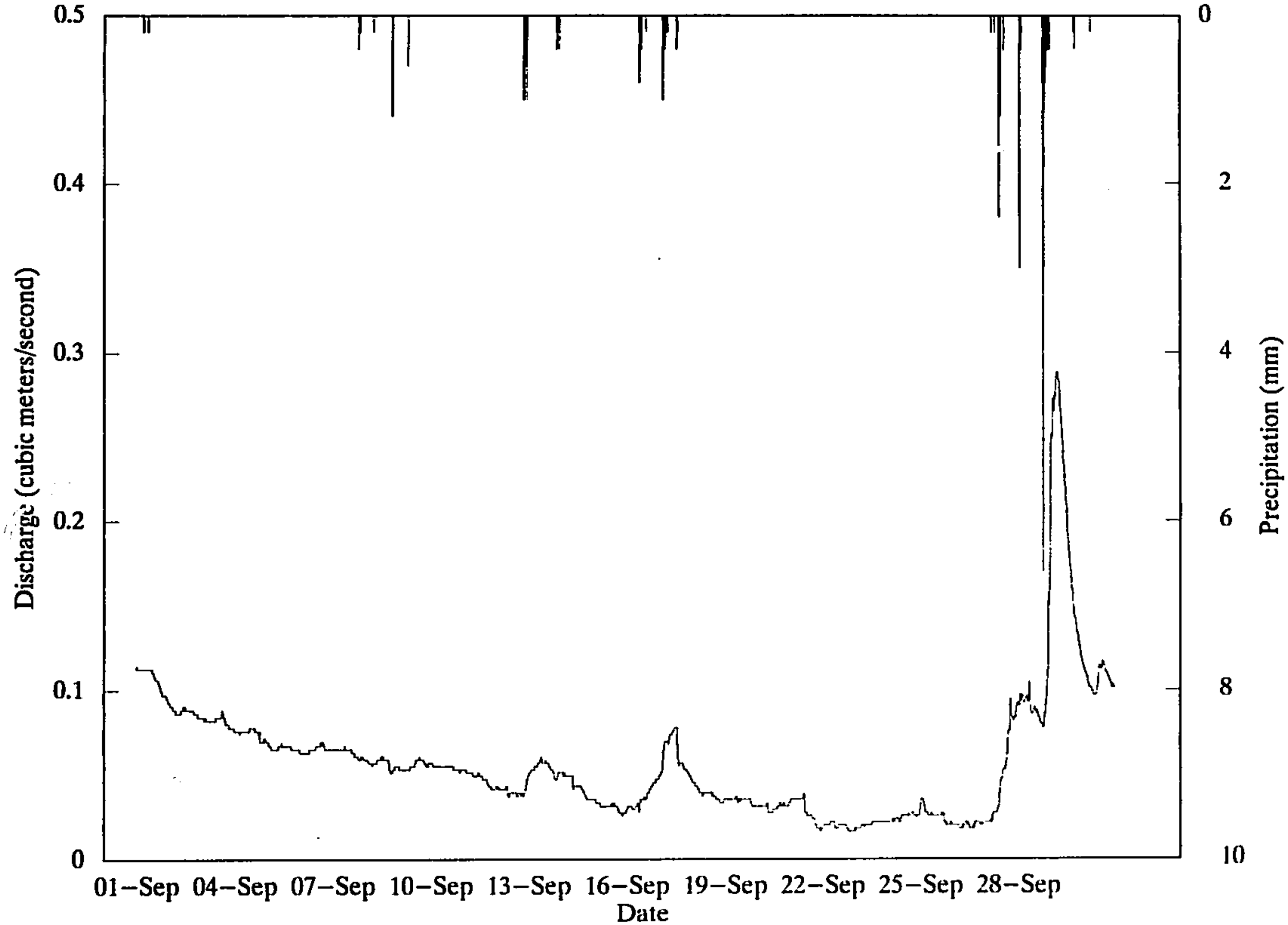

Figure 4.6 Flow and Precipitation – September 1994

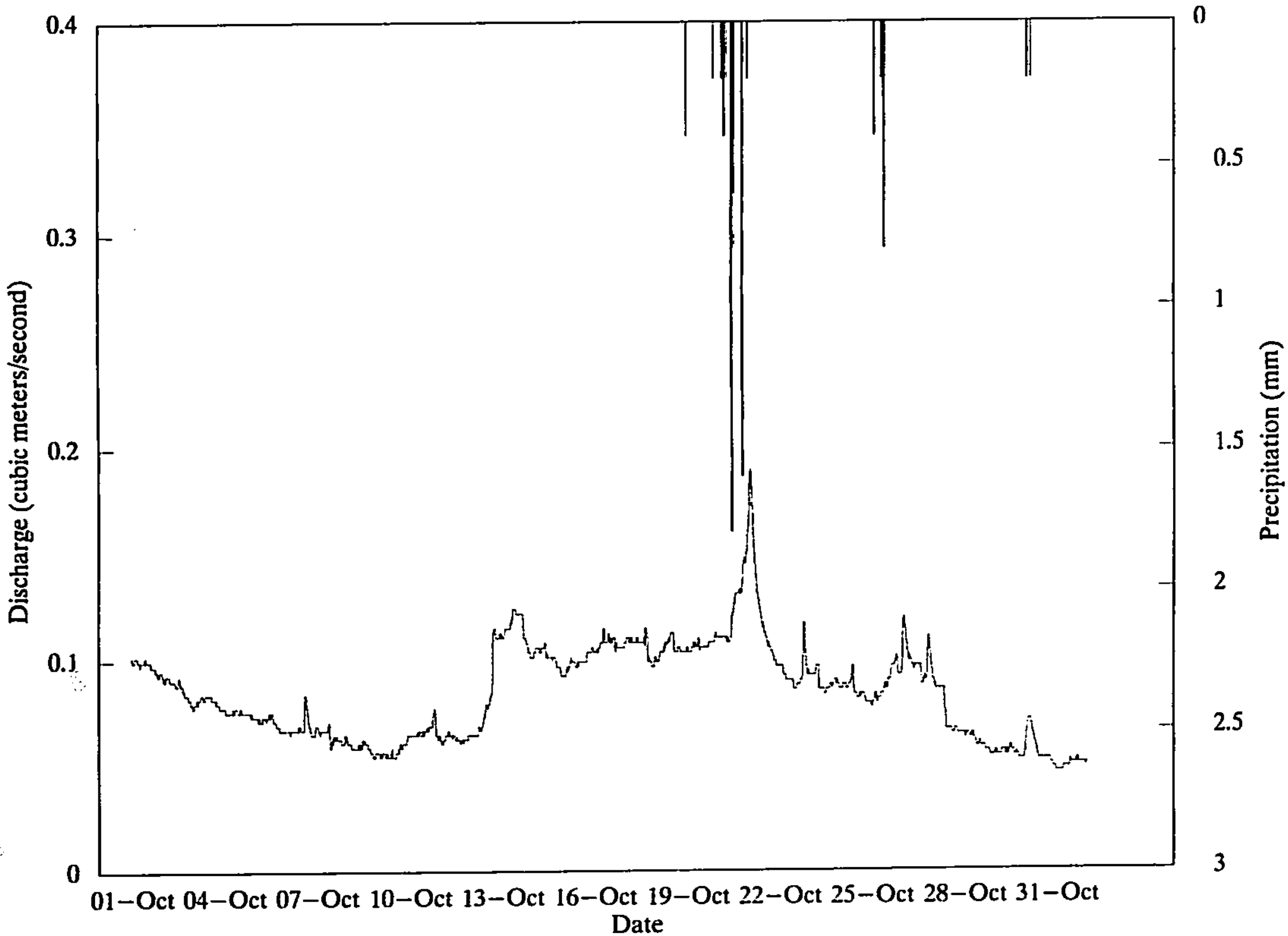

Figure 4.7 Flow and Precipitation – October 1994

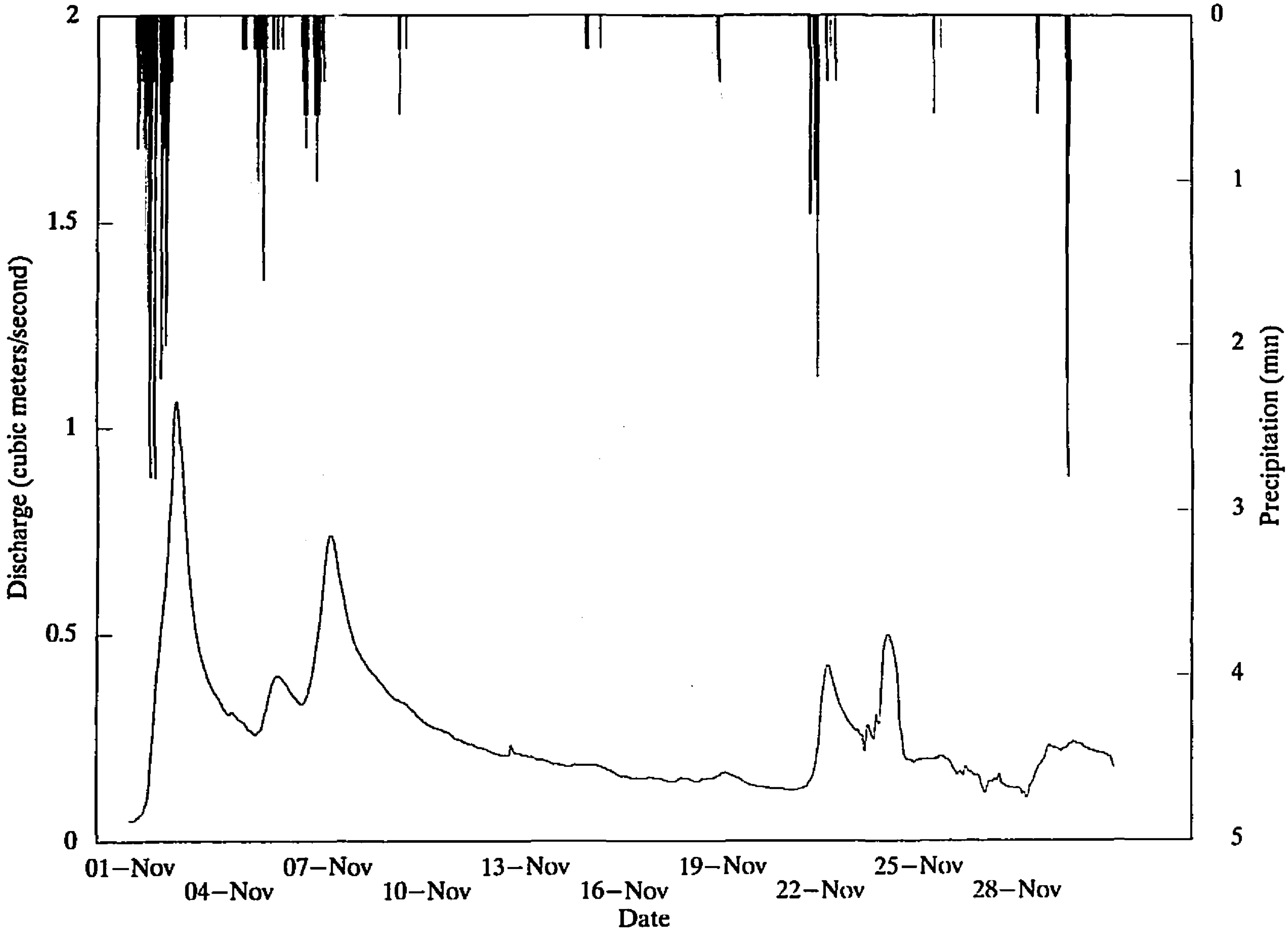

Figure 4.8 Flow and Precipitation – November 1994

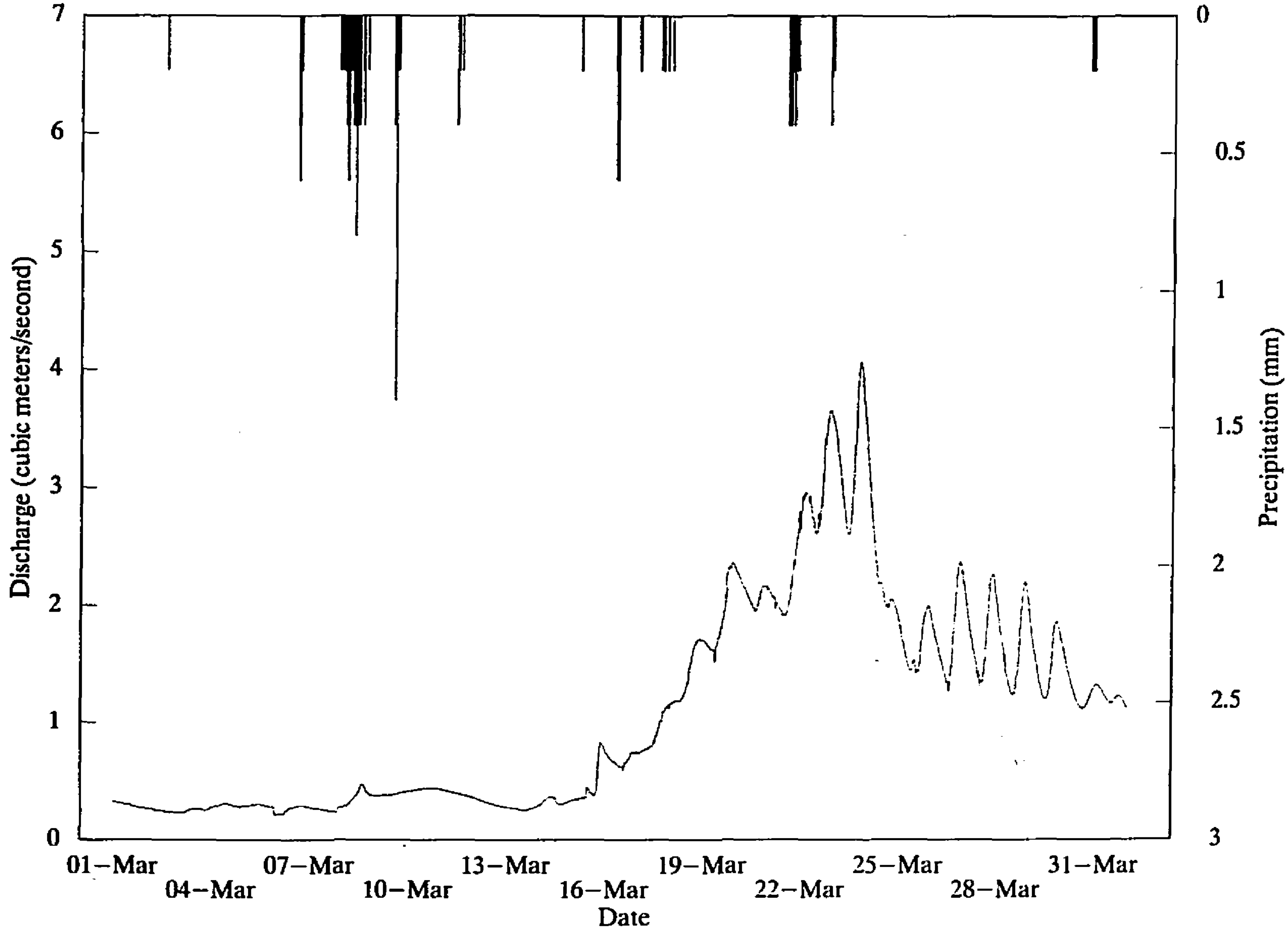

Figure 4.9 Flow and Precipitation − March 1995

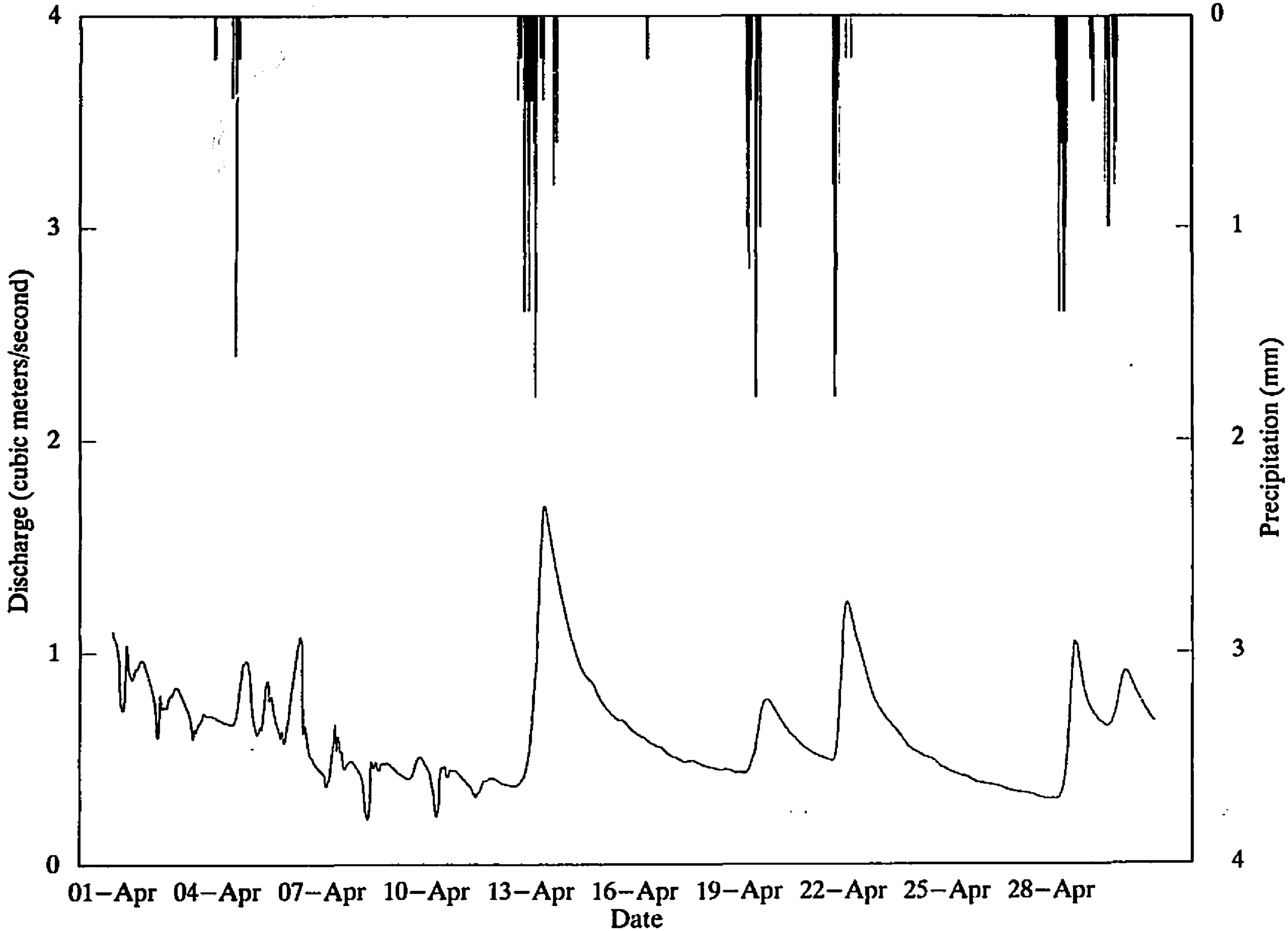

Figure 4.10 Flow and Precipitation – April 1995

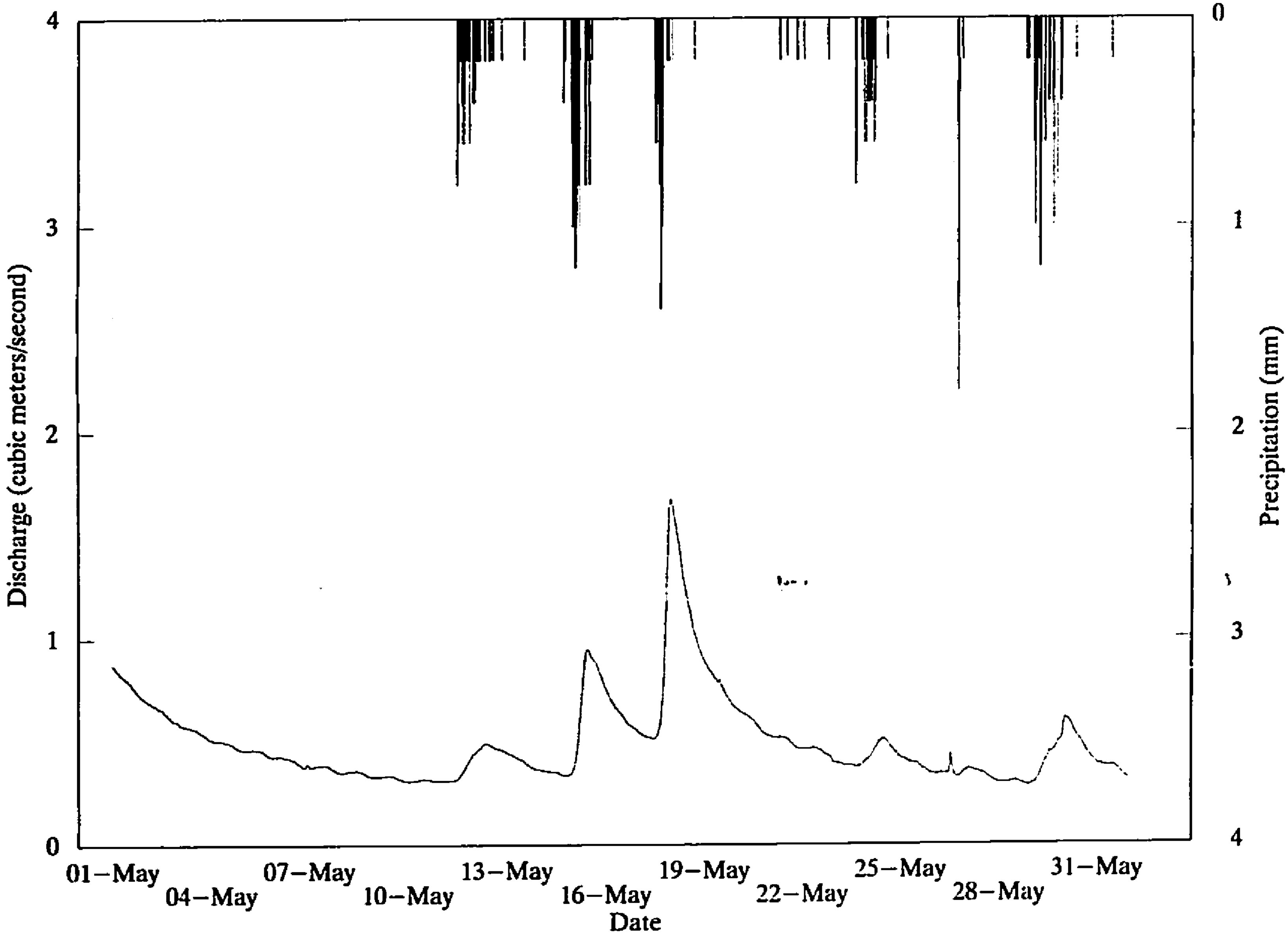

Figure 4.11 Flow and Precipitation − May 1995

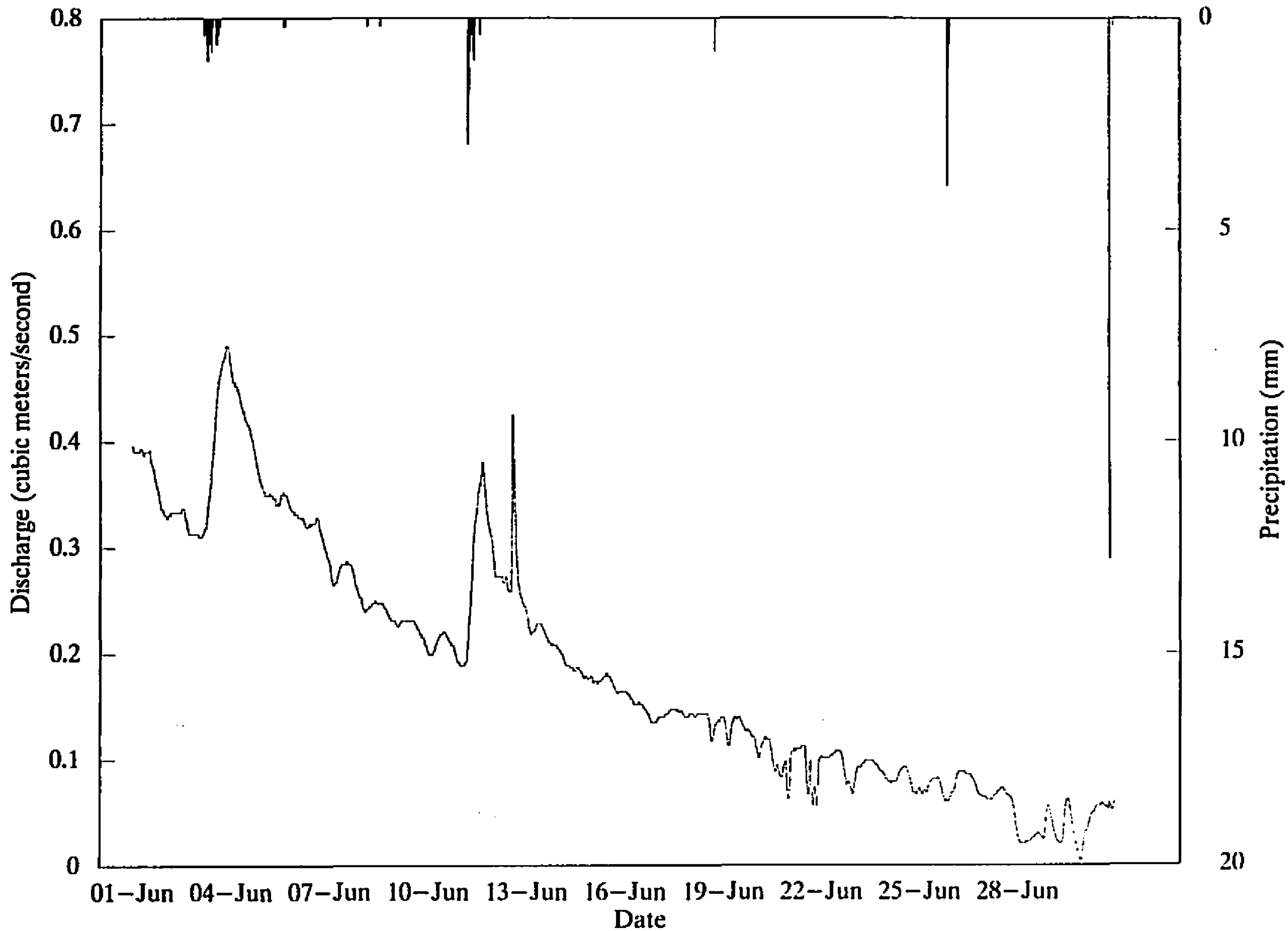

Figure 4.12 Flow and Precipitation – June 1995

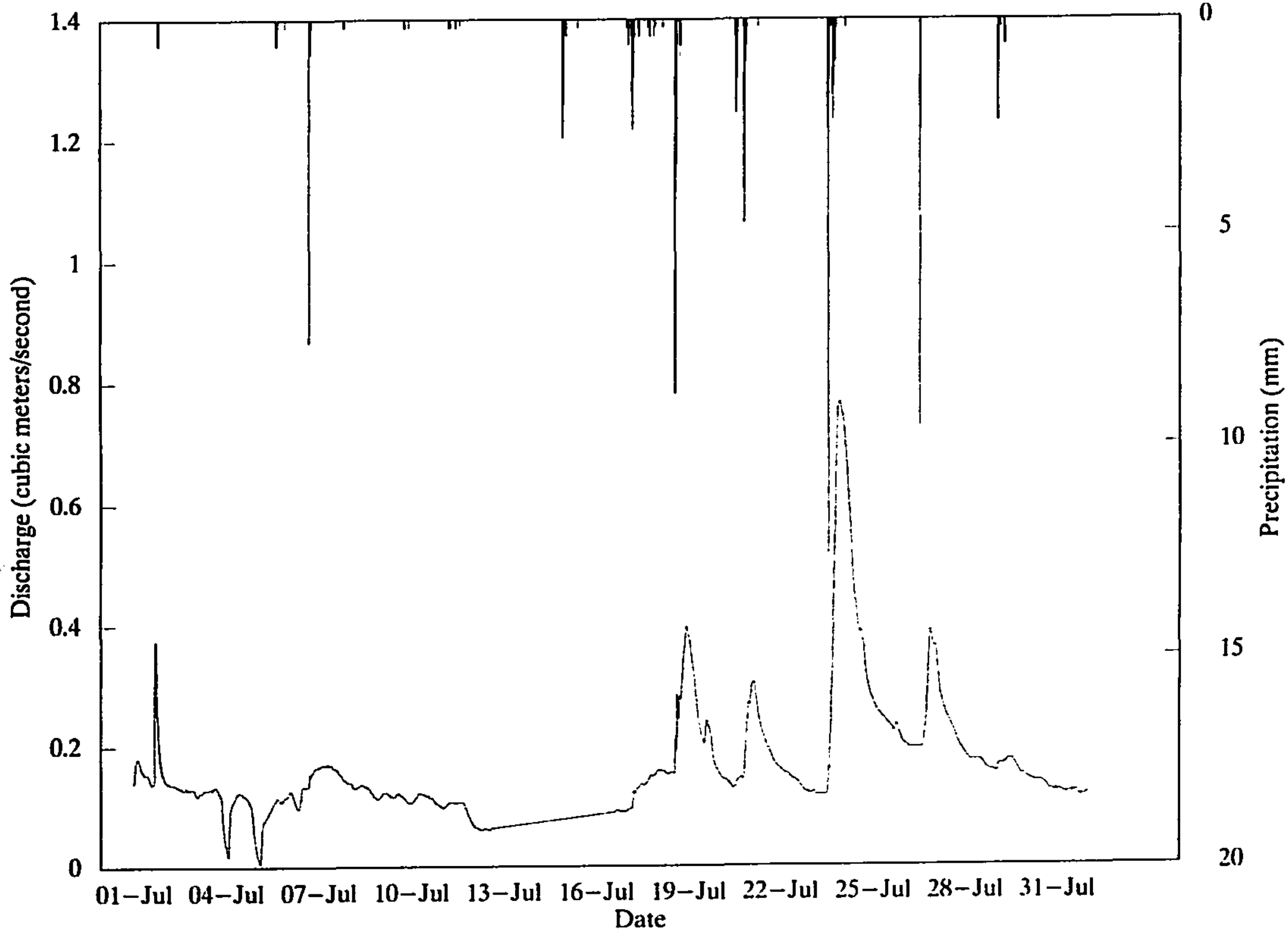

Figure 4.13 Flow and Precipitation – July 1995

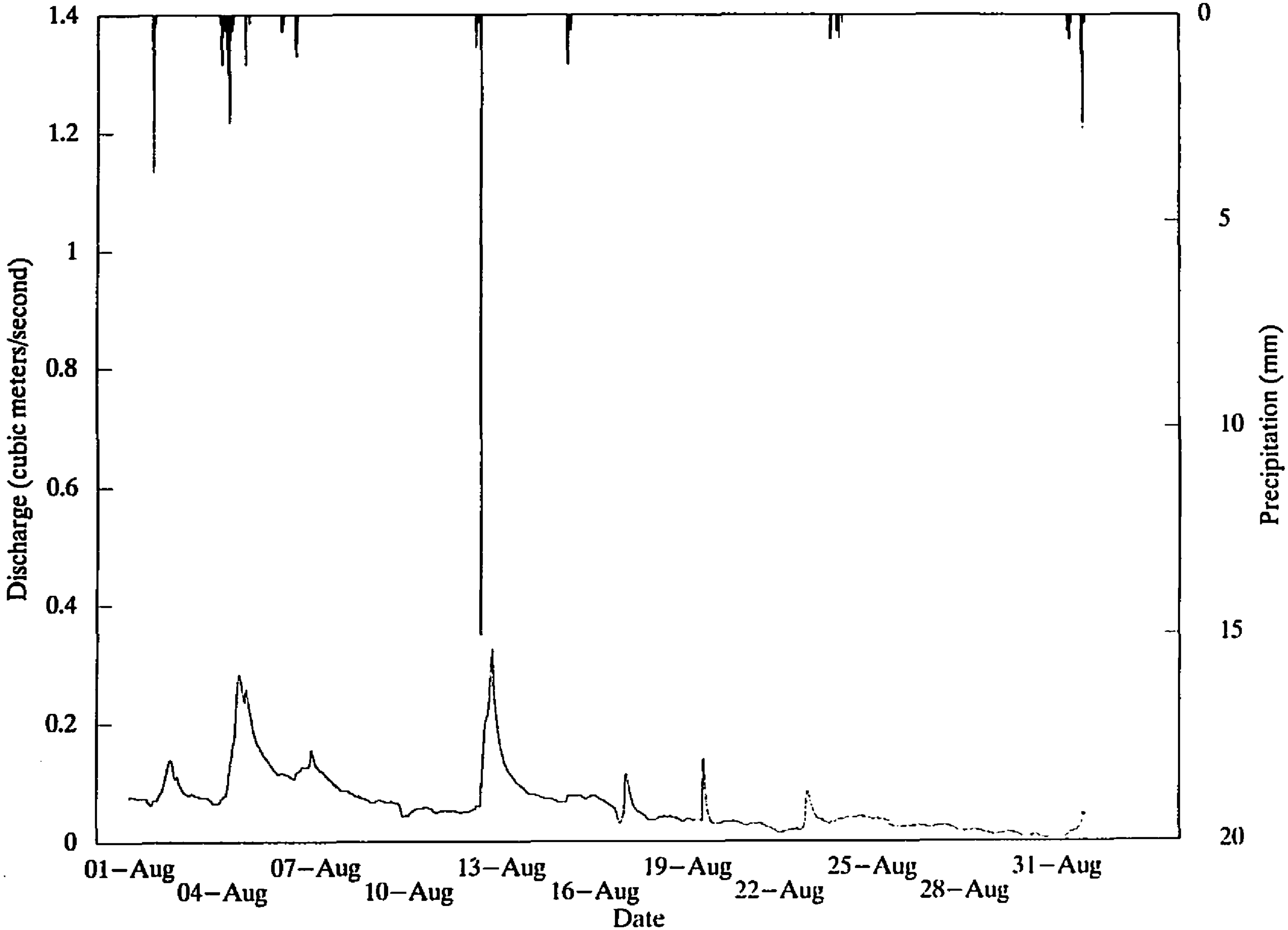

Figure 4.14 Flow and Precipitation – August 1995

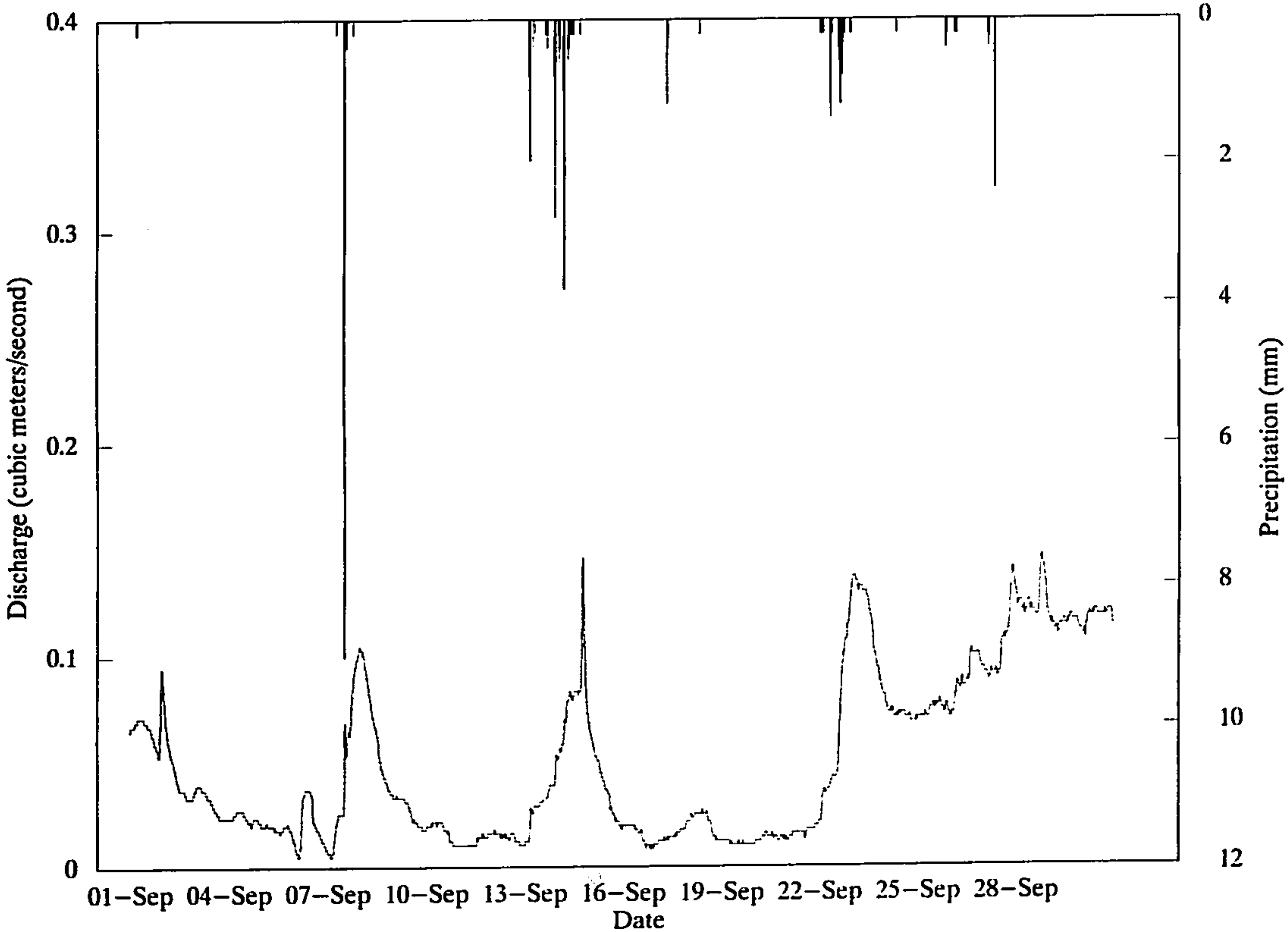

Figure 4.15 Flow and Precipitation − September 1995

soils through the growing season. The frequent change in flow regime in 1994 resulted in the opportunity to observe more dynamic behaviour in water quantity and quality. The dry conditions that prevailed through much of 1995 resulted in a much more static flow regime. This resulted in conditions that can best be described as predominantly base flow.

4.1.1 Hydrograph Analysis

Twenty-five events were chosen for analysis of hydrographic time parameters. Of these 25 events, 18 were chosen from the 1994 season with the remainder coming from the 1995 season. A tabular summary of the hydrologic characteristics of these events is given in Tables 4.3 and 4.4. Sample rainfall and runoff hydrographs are given in Figures 4.16 and 4.17 for the events of May 1, 1994 and June 13, 1994 respectively. The hydrographs and precipitation records for the remainder of the events are found in Appendicies A and B.

The time to peak (t_p) is a function of the storm characteristics and to a limited extent the watershed characteristics. Figure 4.18 shows a plot of t_p versus the storm duration. A linear regression of t_p versus storm duration gives the following equation:

$$t_p = 0.7468 * [d(hr)] + 5.83 \qquad (4.1)$$

The constant (5.83) in the above equation is of some significance as it represents the time to peak for an instantaneous storm. As such, it becomes representative of the flood wave travel time and thus it may be considered an alternative estimate of the lag time (t_l) of the watershed.

A fundamental problem in the analysis of storm hydrographs is that the development of unit hydrograph time parameter theory is based on the uniformly distributed, constant intensity storm.

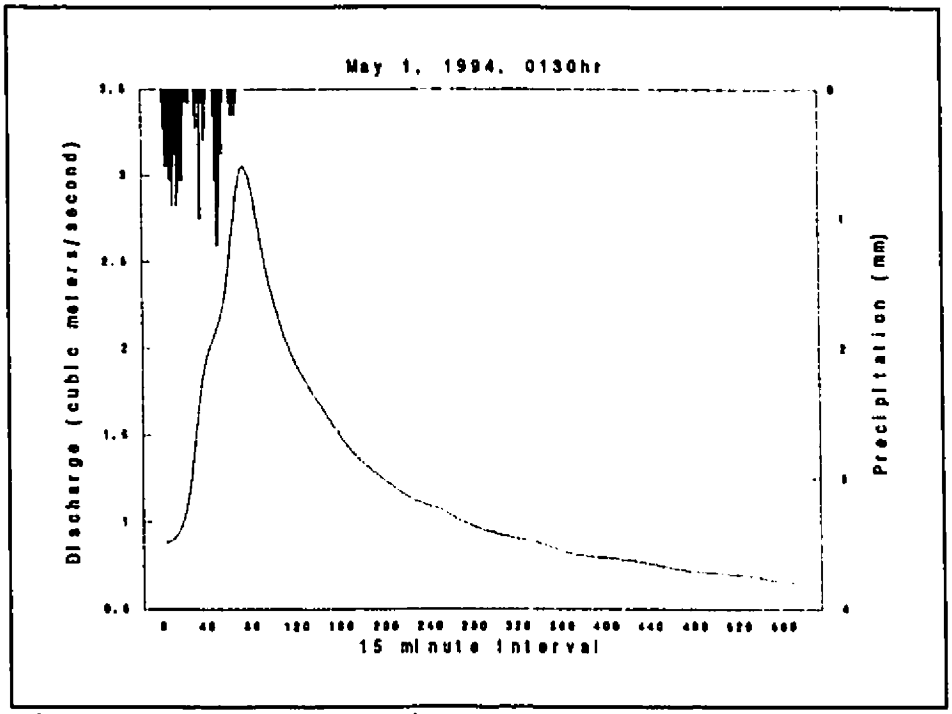

Figure 4.16 Sample rainfall and runoff event

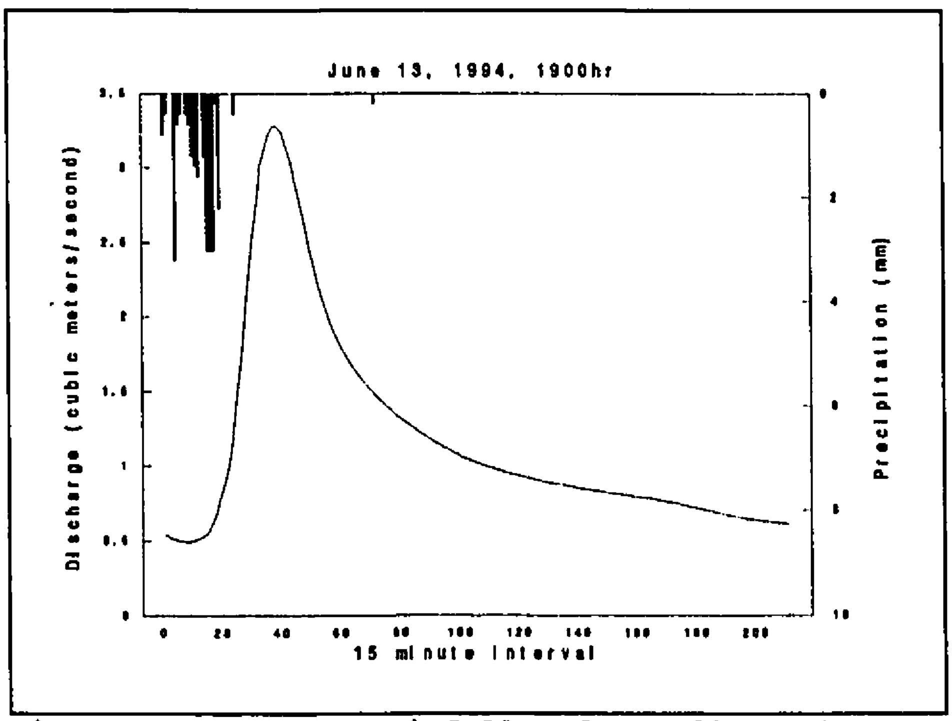

Figure 4.17 Sample rainfall and runoff event

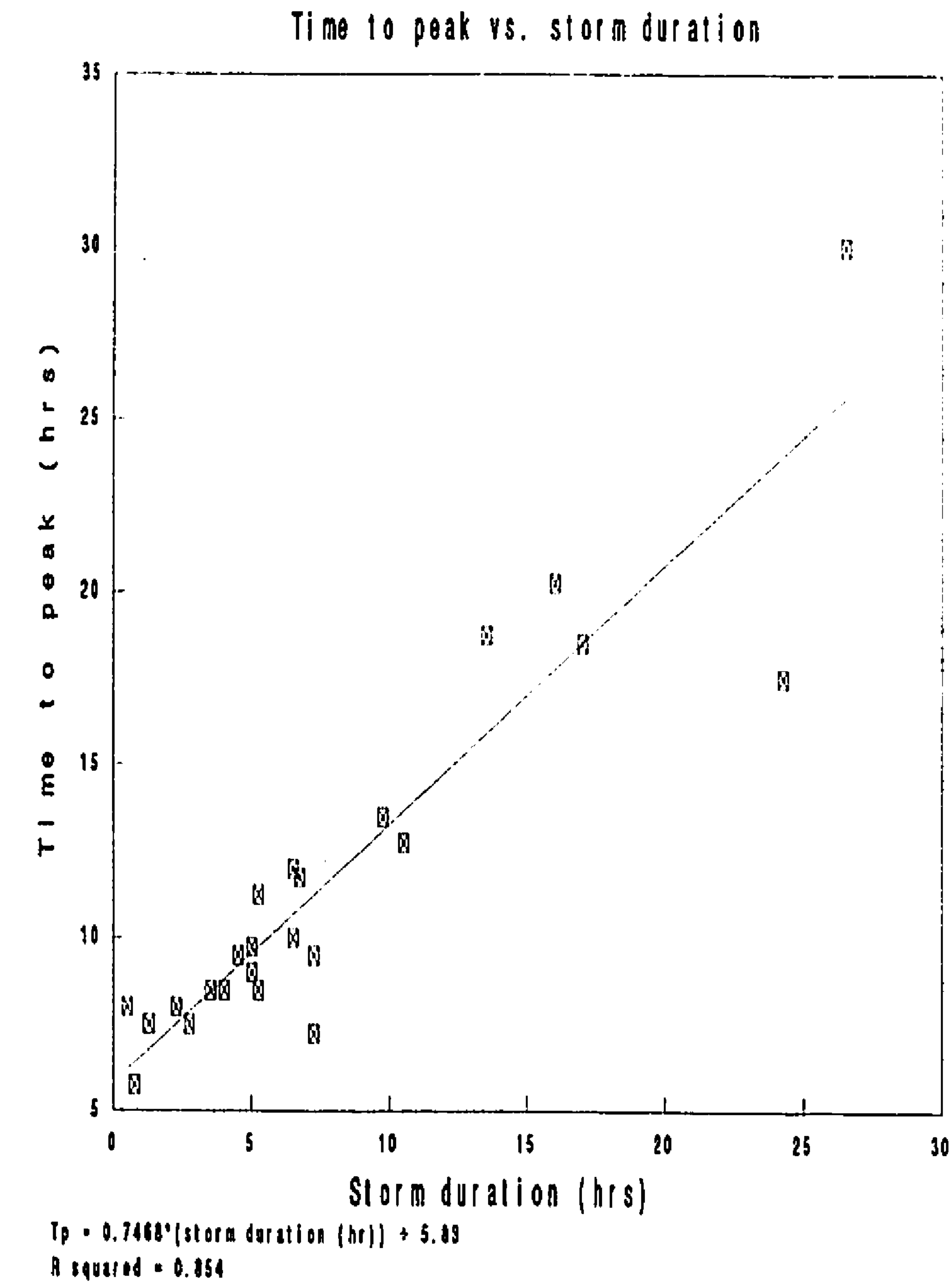
Time to peak vs. storm duration
Time to peak (hrs)
Storm duration (hrs)
Tp = 0.7468*(storm duration (hr)) + 5.89
R squared = 0.854

Figure 4.18

This type of ideal storm does not occur often in nature. Storms which do not conform to the ideal storm present some problems in analysis because of the possible superposition of multiple flood waves from the storm. This would be the case for storms with irregular intensity distributions or storms which exceeded the time of concentration (t_c) of the watershed.

Table 4.3 Selected hydrologic events of 1994

Date	Prec. (mm)	Dur. (hr)	Max. Rain Int. (mm/h)	Peak Flow (m^3/s)	T_p (hr)	T_l (hr)	T_{c1} (hr)	T_{c2} (hr)	Runoff (mm)
Apr.16	14.5	7.25	7.6	11.02	7.25	4.5	4.0	2.75	5.16
Apr.27	8.1	6.75	20.8	2.66	11.75	7.75	5.0	7.75	0.98
May 1	20.8	17.0	4.8	3.06	18.5	11.5	--	4.0	2.98
May 16	46.4	24.25	7.2	3.47	17.5	12.75	11.5	--	5.78
May 26	18.2	10.5	4.8	1.13	12.75	8.0	9.5	6.0	0.86
Jun.13	23.8	5.0	12.8	3.28	9.75	6.25	7.25	7.0	1.94
Jun.27	41.0	5.25	20.0	12.13	8.5	5.75	3.75	6.0	9.68
Jun.29	19.8	4.0	17.6	5.25	8.5	6.75	4.25	7.0	3.24
Jul. 2	9.2	2.75	12.8	1.58	7.5	6.5	5.5	6.75	0.47
Jul. 5	20.2	3.5	21.6	2.31	8.5	6.5	5.75	7.25	1.22
Jul. 9	16.2	0.75	37.6	2.9	5.75	5.0	3.25	7.0	1.56
Jul.16	12	2.25	19.2	0.49	8.0	6.5	4.0	6.75	0.16
Jul.23	21.2	5.25	36.8	2.06	11.25	9	--	8.0	1.51
Jul.26	4.2	1.25	9.6	0.63	7.5	6.75	--	8.0	0.16
Aug. 2	42.6	6.5	25.6	3.46	10.0	7	5.5	6.75	3.55
Aug. 4	19.2	5.0	23.2	2.75	9.0	7.25	5.0	8.0	2.39
Nov. 1	52.2	26.5	11.2	1.06	30.0	16.75	--	6.0	1.85
Nov. 6	13.8	16.0	3.2	0.74	20.25	13.0	--	8.0	0.63

The time of concentration (t_c) is a measure of the maximum runoff travel time for the watershed or alternatively, the time for water to travel from the most remote point of the watershed to the outlet. It should therefore, theoretically, be a constant for the watershed. As previously mentioned, the time of concentration can be measured as the time from the onset of rainfall until the positive inflection point on the hydrograph. The positive inflection point

Table 4.4 Selected hydrologic events of 1995

Date	Prec. (mm)	Dur. (hr)	Max. Rain Int. (mm/h)	Peak Flow (m^3/s)	T_p (hr)	T_L (hr)	T_{c1} (hr)	T_{c2} (hr)	Runoff (mm)
Apr. 12	20.4	13.5	7.2	1.69	18.75	10.25	15.0	6.75	1.33
Apr. 19	11.4	9.75	7.2	0.78	13.5	9.25	--	8.25	0.5
Apr. 21	14	4.5	7.2	1.23	9.5	7.5	--	7.5	0.8
May 17	15.8	6.5	5.6	1.68	12	8.0	9.25	7.25	0.88
Jul. 20	12.2	2.75	19.2	0.30	7.5	6.0	--	6.75	0.17
Jul. 23	35.8	7.25	50.4	0.77	9.5	7.0	6	6.75	0.81
Jul. 26	12.2	0.5	38.4	0.39	8	7.75	6.5	9.0	0.19

represents the time at which the rate of flow is increasing the greatest and thus it represents the time at which all areas of the watershed are contributing to runoff at the outlet. This assumes a uniformly distributed, constant intensity storm.

There are however two problems to using this method of identification in practice. The first is that storms which have an irregular intensity distribution, as with most storms, may produce multiple flood waves of varying magnitude. The superposition of these flood waves may result in multiple inflection points or it may result in an inflection point which does not represent the true time of concentration owing to the disproportionate influence of an intense period of the storm on the resulting hydrograph. Figures 4.19 and 4.20 are the hydrographs and first derivative

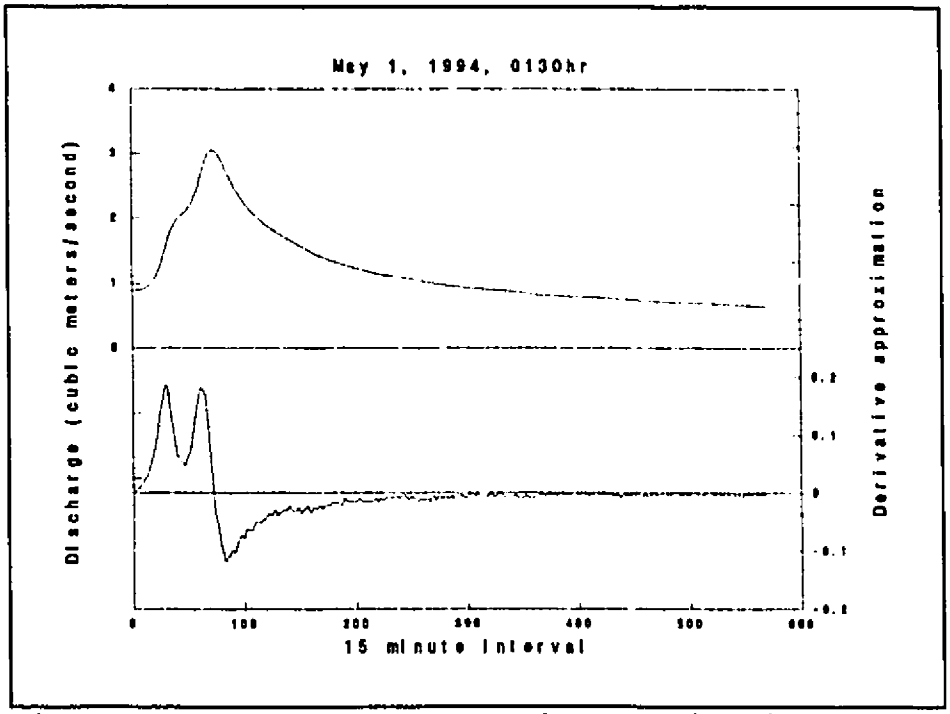

Figure 4.19 Hydrograph and first derivative curve

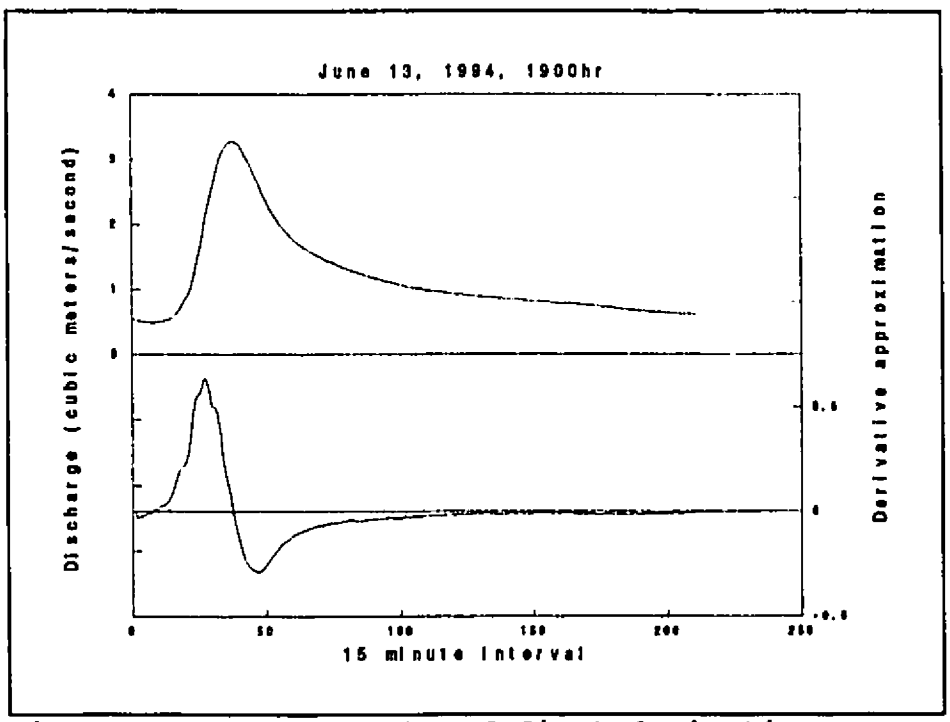

Figure 4.20 Hydrograph and first derivative curve

curves for the events of May 1, 1994 and June 13, 1994 respectively. The hydrograph for the May 1 event exhibits two inflection points on the concentration side of the hydrograph due to the superposition of multiple flood waves during the event. The event of June 13 has only one positive inflection point.

The second problem occurs if the storm duration does not exceed the time of concentration. In this case, the flood wave may crest before runoff from the most remote part of the watershed is able to reach the outlet. In this case the inflection point cannot represent the time of concentration. In all of the above cases, the inflection point of the hydrograph can be seen to be primarily a function of the storm characteristics and therefore not representative of the watershed itself. The time of concentration measured using the positive inflection point is shown as t_{c1} in Tables 4.3 and 4.4. For some storms, this time could not be determined because of the presence of multiple inflection points. The mean of t_{c1} is 6.53 hr. with a standard deviation of 3.04 hr.

An alternative method to measure the time of concentration is to take the time interval between the cessation of rainfall and the inflection point on the receeding limb of the hydrograph (Madramootoo and Enright 1988). The inflection point on the receeding limb is taken to be the point where all runoff has passed the outlet. This method is preferable to the former because the interval will not be affected by storm pattern or duration as it is only dependant on the time when precipitation ceases, and flow characteristics of the watershed. The mean of t_{c2} is 6.89 hr. with a standard deviation of 1.3 hr.

The large standard deviation observed for t_{c1} can be explained by observing the values for t_{c1} for storms of duration exceeding, or much lower, than the mean value for t_{c1}. In most cases they could not be determined due to multiple inflection points or the value was much higher or lower than what might be expected. Therefore one can conclude that the storm duration had an effect on the observed value of t_{c1}. For all storm durations, t_{c2} gave more consistent results as can be seen by the lower standard deviation. Further, the method for determining t_{c2} was applicable even for storms where the method for determining t_{c1} could not be used.

The lag time (t_l) is the mean flood wave travel time. It is defined as the interval between the center of mass of observed rainfall and the center of mass of runoff. A method to estimate the lag time is to measure the time from the center of mass of observed rainfall to the time of peak flow at the outlet. The values for t_l for the observed events on this watershed are shown in Tables 4.3 and 4.4. The lag time is also a measure of watershed properties and thus it should be expected to be a constant regardless of storm duration. However the estimate is dependant upon the time when peak flow is reached which has already been demonstrated to be dependant on the duration of the storm. If one takes the mean and standard deviation of the lag times, the result is a mean of 8.13 hr and a standard deviation of 2.76 hr. However, if one considers only those storms where the duration does not exceed the time of concentration, then the mean is 6.89 hr with a standard deviation of 0.94 hr. This would seem to be a reasonable assumption since the lag time is a measure of the average flood wave travel time. Storms with a duration less than the time of concentration should have a flood wave whose characteristics are not as dependant on the duration of the storm and therefore should give a better estimate of the lag time.

The SCS nomograph method, the Kirpich formula and the Bransby Williams formula were used to derive calculated values of t_c and t_l. The SCS nomograph method gave a value for t_l of 4.6 hours. Of the two measured values of t_l, the calculated value is in closer agreement with the constant in the regression equation for t_p versus storm duration of 5.83 hours.

The calculated values for t_c are given in Table 4.5. The Kirpich method underpredicted

Table 4.5 Measured and Calculated values of t_c

Method	t_c(hr)
Measured	6.9
Kirpich	3.1
SCS	7.7
Bransby Williams	8.4

the time of concentration. This was noted as well by Madramootoo and Enright (1988) for watersheds in the Ottawa - St. Lawrence lowlands. They attributed their result to the fact that the Kirpich formula was developed for steeper watersheds. The SCS method yielded the closest result to the measured value. It would appear that the Kirpich method is not appropriate for the relatively flat agricultural watersheds in Quebec.

The above time parameters describe the behaviour of a hydrograph in the ascending portion of the curve. What follows is a discussion of the behaviour of the receeding limb of hydrographs from this watershed. There are two distinct sections of the recession of a hydrograph as can be seen by examining the curves of $\Delta q/\Delta t$ in Figures 4.19 and 4.20. The first section is a short period from the time of peak flow until the inflection point on the receeding limb is reached. The second section is from the inflection point onwards. The approach used is to determine recession constants for these two sections. This is done by plotting q_0 versus q_t for each time interval in the recession phase where q_0 is the flow at the beginning of the interval and q_t is the flow at the end of the interval. The interval that was used was 15 minutes. The resulting plots are straight lines with a slope K and an intercept C. This was done for each event tabulated in Table 4.3 and 4.4, and the resulting K and C values were averaged. The K and C values for the first recession phase are denoted by the subscript '1' and those from the second phase are denoted by the subscript '2'. The value of R^2 as a measure of goodness of fit exceeded 0.93 for all events for the determination of K_1 and C_1 and it exceeded 0.99 for all events for the determination of K_2 and C_2.

The value of C_2 is approximately equal to zero. Therefore, the recession in this phase is governed only by the value of K_2, the mean of which was found to be 0.97. The average value for K_1 was found to be 1.15. The value of C_1 was found to be related to the magnitude of the flow. This is shown in Figure 4.21. The R squared value for this curve is 0.906. Based on these results, the recession phase of hydrographs on this basin can be described from the time of peak flow until the inflection point on the receeding limb by the following relation:

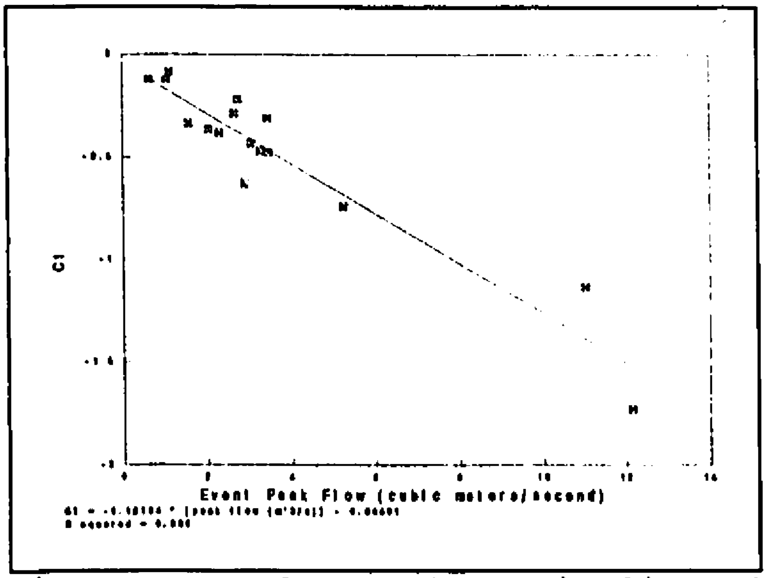

Figure 4.21 Plot of best fit line of recession coefficient C_1 versus magnitude of peak flow

$$q_1 = 1.15*q_0 - 0.12*[\text{peak flow}(m^3/s)] - 0.04 \quad (4.2)$$

and from the inflection point onward, the recession can be described by the relation:

$$q_1 = 0.97*q_0 \quad (4.3)$$

4.1.2 Empirical relationships

A number of empirical relationships were examined with respect to the hydrology of the basin. The objective of this section is to assess whether simple mathematical models are adequate to explain the hydrology of the watershed.

In general, it can be said that none of the relationships tested provided a satisfactory model for any component of the hydrology of this watershed. Figure 4.22 shows a scatter graph of peak rainfall intensity versus peak flow for the 25 events under study. No satisfactory regression relationship was found for this data set.

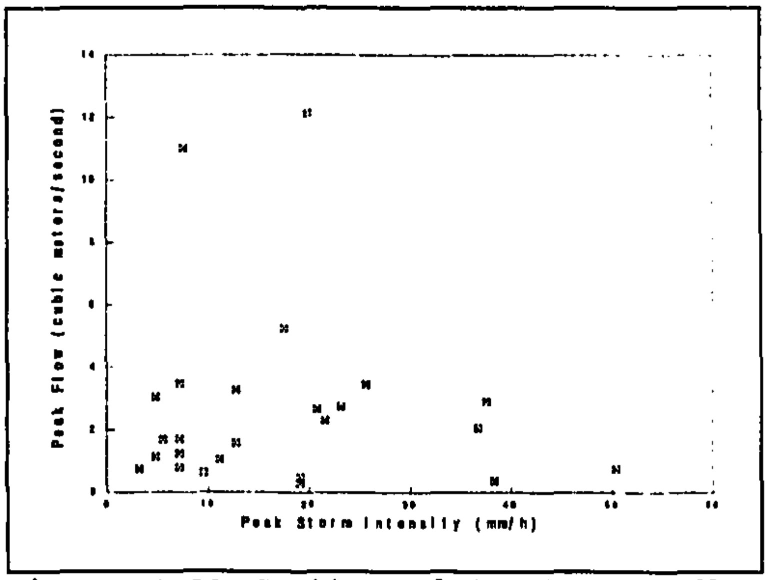

Figure 4.22 Scatter plot of peak flow versus rainfall intensity

Figure 4.23 is a plot of total rainfall versus total runoff for each of the 25 events. A best fit straight line has been drawn for this data however the R squared value for this curve is 0.35 so the relationship is not strong. The equation of the best fit line is:

$$\text{Runoff(mm)} = \text{Rainfall(mm)} * 0.10 - 0.20 \qquad (4.4)$$

Figure 4.24 is a plot of the best empirical model that was found for these events. This figure represents the percentage of rainfall from a storm appearing as surface runoff versus the

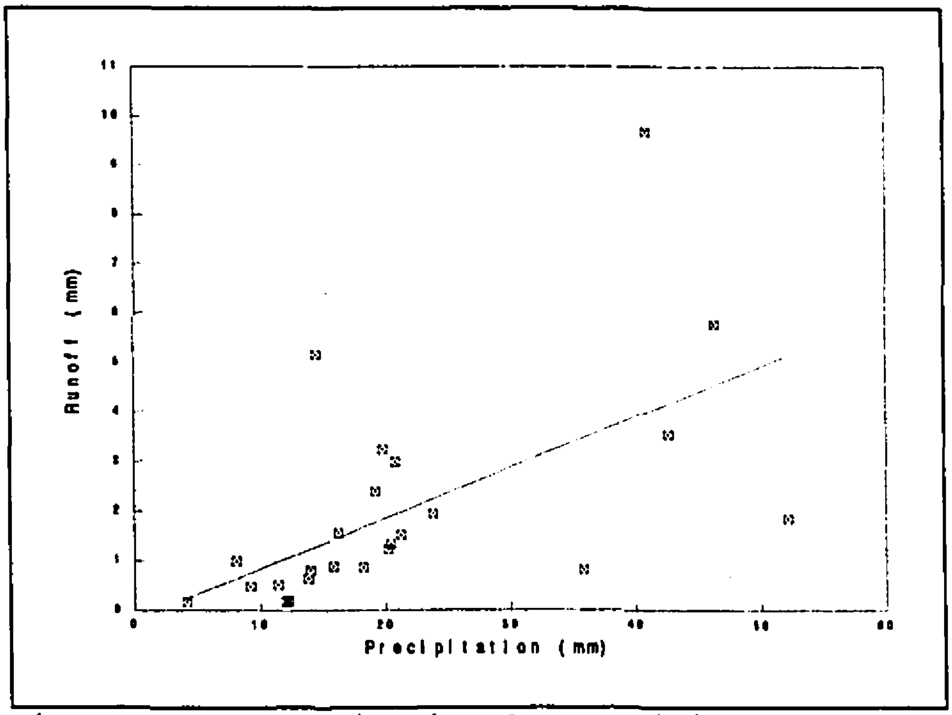

Figure 4.23 Best fit line for precipitation versus runoff volume

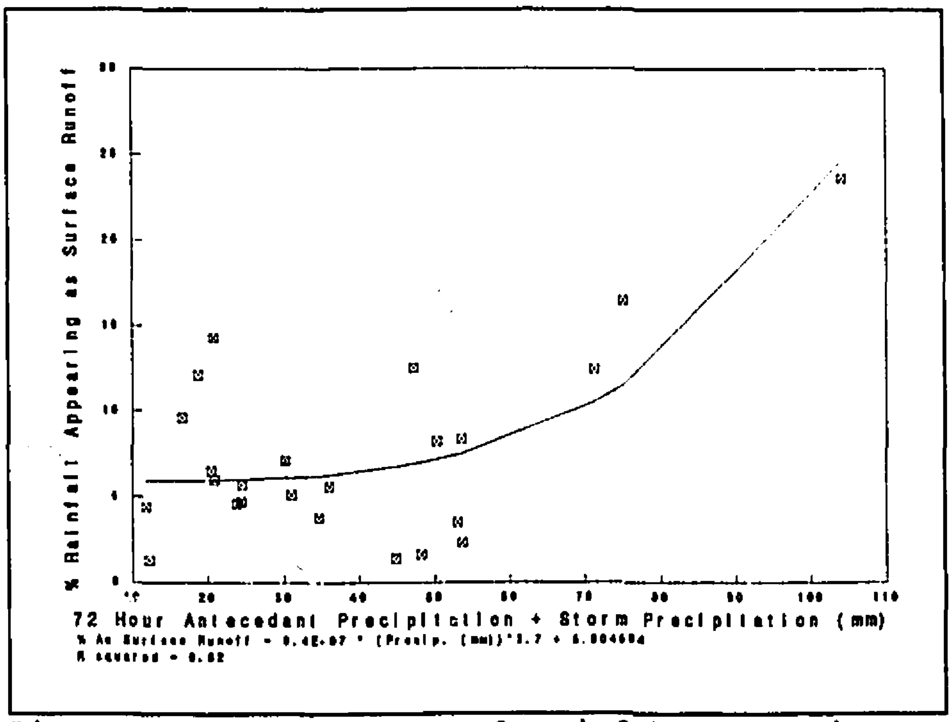

Figure 4.24 Percentage of rainfall appearing as surface runoff versus the cumulative 72 hour antecedant rainfall and event rainfall

sum of the 72 hour antecedant rainfall and the storm rainfall. The R squared value for this model is 0.52. The equation of the best fit curve is:

$$\%Rr = 6.4 \times 10^{-07} * (P_{72} + P_s)^{3.7} + 5.9 \qquad (4.5)$$

It appears that the most likely reason for the poor performance of empirical models on this watershed is the seasonal changes in the hydrology of the watershed. As only two years of record are available, seasonal variations in the hydrology will significantly affect efforts to develop a comprehensive empirical model of the watershed. Seasonal variations in the hydrology are likely influenced by factors such as changing ground cover through the growing season and seasonal influences on the hydrologic cycle such as increased rates of evapotranspiration through the mid-summer months. As more years of record become available and more storms from all seasons are added to the database of this watershed, then perhaps models which are applicable on a seasonal basis could be developed.

4.2 Water Quality Analysis

4.2.1 Statistical Analysis

The data in this section consists of 206 water samples taken in 1994 and 50 water samples from 1995. The difference in the number of samples for each season is primarily a result of the flow conditions in the river. The predominantly low flow conditions of 1995 did not require that samples be taken at the same frequency as for the 1994 season. This section will report on the water quality results for nitrate (NO_3), phosphate (PO_4), suspended sediment (SS), and atrazine.

Statistical results for the measured water quality parameters are given in Table 4.6. As previously noted, atrazine was not detected in a sufficient number of samples in 1995 to be able to draw any conclusions as to its behaviour.

Table 4.6 Statistical results for measured water quality data

Year	Parameter	Mean	Coefficient of Skew	Variance
1994	NO3 (mg/l)	2.78	1.08	1.71
	PO4 (mg/l)	0.05	1.91	0.05
	SS (g/l)	0.05	4.29	0.09
	Atrazine (ug/l)	1.41	1.89	1.45
1995	NO3 (mg/l)	2.53	-0.14	1.10
	PO4 (mg/l)	0.05	1.13	0.02
	SS (g/l)	0.04	4.82	0.07

The high coefficient of skew observed for most of these parameters causes the variance statistic to loose relevance as an analysis tool. The observed mean concentrations for these parameters do not exceed drinking water quality standards in Canada (CCME 1994).

4.2.2 Material Export Analysis

The measured water quality parameters were matched in a monthly flow record to the 15 minute interval in which they were taken. An algorithm programmed into a LOTUS 1-2-3 spreadsheet was then used to interpolate between measured points to determine a concentration at each 15 minute interval in the flow record. The resulting concentrations were then multiplied by the flow volume to determine the mass or load of pollutant material carried by the river during that 15 minute interval. The data were then analyzed by several methods.

The material export data were tabulated on a daily basis for each month. Figures 4.25 to 4.54 give the daily average concentration and load for nitrate, phosphate, suspended sediment and atrazine for the months of April, May, June, and July 1994. Graphs of each water quality parameter are not shown for every month in order to avoid redundancy. Due to the higher number of water samples taken in 1994, data primarily from that year will be used to develop trends in parameter behaviour.

Examining the daily variation in concentration and loading in relation to the observed flow on the basin is useful for determining behaviour of pollutant materials in relation to flow characteristics.

Flow during the month of April 1994 was characterized by snowmelt. This process began around the 9th of April and continued through to about the 17th. Examining the concentration and material export for April (Figures 4.25 to 4.30), it can be seen that the concentration of nitrate decreased during the snowmelt period while the concentration of sediment and PO_4 both increased as the flow increased. This indicates a dilution effect is occurring with respect to the concentration of nitrate at this time of the year. It is known that nitrates moves primarily

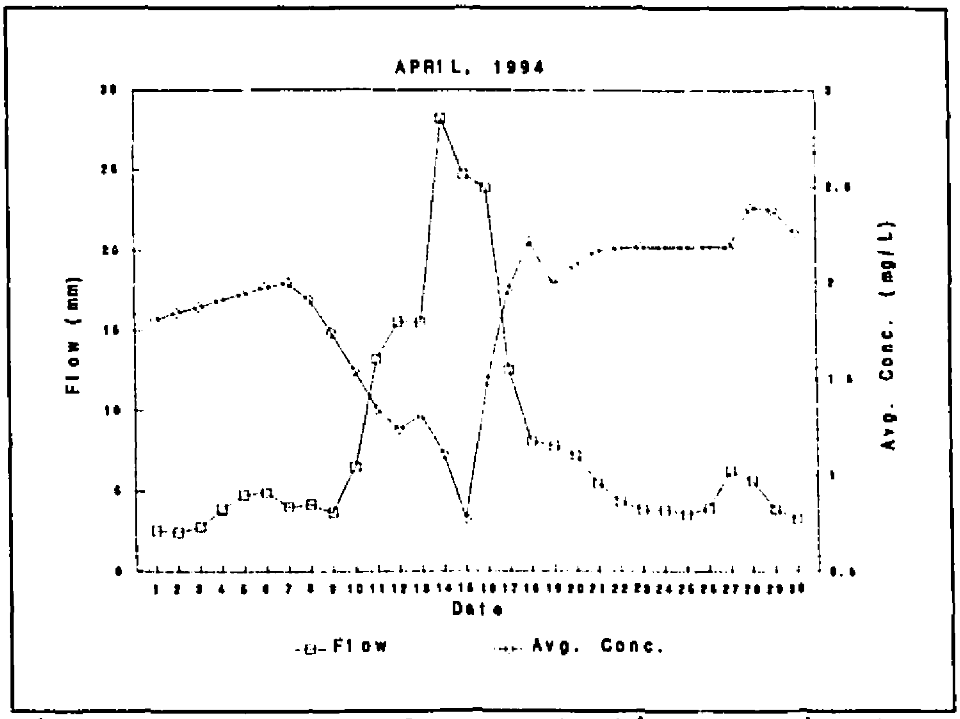

Figure 4.25 Flow and concentration of nitrate - April 1994

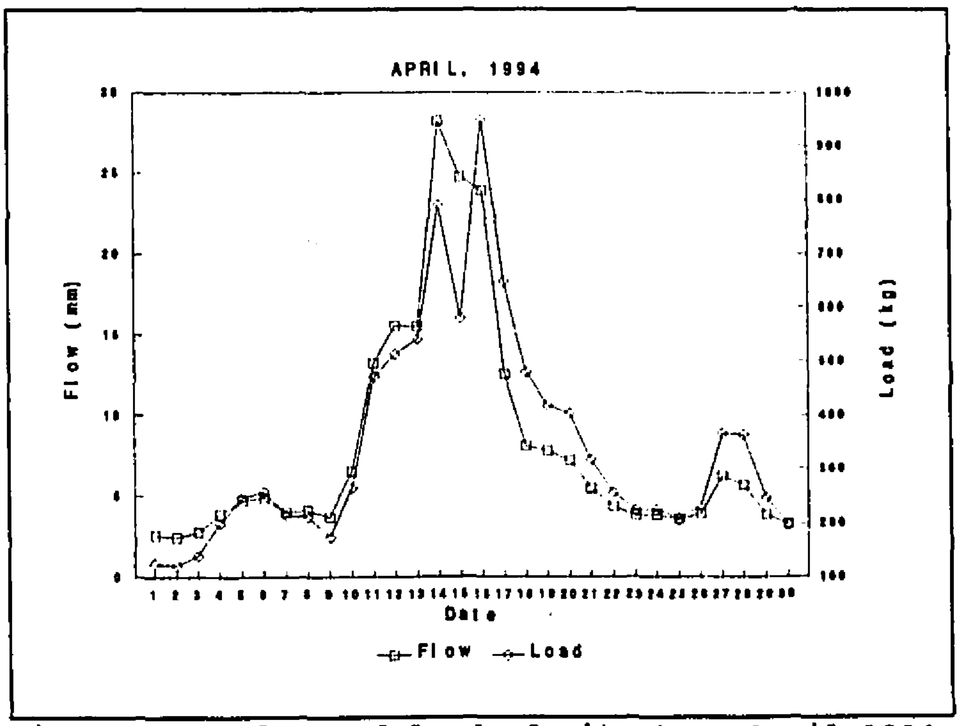

Figure 4.26 Flow and load of nitrate - April 1994

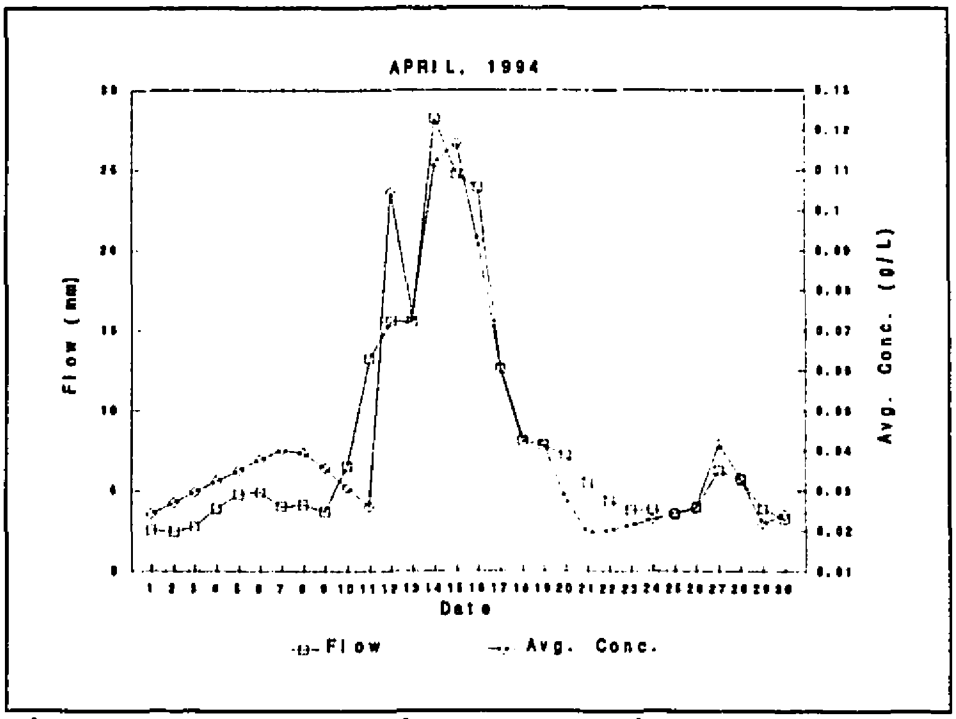

Figure 4.27 Flow and concentration of suspended sediment - April 1994

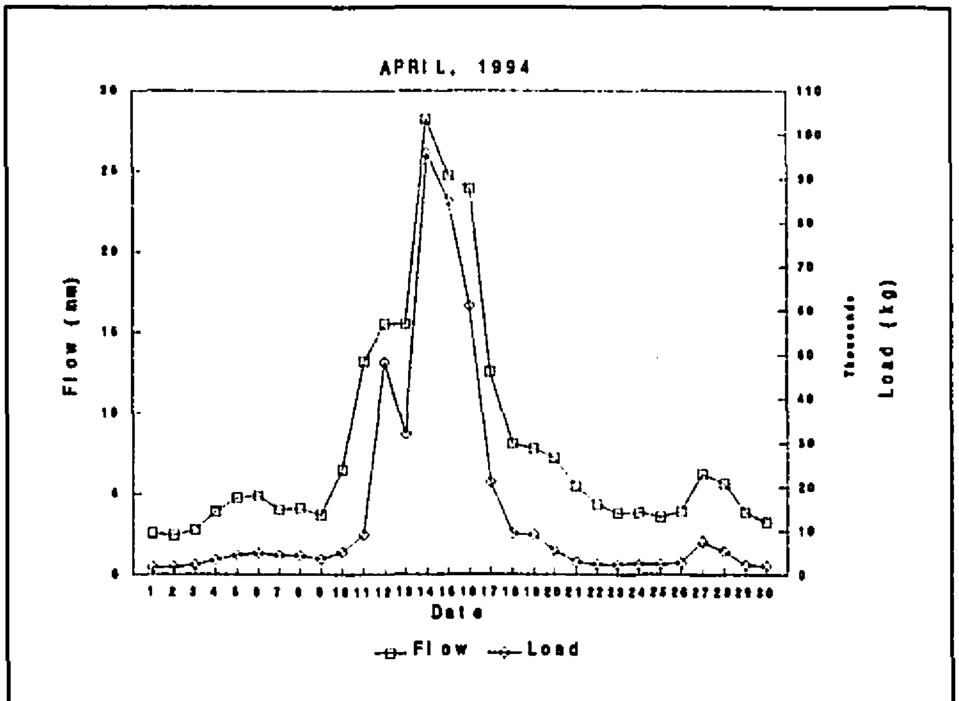

Figure 4.28 Flow and load of suspended sediment - April 1994

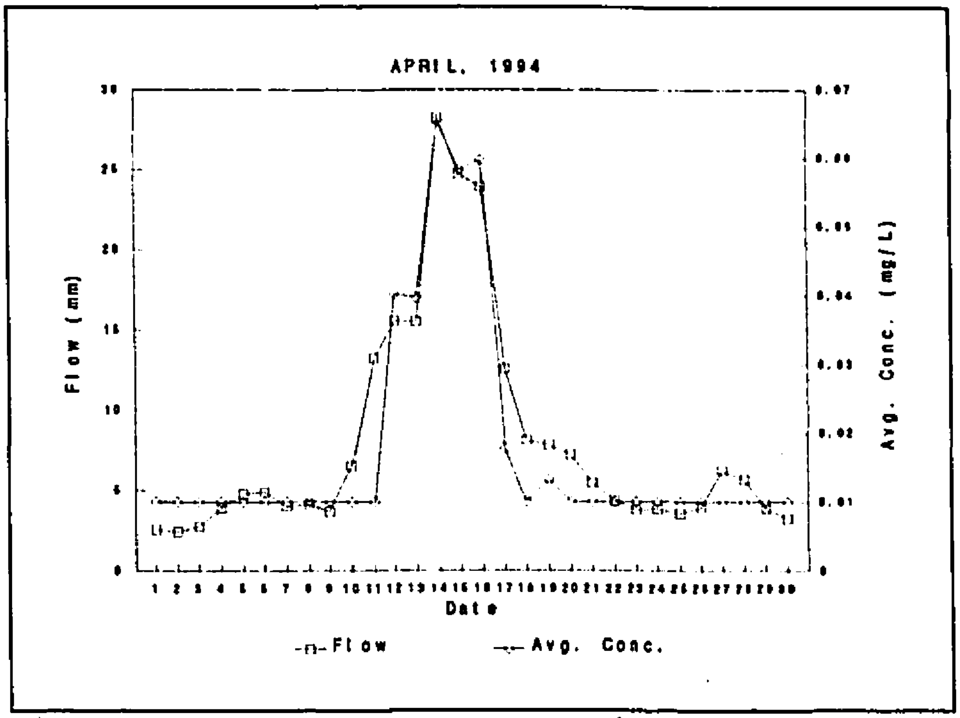

Figure 4.29 Flow and concentration of phosphate - April 1994

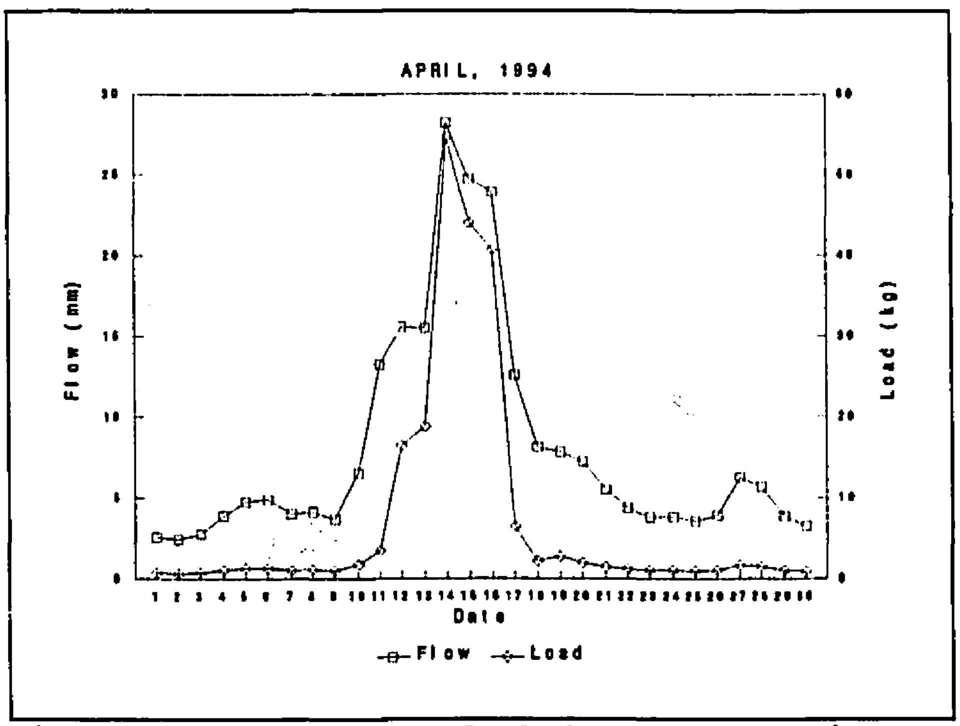

Figure 4.30 Flow and load of phosphate - April 1994

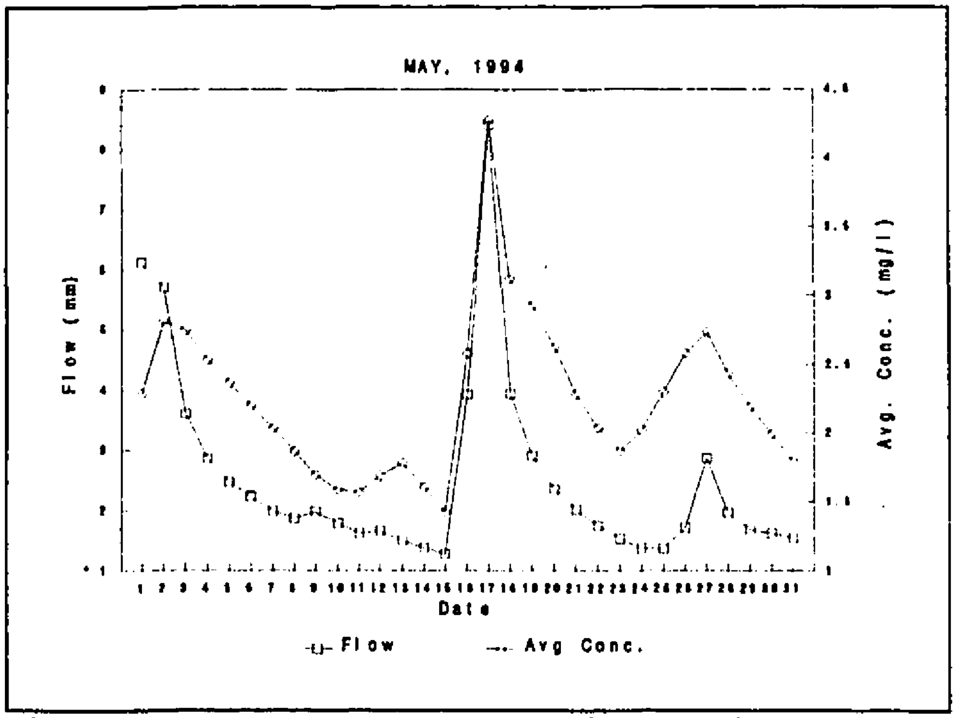

Figure 4.31 Flow and concentration of nitrate - May 1994

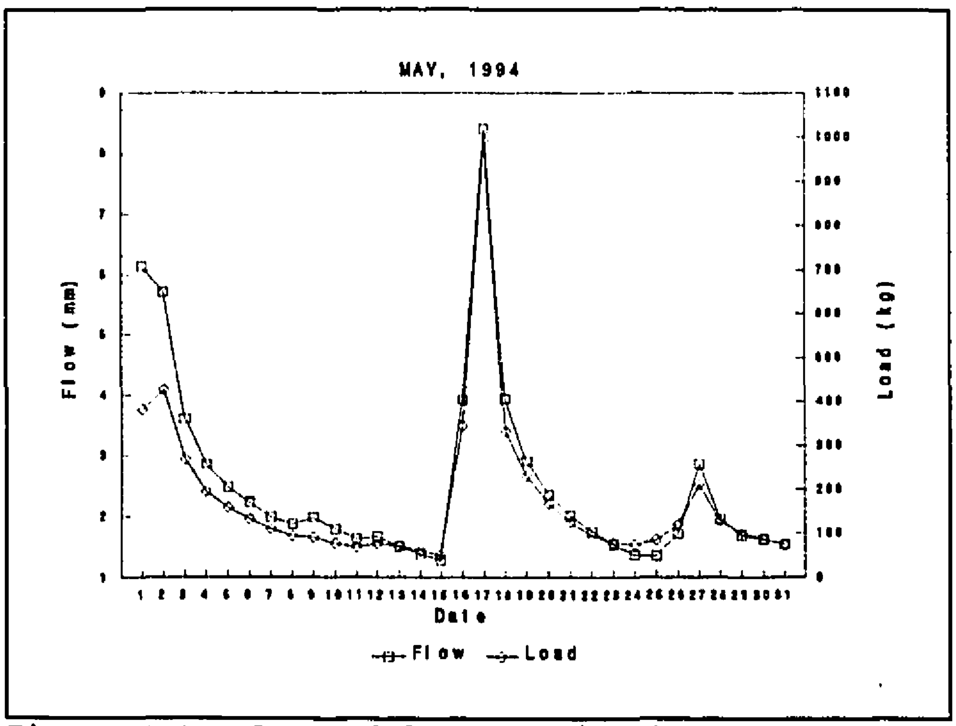

Figure 4.32 Flow and load of nitrate - May 1994

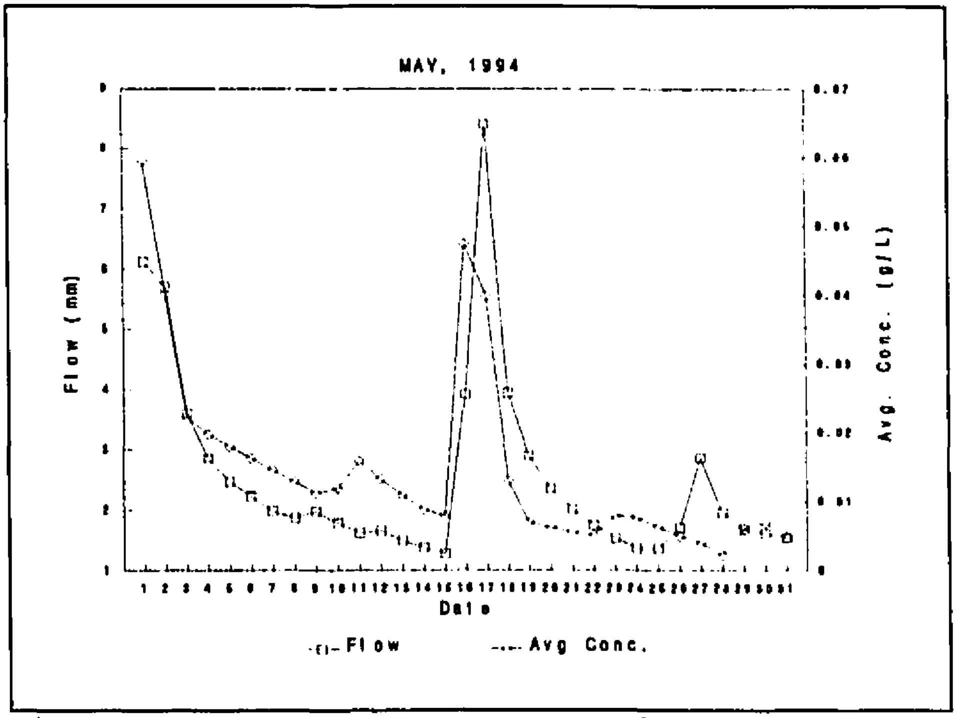

Figure 4.33 Flow and concentration of suspended sediment - May 1994

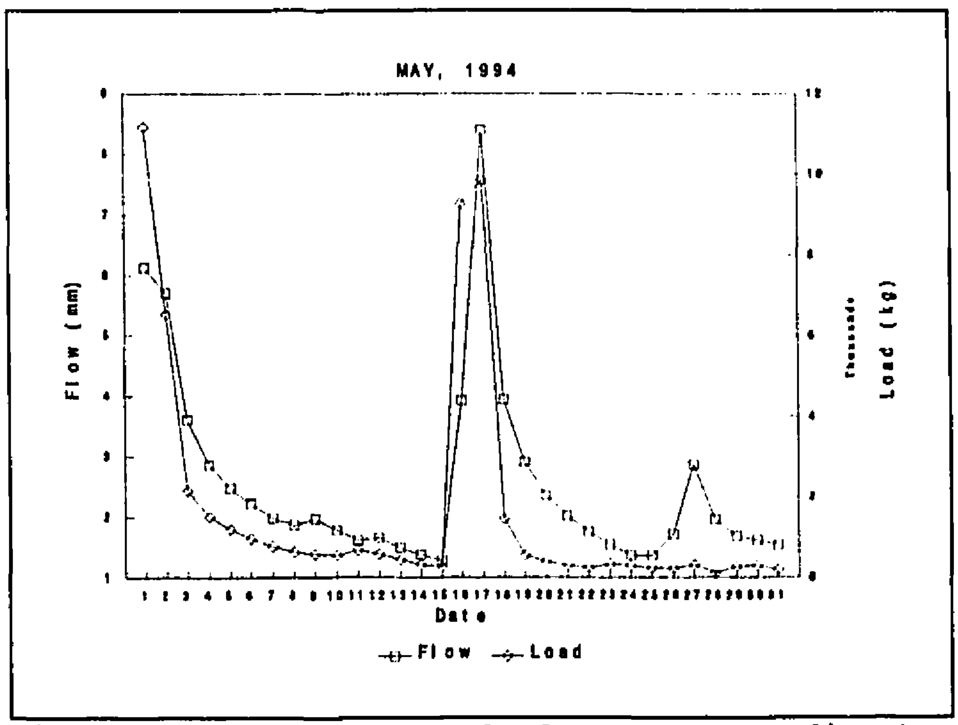

Figure 4.34 Flow and load of suspended sediment - May 1994

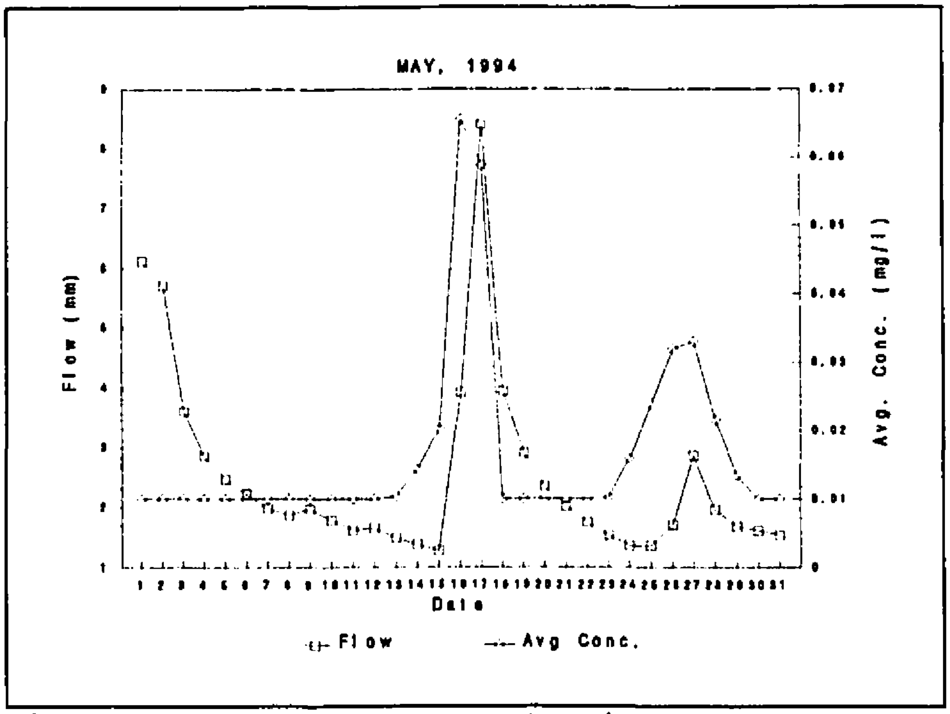

Figure 4.35 Flow and concentration of phosphate - May 1994

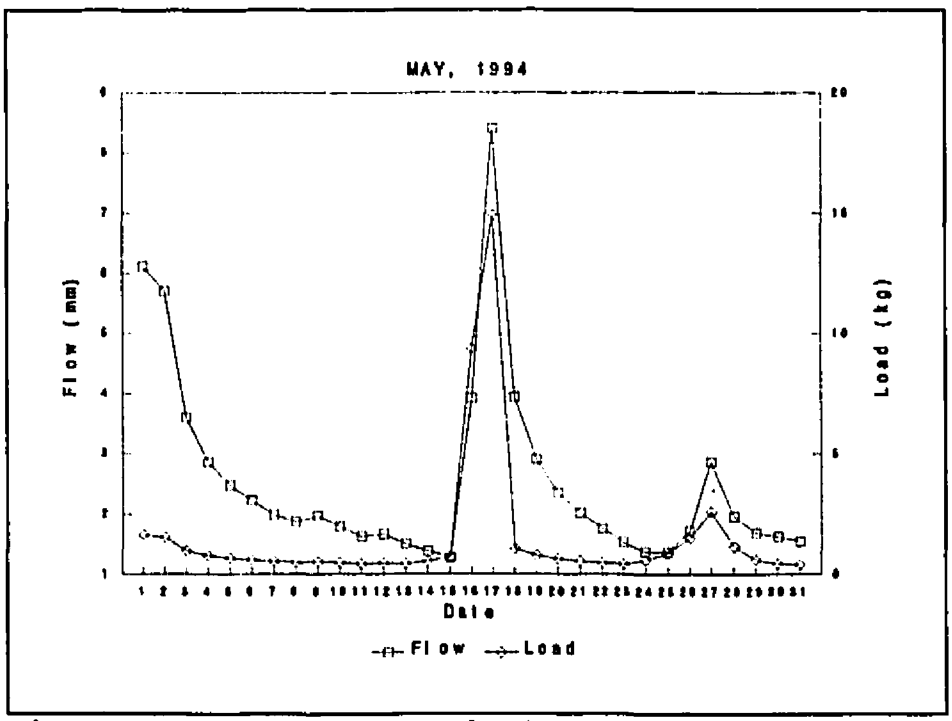

Figure 4.36 Flow and load of phosphate - May 1994

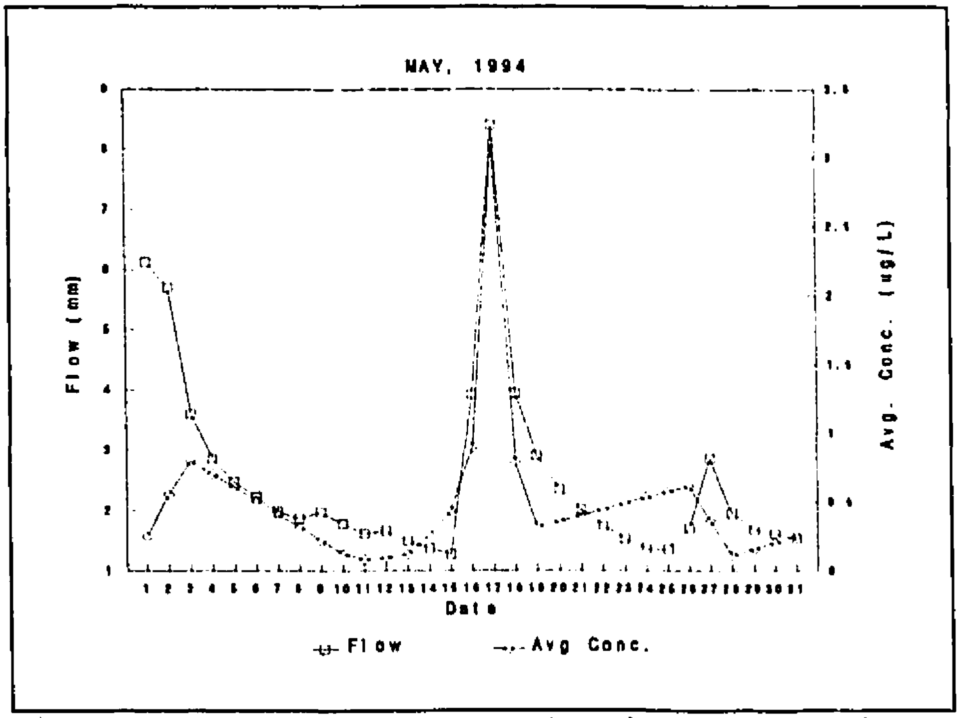

Figure 4.37 Flow and concentration of atrazine - May 1994

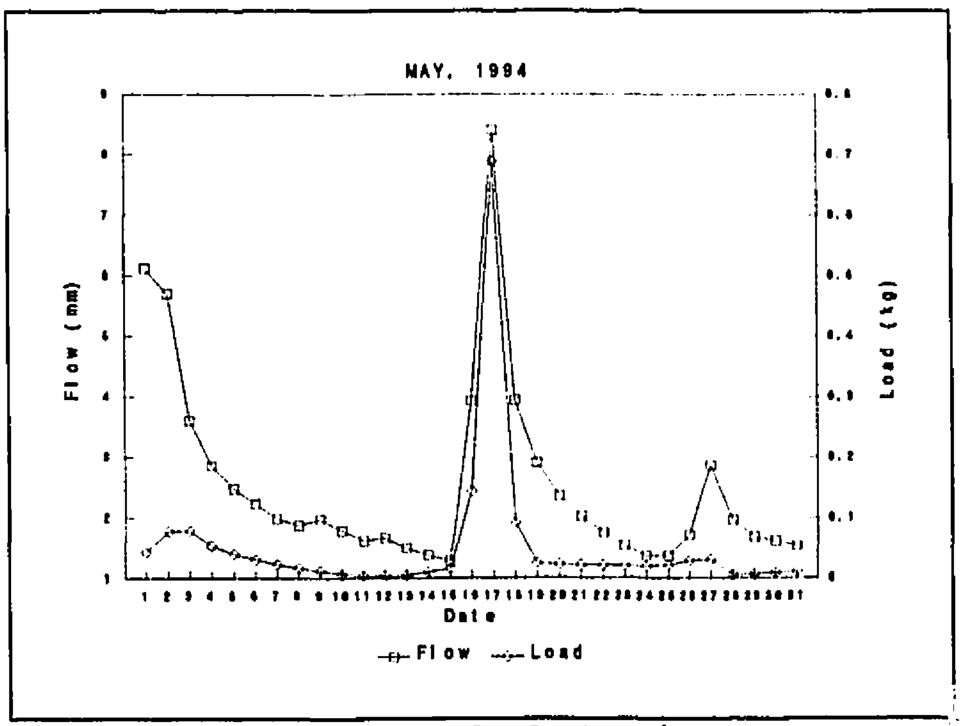

Figure 4.38 Flow and load of atrazine - May 1994

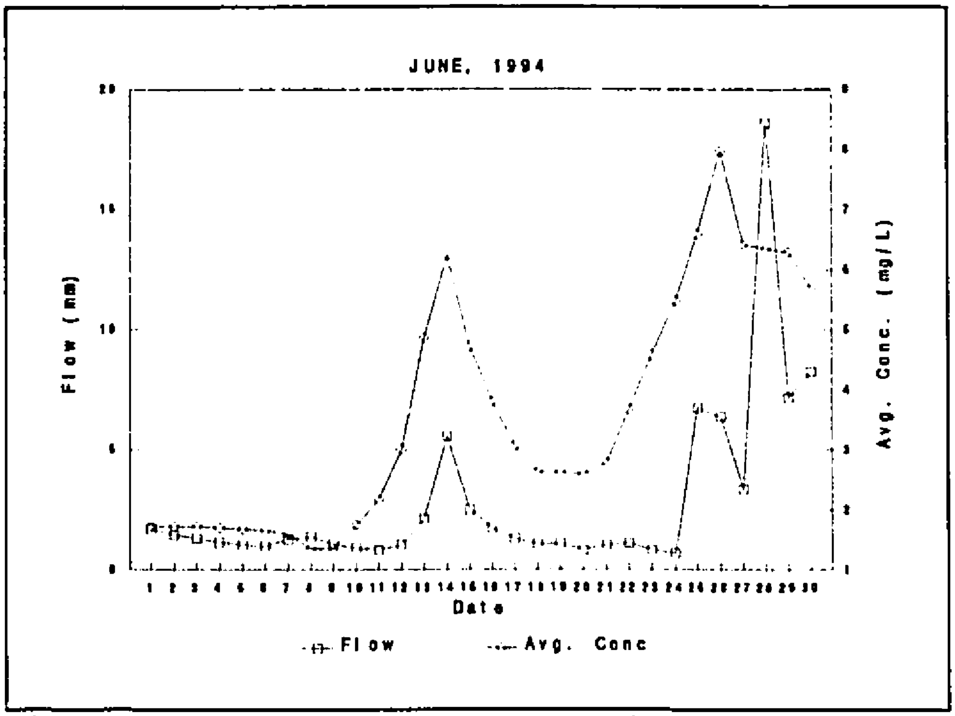

Figure 4.39 Flow and concentration of nitrate - June 1994

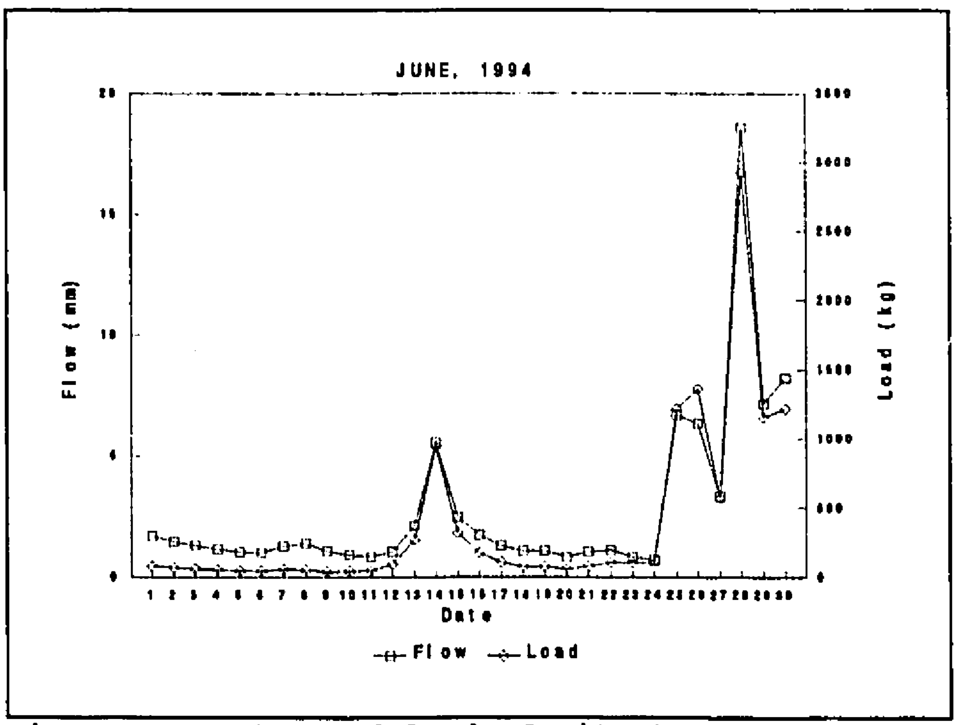

Figure 4.40 Flow and load of nitrate - June 1994

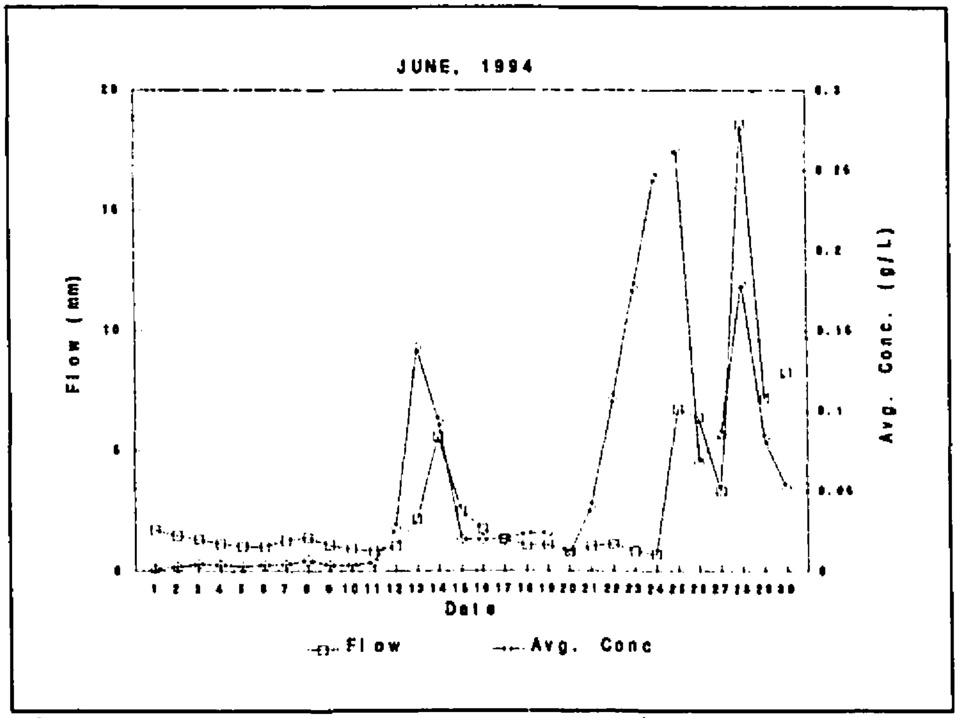

Figure 4.41 Flow and concentration of suspended sediment - June 1994

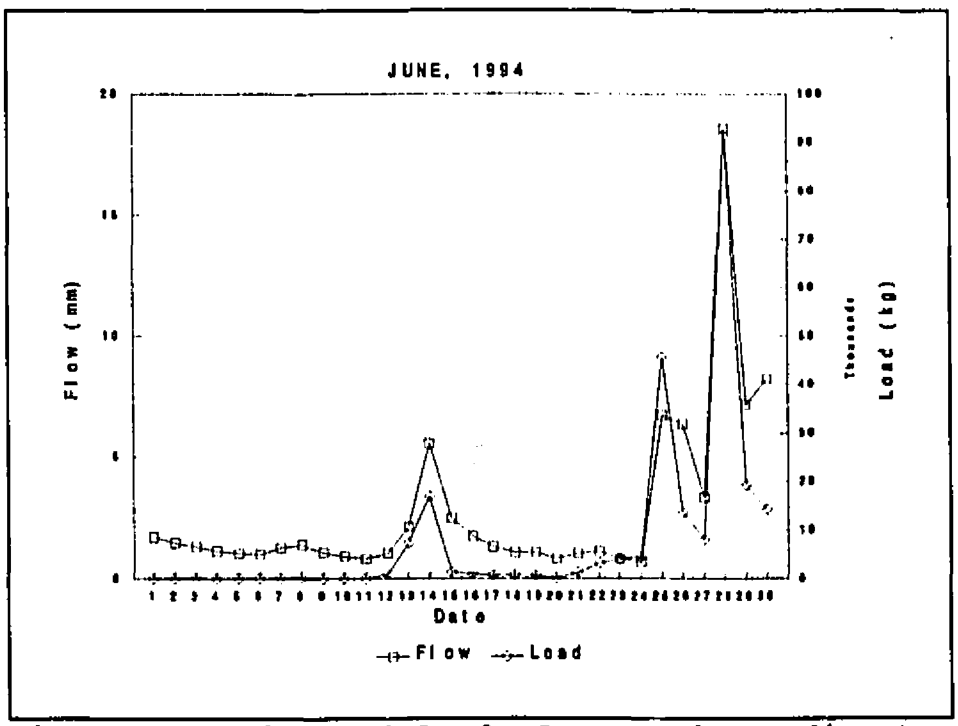

Figure 4.42 Flow and load of suspended sediment - June 1994

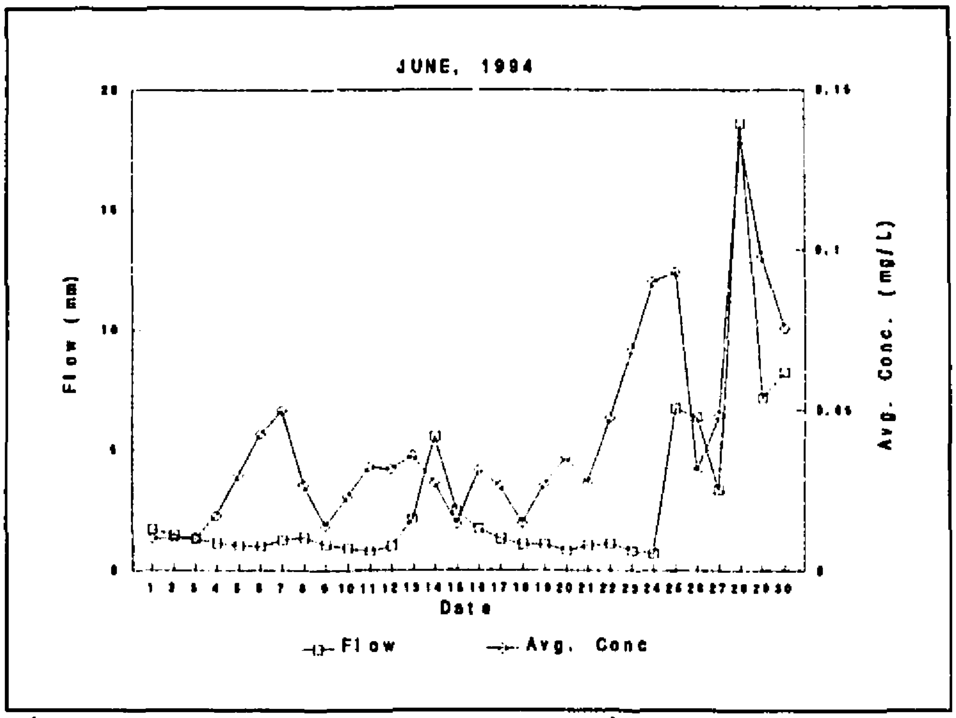

Figure 4.43 Flow and concentration of phosphate - June 1994

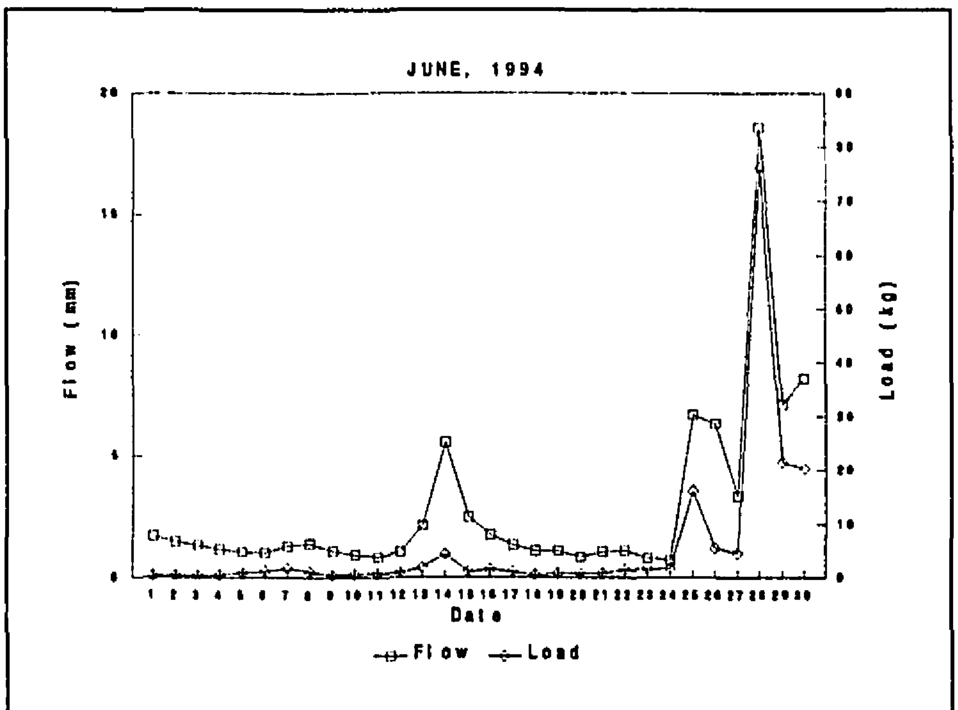

Figure 4.44 Flow and load of phosphate - June 1994

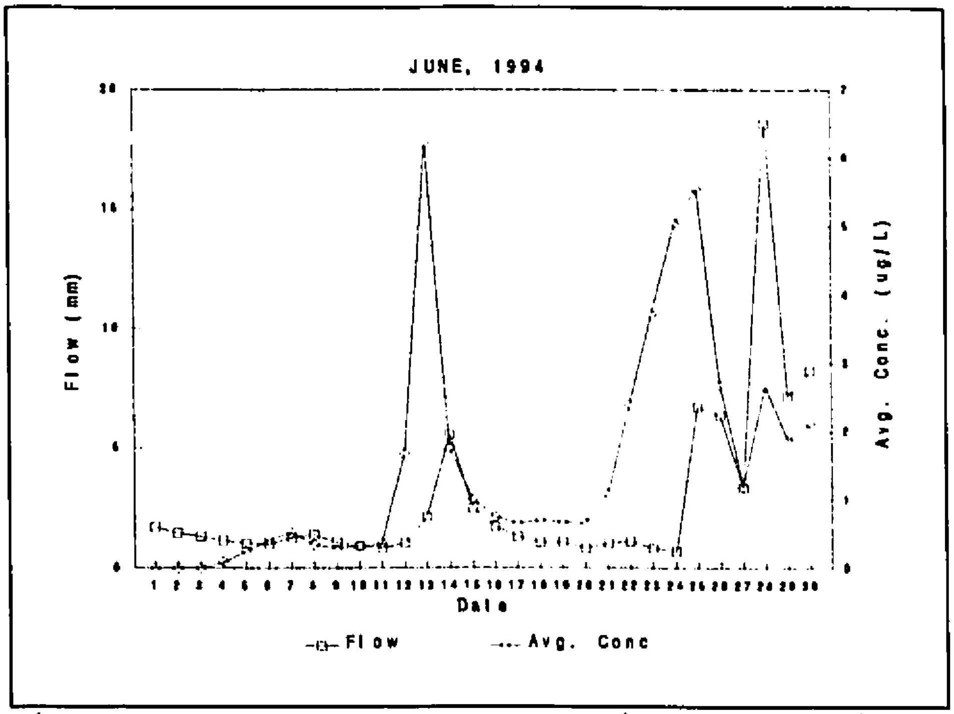

Figure 4.45 Flow and concentration of atrazine - June 1994

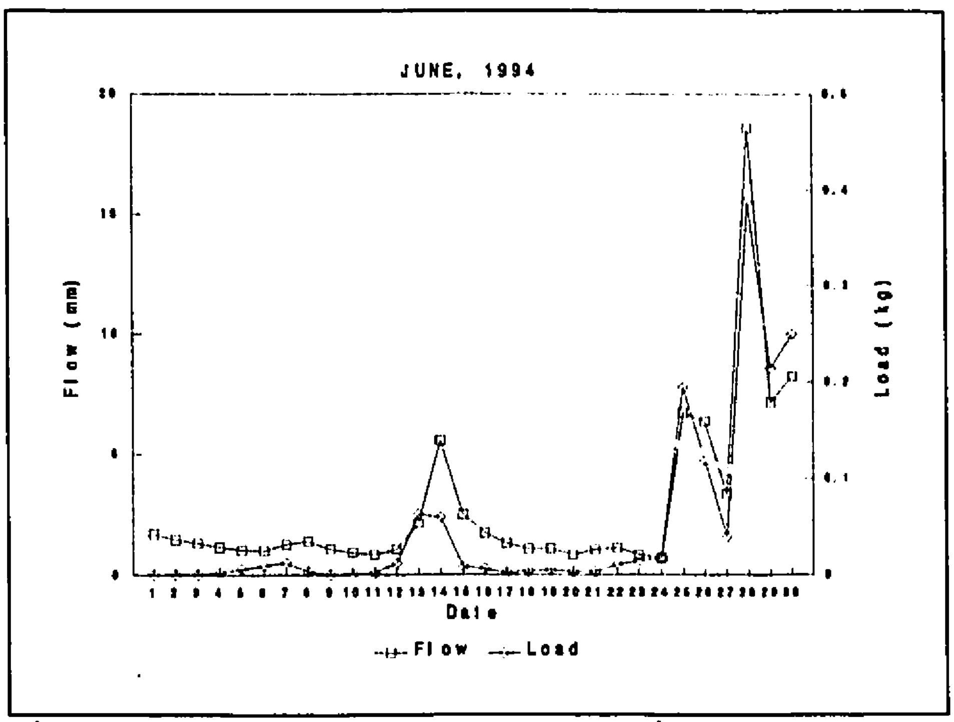

Figure 4.46 Flow and load of atrazine - June 1994

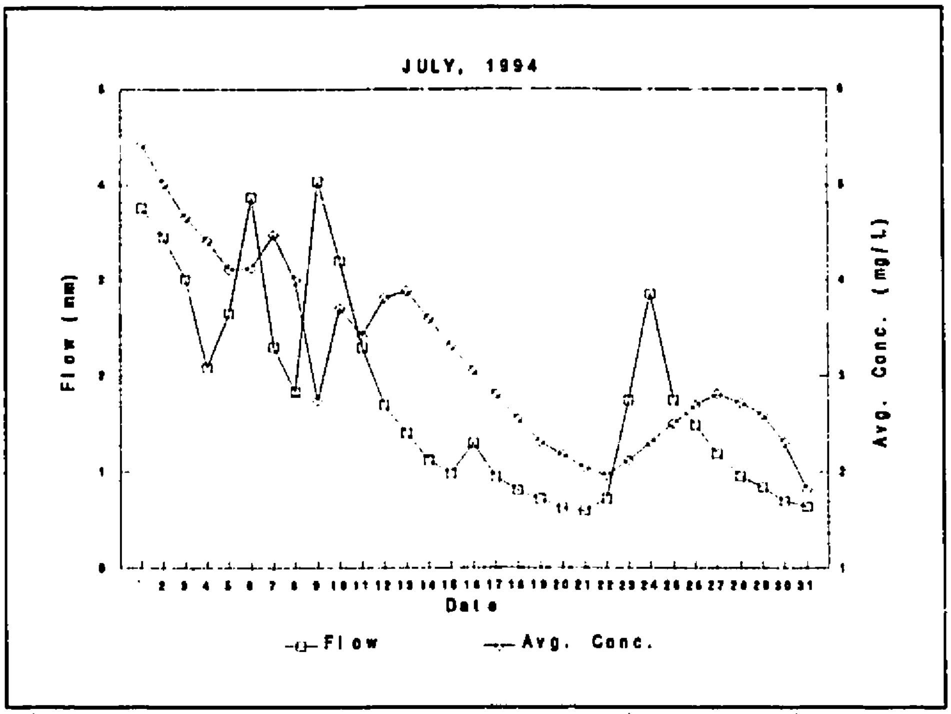

Figure 4.47 Flow and concentration of nitrate - July 1994

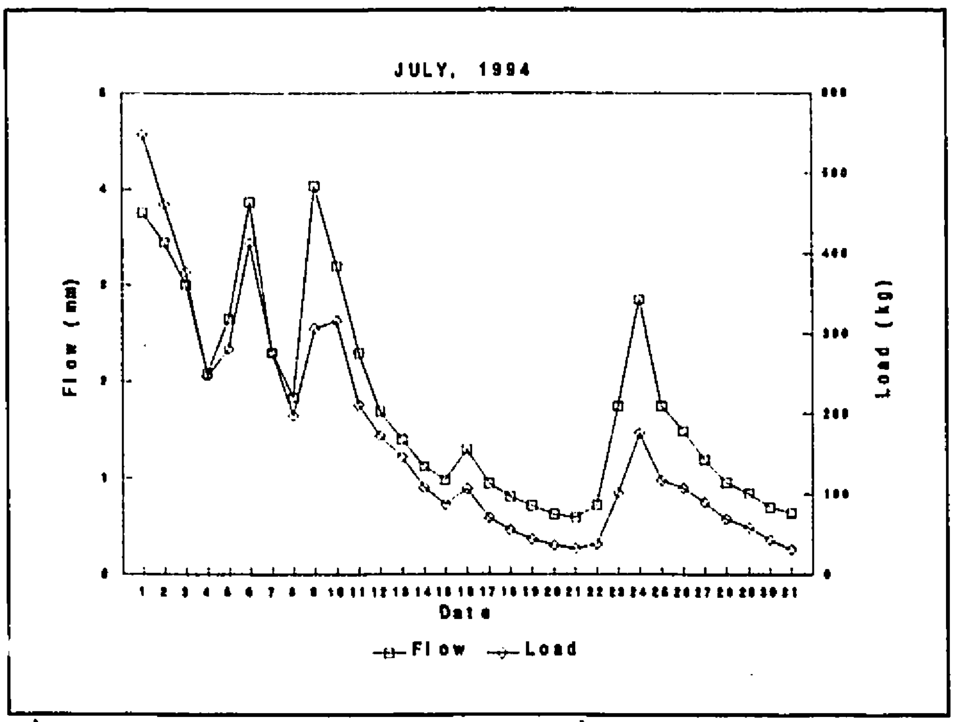

Figure 4.48 Flow and load of nitrate - July 1994

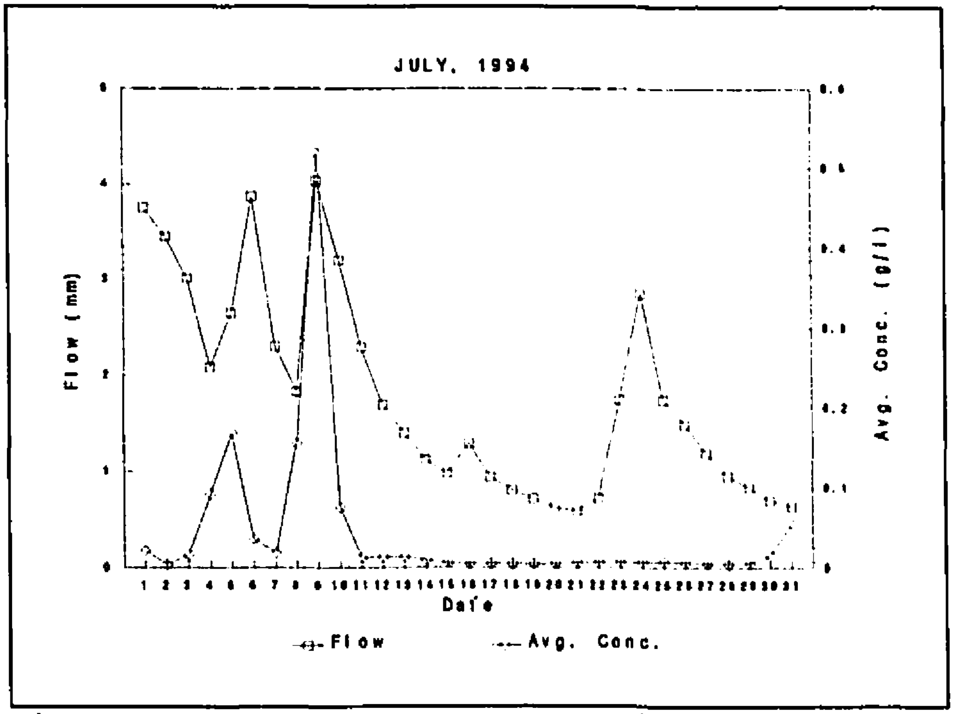

Figure 4.49 Flow and concentration of suspended sediment - July 1994

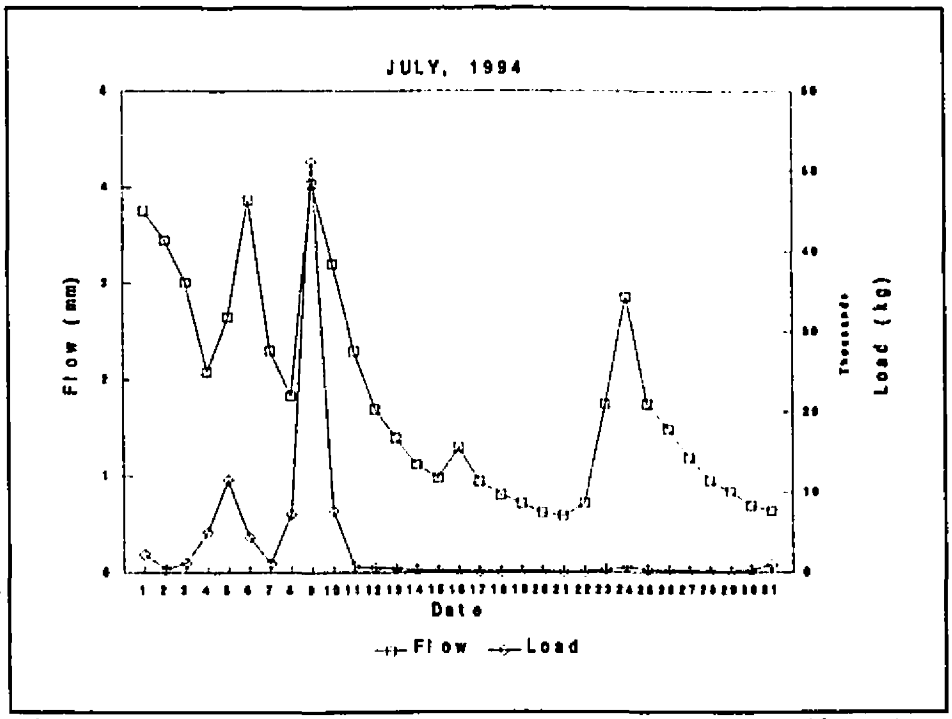

Figure 4.50 Flow and load of suspended sediment - July 1994

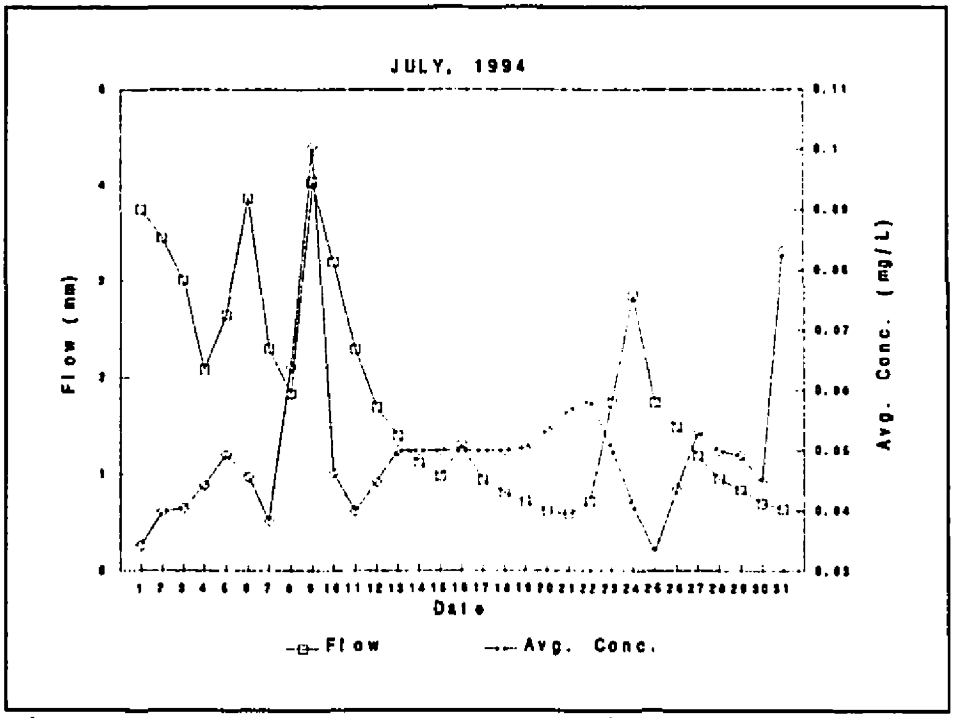

Figure 4.51 Flow and concentration of phosphate - July 1994

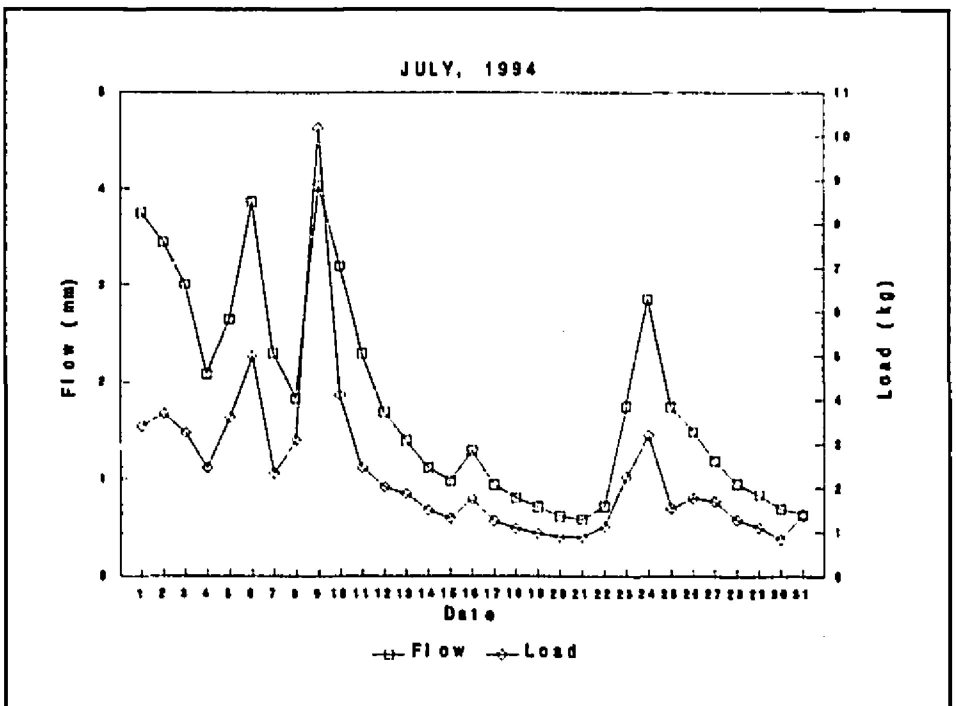

Figure 4.52 Flow and load of phosphate - July 1994

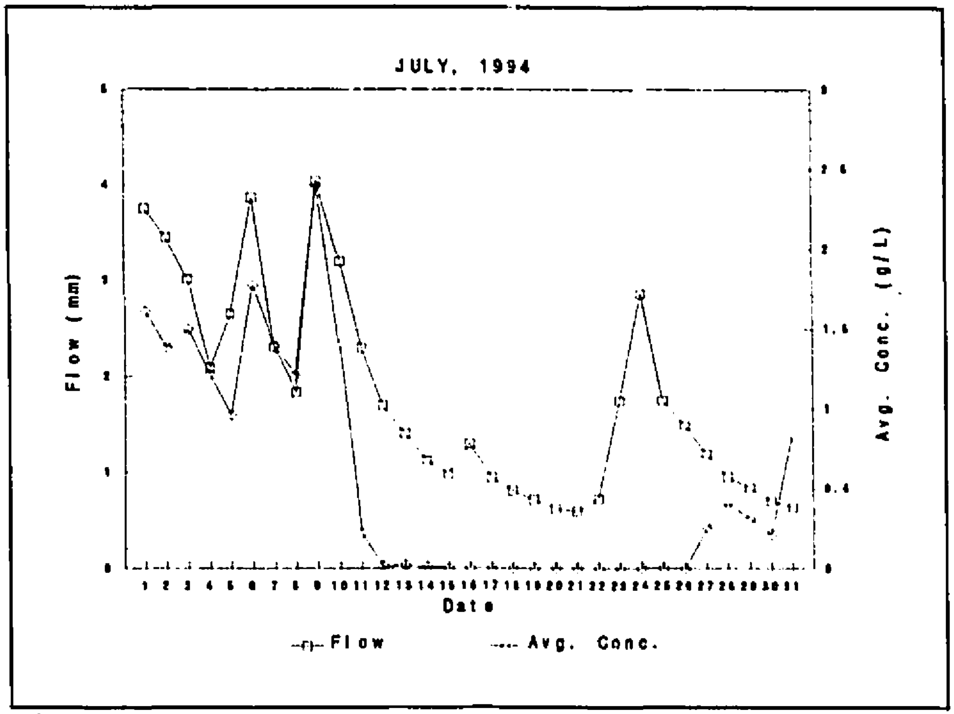

Figure 4.53 Flow and concentration of atrazine - July 1994

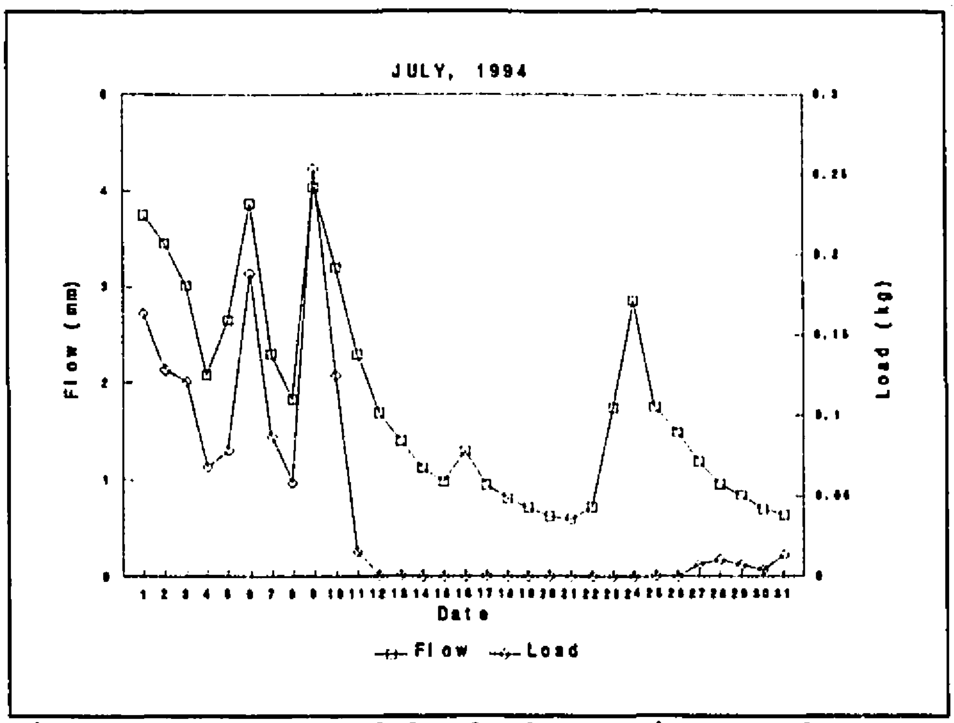

Figure 4.54 Flow and load of atrazine - July 1994

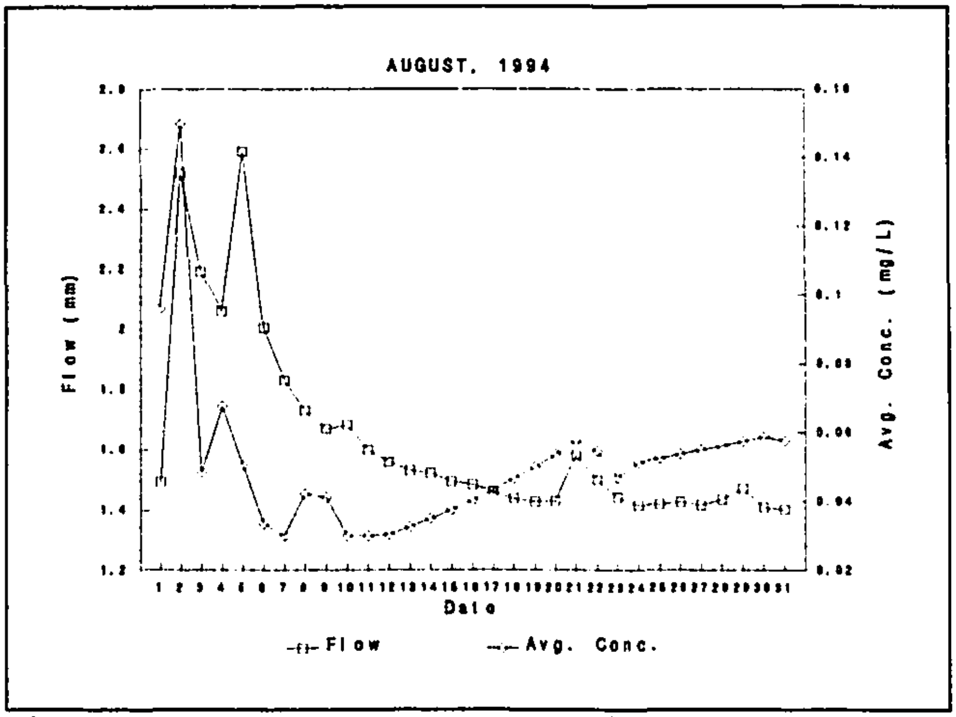

Figure 4.55 Flow and concentration of phosphate - August 1994

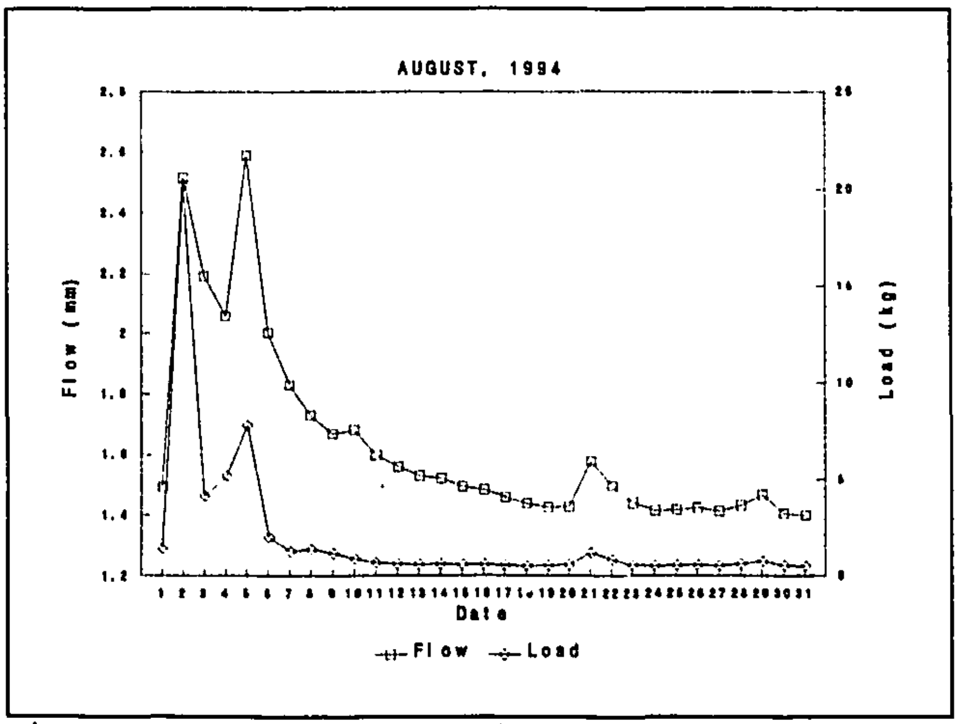

Figure 4.56 Flow and load of phosphate - August 1994

through tile drains, or to groundwater, whereas sediment moves primarily in surface runoff. It is possible that large volumes of surface runoff are diluting the nitrate levels in the watercourse. As the snowmelt waters receded, groundwater discharge began to occur and as can be seen, the concentration of nitrate increased to pre-snowmelt levels.

During the month of May, the concentration and loading of suspended sediment, atrazine, and PO_4 (Figures 4.31 to 4.38), are correlated closely with flow in the watercourse. The flux and concentration of NO_3 also correlates closely with the observed flow with the exception of nitrate on the receding limb of the hydrographs, which tends to decline much more slowly than other materials.

During the month of June (Figures 4.39 to 4.46), the same observations as for May can be made for each pollutant material. Sediment moves through surface water so the load drops off in the recession phase since it is subsurface drainage water and shallow groundwater which sustain the flow. As well, the decrease in discharge results in a decrease in flow velocity which decreases the carrying capacity of the river. The parallel in the movement patterns of atrazine and PO_4 to that of suspended sediment suggests that the movement of these materials on this basin is similar to that observed for suspended sediment. Surface runoff is the contributing factor.

Since nitrates move primarily through drainage water or groundwater, the average concentration should be expected to decline slowly since these sources of water sustain the receding flow.

Through the month of July (Figures 4.47 to 4.54), the observed pattern for suspended sediment and atrazine remained similar to what was observed in previous months. It will be noted that events towards the end of the month failed to generate significant concentrations of suspended sediment or atrazine, likely due to complete crop canopy cover and well developed vegetation along the watercourse which likely impeded the transport of sediment to the watercourse and certainly limited the carrying capacity of overland flow. The observed behaviour in concentration of PO_4 appears to change somewhat. Through the beginning of the month, the same behaviour in concentration variation as was observed for previous months is seen. However, towards the end of the month, the concentration increases during the recession phase of the hydrographs. This suggests that through the summer months, groundwater flow may become a significant pathway for movement of PO_4.

The observed behaviour of nitrate changes as well during the month of July. The peaks in concentration no longer correlate with the peaks in flow. Instead, the peaks in nitrate concentration occur 1 to 3 days after the flow has peaked. The concentration continues to recede slowly after events.

As confirmation of trends that were observed in July, the graphs of concentration and load for PO_4 for August are shown in Figures 4.55 and 4.56. The concentration of PO_4 responds to rainfall events, and that there is a gradual increase in concentration during long periods of base flow.

The observed behaviour of these materials as shown in the months profiled, gives some insight into the processes of material movement on this watershed. Sediment load is due to erosion and suspended sediment movement increased with higher flows observed during hydrologic events. This would be expected if overland flow was the primary mover of the material.

Literature on atrazine movement suggests that it can move from fields by several means including surface runoff, seepage to drains or by deep percolation to groundwater. From the results obtained, it would appear that atrazine behaviour parallels that of suspended sediment which suggests that surface flow is the primary mover of atrazine.

Phosphate, like atrazine is also capable of moving by several pathways. Phosphate phosphorous is water soluble. However in soil solution it is often quickly incorporated by micro-organisms or bound to soil particles. Therefore it moves slowly through the soil profile as leachate. However, since it is bound to organic matter and soil particles, it is moved by surface erosion as well. The behaviour of PO_4 concentration suggests that on this watershed it is moved primarily by surface flow particularly early in the season. There would appear to be some evidence however of deep groundwater conveying PO_4 to the stream. Sustained rises in concentration are seen during long periods of low flow. It is possible that this groundwater phosphate only becomes apparent in the watercourse when deep groundwater is the primary source of flow in the river. At other times, water from shallower groundwater or drainflow may dilute the phosphate.

Nitrate is highly soluble and is lost primarily through leaching to drains or groundwater. The slow recession of nitrate concentration through the observed months and the slow response in the peak of nitrate concentration to rainfall events in July suggest that leaching to groundwater is an important pathway. However the quick response of nitrate concentration to events in late spring and early summer suggest a quick flushing of nitrate to the watercourse. Nitrate has been observed to move in surface runoff (Baker and Laflen 1983), particularly after fertilization. Another possible pathway is by preferential flow through the soil profile to the drains.

4.2.3 Monthly Export

Tables 4.7 and 4.8 show the load of material lost per unit cropped area on the watershed for 1994 and 1995 respectively.

Table 4.7 Material lost per cropped hectare - 1994

Month	Material export (kg/ha)			
	NO_3	SS	PO_4	Atrazine
April	6.26	267.48	0.13	0.002
May	3.30	31.79	0.028	0.001
June	6.97	142.49	0.10	0.0009
July	3.21	59.33	0.043	0.0008
August	1.64	13.95	0.034	0.0003
September	0.11	0.09	0.003	0.0001
October	0.12	0.93	0.004	0.0003
November	1.00	11.15	0.024	0.00005
Total	22.61	527.21	0.366	0.00545

Table 4.8 Material lost per cropped hectare - 1995

Month	Material export (kg/ha)		
	NO_3	SS	PO_4
March	3.7	84.7	0.1
April	2.07	20.5	0.03
May	1.44	12.2	0.03
June	0.46	4.6	0.01
July	0.43	6.3	0.02
August	0.09	1.7	0.1
September	0.05	2.0	0.004
Total	8.24	132	0.294

The period of greatest loss of these materials was generally in the early spring in 1994. In 1995, the highest losses tended to occur in the spring as well. These observations are not surprising given the high flow rates generally seen in the spring as well as the predominantly bare or uncovered soil that is characteristic of agricultural areas in the spring.

Further insight into the pathways of material loss can be gained by examining the change in pollutant monthly average concentration of pollutants as determined from interpolated values. This is shown in Tables 4.9 and 4.10.

Table 4.9 Monthly average concentration of pollutant material - 1994

Month	Average Concentration			
	NO_3 (mg/l)	SS (g/l)	PO_4 (mg/l)	Atrazine (ug/l)
April	1.88	0.043	0.017	0.50
May	2.26	0.015	0.016	0.49
June	3.59	0.060	0.041	1.50
July	3.21	0.042	0.05	0.55
August	2.33	0.011	0.051	0.31
September	1.18	0.001	0.037	1.27
October	0.88	0.006	0.031	2.28
November	2.27	0.017	0.052	0.15

There are several trends in the data that will be noted for each material. Firstly, for nitrate, it can be seen that the month with the highest export of material is the month associated with snowmelt. That is April 1994 and March 1995. The load of material per month tends to decrease after these times. However the highest concentrations of nitrate are not associated with snowmelt. The highest concentrations for the season for both these years was found during the two months after snowmelt. This would coincide with a period of increased activity

Table 4.10 Monthly average concentration of pollutant material - 1995

Month	Average Concentration		
	NO_3 (mg/l)	SS (g/l)	PO_4 (mg/l)
March	1.89	0.034	0.043
April	2.12	0.018	0.029
May	1.73	0.014	0.036
June	1.52	0.022	0.054
July	1.52	0.024	0.067
August	0.89	0.016	0.067
September	0.69	0.027	0.049

on fields in agricultural areas and therefore, it can be speculated that the periods of peak concentration are associated with spring preparation for planting and early establishment of the crop. This would be the period of heaviest tillage as well as the period of heaviest applications of manure and fertilizer. These activities would increase the amount of nitrate available to be leached through the profile or to be moved by surface water. The mass of nitrate lost per cropped hectare is comparable to losses reported by Neilson et al., (1982) for agricultural watersheds in southwestern Ontario.

For suspended sediment, the periods of highest loss and highest concentration are closely associated with months with high levels of flow.

The loss pattern of atrazine is somewhat similar to that observed for suspended sediment. The highest load of atrazine is associated with periods of high flow which indicates that surface water is an important transport path. The highest concentrations in the early part of the growing season are found in June which is just after the usual application periods for atrazine in this region. The high concentrations observed in the fall cannot be explained in terms of standard agricultural practices or the hydrology of the basin. A point source cannot be excluded as a possible source of the high levels of atrazine through the fall. The pattern of loss of this material suggests that the occurrence of significant runoff in the period just after the time of application is the primary means by which high concentrations of atrazine are moved to the watercourse. This conclusion was also reached in CCME (1994) after a review of more rigorous studies in atrazine loss patterns.

The behaviour of phosphate suggests that a number of paths exist for this material to move into the watercourse. Generally, the highest average concentration is found through the summer months during low flow conditions. However, the highest rate of export tends to occur during months with the highest flow. At least two paths appear to be significant for phosphate loss. The relatively high concentrations observed during very low base flow conditions may be due to a number of possible sources including release from sediment deposited in the channel or geologic sources. It suggests a constant base level of material export. The actual mass of material lost by this path would appear to be small, but it's presence becomes noticeable during times of very low flow. It should be noted that the entire 1995 season was characterized by predominantly low base flow conditions and that of the materials discussed, only the average concentration of phosphate is greater in 1995 than in 1994. The highest loading of phosphate occurred during periods of high flow and the highest concentrations are found during high flow events. This suggests a second transportation path by surface runoff. It is likely that agricultural practices have an impact on the mass of material exported by this path. High loads of material occur in the early summer which coincides with periods of fertilizer application. Because phosphate is quickly immobilized in the soil, fertilizer applications which do not incorporate phosphate below the surface layer are likely to experience loss by surface water movement.

4.2.4 Material Loss by Flow Regime

The water quality data was analyzed by developing an algorithm which surveyed each 15 minute flow interval and determined whether the interval represented runoff, interflow, or deep groundwater flow. A fourth category was defined as well which is snowmelt, but these intervals were assigned before the algorithm was run on the data.

Once the interval was assigned to a particular flow regime, the material export load for that interval was assigned to that particular flow regime. Summing the load of material by regime allows for a profile of material loss by path. The results are shown in Tables 4.11 and 4.12 for 1994 and 1995 respectively.

Table 4.11 Material export by flow path - 1994

Parameter	Total (kg)	Percent loss by flow regime			
		Meltwater	Runoff	Interflow	Groundwater
NO_3	37532	17.7%	23.1%	36.2%	23.0%
PO_4	614	34.7%	34.2%	21.3%	18.0%
SS	875169	39.8%	34.1%	17.3%	8.8%
Atrazine	8.99	18.9%	24.2%	36.9%	19.5%

Table 4.12 Material export by flow path - 1995

Parameter	Total (kg)	Percent loss by flow regime			
		Meltwater	Runoff	Interflow	Groundwater
NO_3	13847	55.0%	7.5%	7.4%	30.1%
PO_4	479.4	37.3%	9.7%	9.5%	43.5%
SS	222130	70.8%	6.5%	6.7%	16.0%

The values for loss by flow regime are best presented on an annual basis because the variability in flow from month to month would not allow an objective comparison without considering the flow pattern in each month. With the two years of data profiled there is a chance to compare the distribution of material loss through the year for years with very different flow profiles.

An observation that is to be expected based on the flow records is that the overall loss of material in 1995 is much less than the loss observed in 1994. The greatest difference is for suspended sediment where the observed loss in 1995 was only about 1/4 of the observed loss for 1994. The observed loss of nitrate in 1995 was about 1/3 of that observed for 1994. The loss of phosphate in 1994 is about 25% higher than in 1995.

The results in the above tables highlight the significant role played by the snowmelt period in the total loss of pollutant material from the watershed. The snowmelt period usually lasts for only one or two weeks during the spring, yet even in a year such as 1994, with high precipitation levels through most of the growing season, the snowmelt period accounted for over 1/3 of the sediment and phosphate lost for the year. The importance of the snowmelt period for material export becomes more pronounced in a year such as 1995 which had very few significant flow events.

The runoff and interflow phases are essentially the cresting and receding phases of an event hydrograph, respectively. Therefore they can be considered together as the result of rainfall events through the growing season. In 1994, these two phases combined to carry over 50% of the total material exported for each parameter. However, in 1995 with few rainfall-runoff events, the impact of the runoff and interflow phases on total export was minimal.

The loss of material through groundwater flow is not insignificant for nitrate, phosphate and atrazine. This is to be expected for parameters such as nitrate and phosphate, based on previous observations that groundwater flow was a significant transportation pathway for both of these materials. The fact that atrazine was not detectable in most samples in 1995 suggests that the presence of significant quantities of atrazine in the groundwater flow phase in 1994 may have been due to earlier deposition of atrazine holding sediment into the stream channel by runoff events. It's lack of detection in 1995 under drier conditions suggests that runoff is the major transportation pathway from fields to the watercourse.

4.2.5 Exceedancy Curves

The data from the sampling program for each year were plotted on an exceedancy curve. These are shown in Figures 4.57 to 4.62. These graphs show the percentage of occasions a measured value was exceeded as well as a best fit curve which indicates the probability of a certain concentration being exceeded.

An observation that can be made regarding these curves is with respect to the exponent in the regression equation of the best fit curve. For both years, it was found that the exponent for nitrate was greater than that for phosphate which in turn was greater than that for suspended sediment. The exponent in the regression equation may be an indication of the degree to which the loss of the particular material from the watershed is affected by runoff processes. The low exponent in the probability curve for suspended sediment is caused by a small number of samples

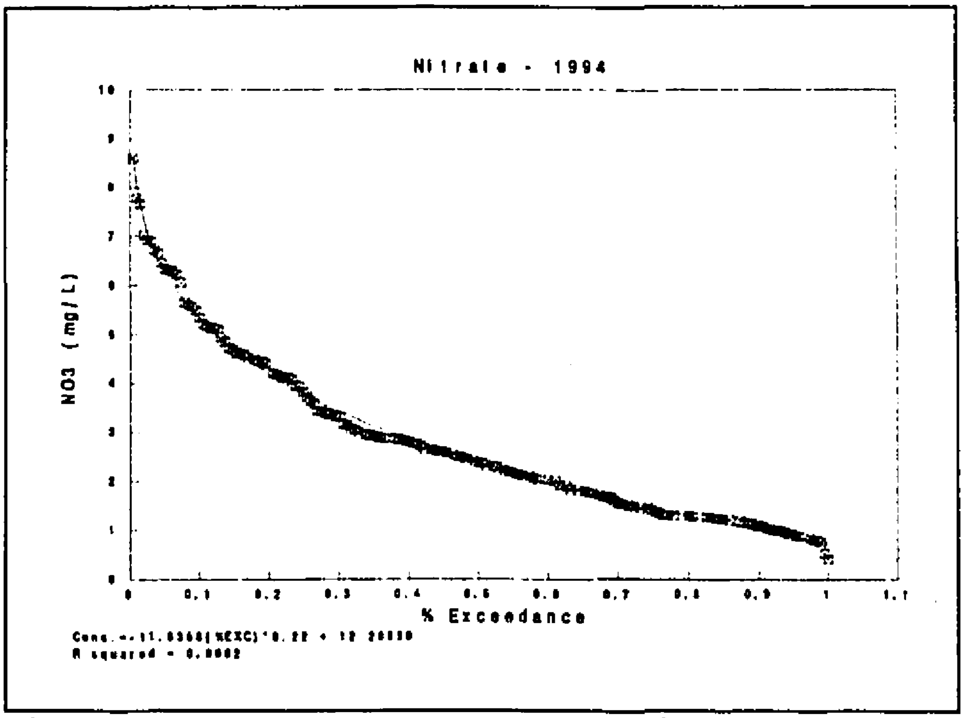

Figure 4.57 Exceedancy curve for nitrate - 1994

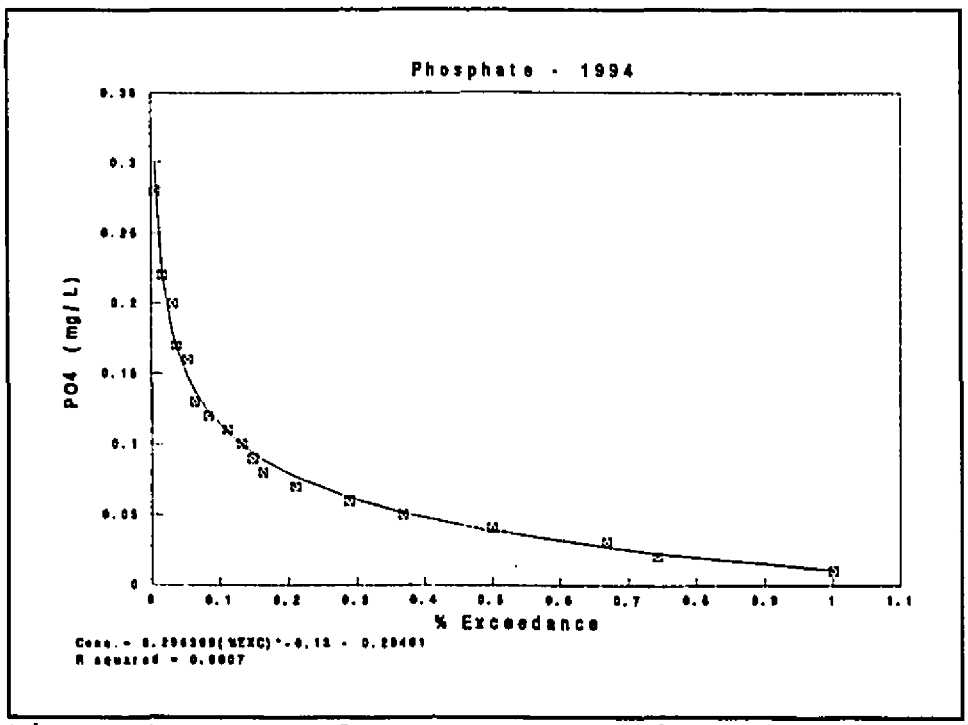

Figure 4.58 Exceedancy curve for phosphate - 1994

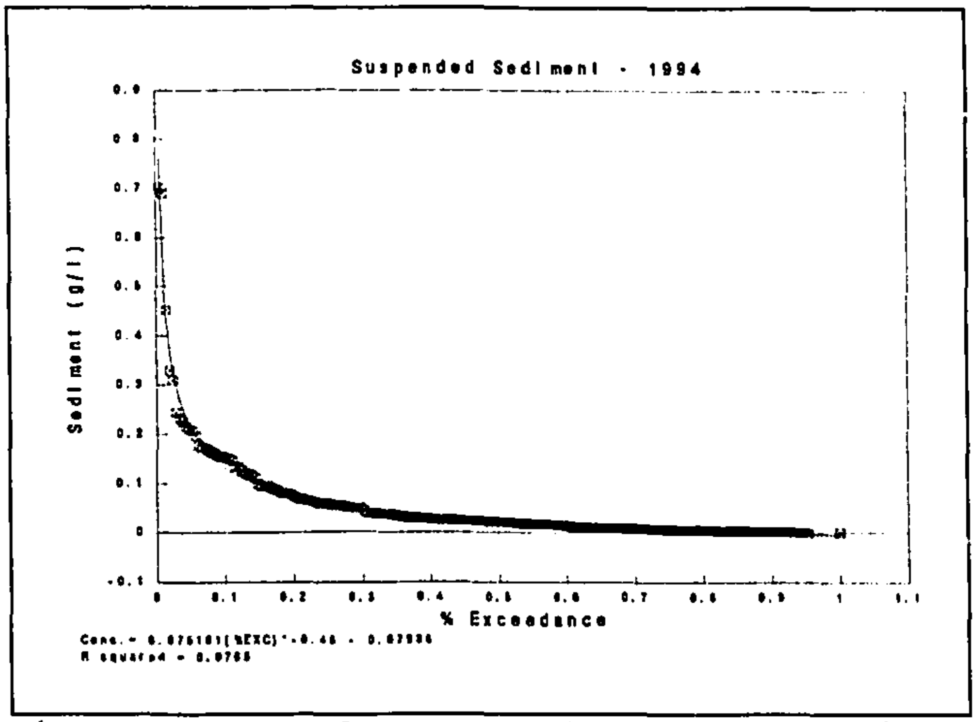

Figure 4.59 Exceedancy curve for suspended sediment - 1994

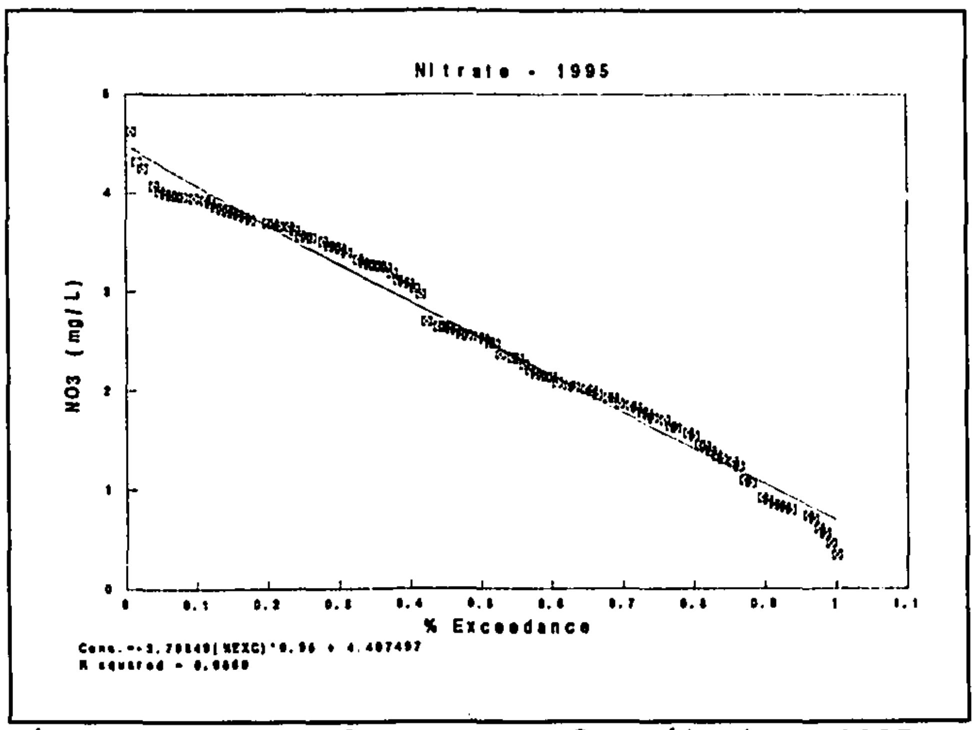

Figure 4.60 Exceedancy curve for nitrate - 1995

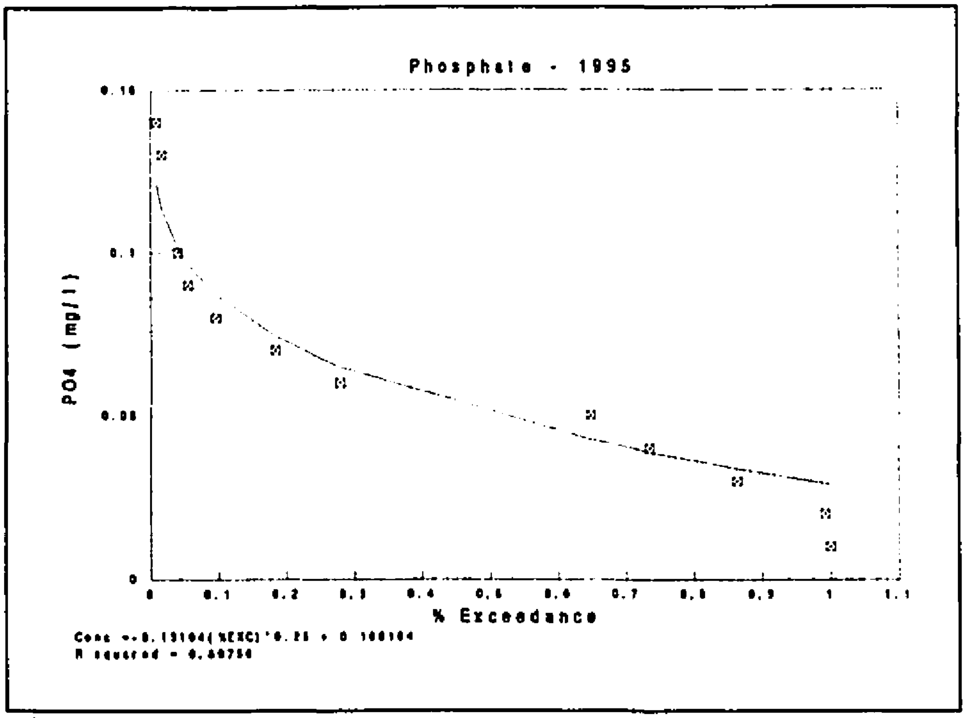

Figure 4.61 Exceedancy curve for phosphate - 1995

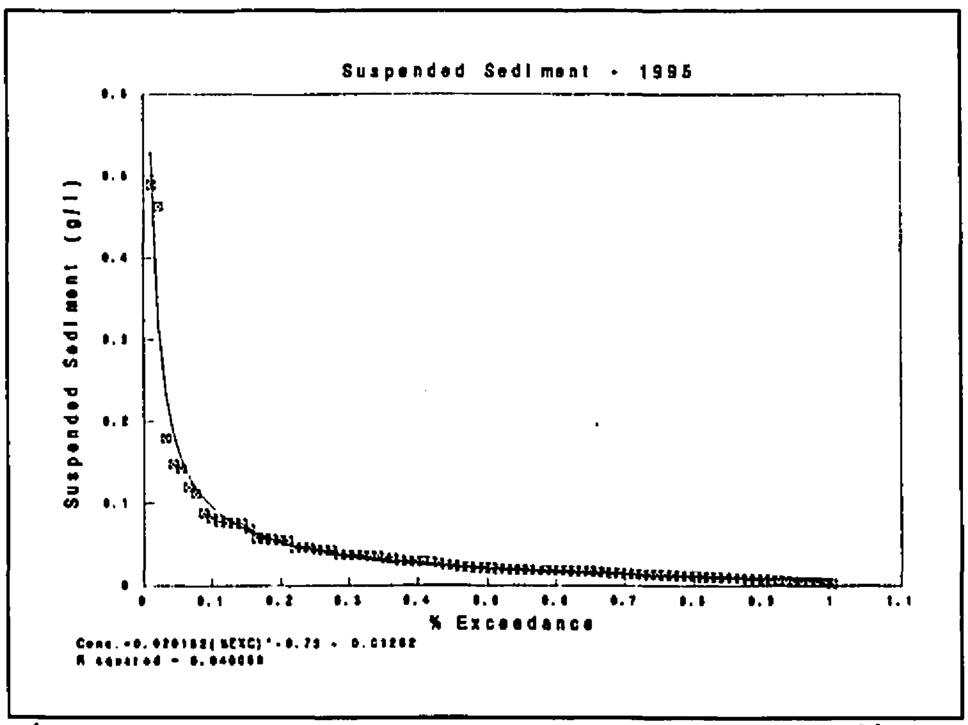

Figure 4.62 Exceedancy curve for suspended sediment - 1995

from high flow events which gave very high concentrations of suspended sediment. The same pattern of loss was not observed for nitrate which resulted in a higher exponent and a flatter exceedancy curve. This is likely the result of sustained, consistent levels of the material in the watercourse which is the behaviour that is expected for a soluble material such as nitrate. Phosphate would appear to be intermediate between the two which confirms previous observations that the majority of the phosphate loss on the basin is through surface runoff but that a deep groundwater conveyance of phosphate serves to sustain the observed concentration through low flow periods.

The development of exceedancy curves for the analysis of material loss would appear to be a useful tool in assessing loss patterns. Evaluation of exceedancy curves from successive years of a water quality improvement program could be a useful assessment and decision making exercise.

4.2.6 Concentration versus Flow Relationships

Empirical regression relations were developed to test the relationship between the observed concentration of pollutant material versus the recorded flow, and the material export during a runoff event versus the volume of runoff for the event.

The scatter plots for concentration versus flow are shown in Figures 4.47 to 4.50 for atrazine, nitrate, phosphate, and suspended sediment respectively. It was not possible to obtain satisfactory regression equations for any of these plots.

The plot of concentration versus flow for atrazine as shown in Figure 4.63 indicates a weak relationship between concentration and flow. One of the reasons for this observation may be due to the high concentration of atrazine observed in the months of September and October, 1994 when the flow was very low. The source of these high concentrations is not known. Atrazine attached to sediments deposited in the main channel may be a possible source of high concentrations of atrazine during low flow periods.

The plot of nitrate concentration versus flow as shown in Figure 4.64 did not result in a satisfactory empirical model. There is however and interesting feature of this plot that bears discussion. There appears to be two distinct sets of data points associated with high flow periods. These two sets of data are associated with high flow events that took place in April and June, 1994. The upper set of points is associated with a June storm while the lower set of points is associated with the April snowmelt event. These two sets illustrate clearly the seasonal variation in nitrate concentration in response to two events of equivalent magnitude. The high

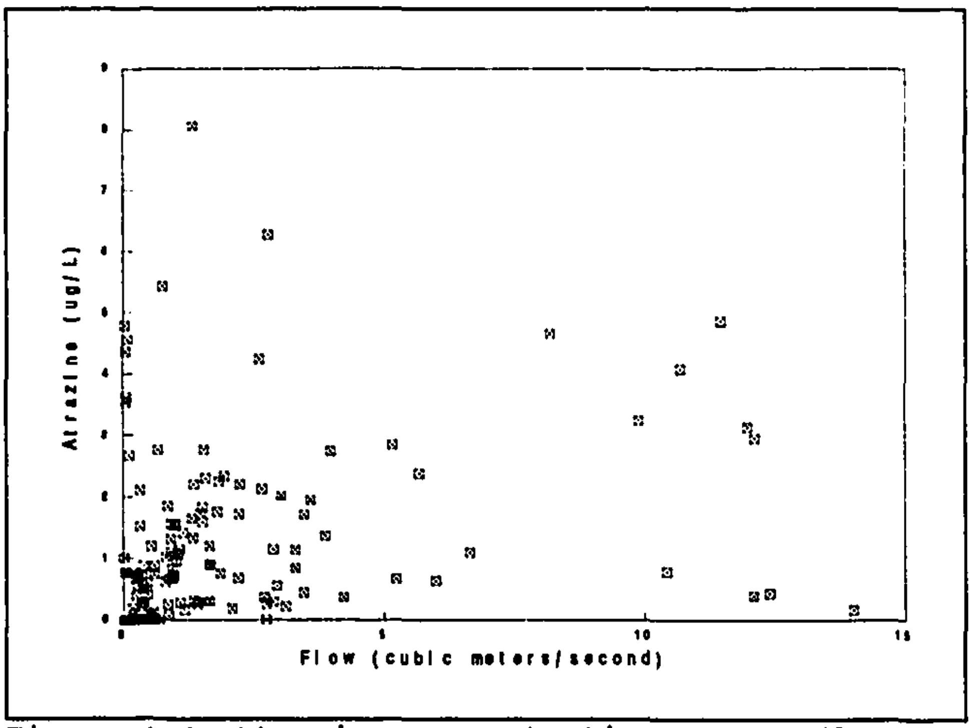

Figure 4.63 Atrazine concentration versus flow

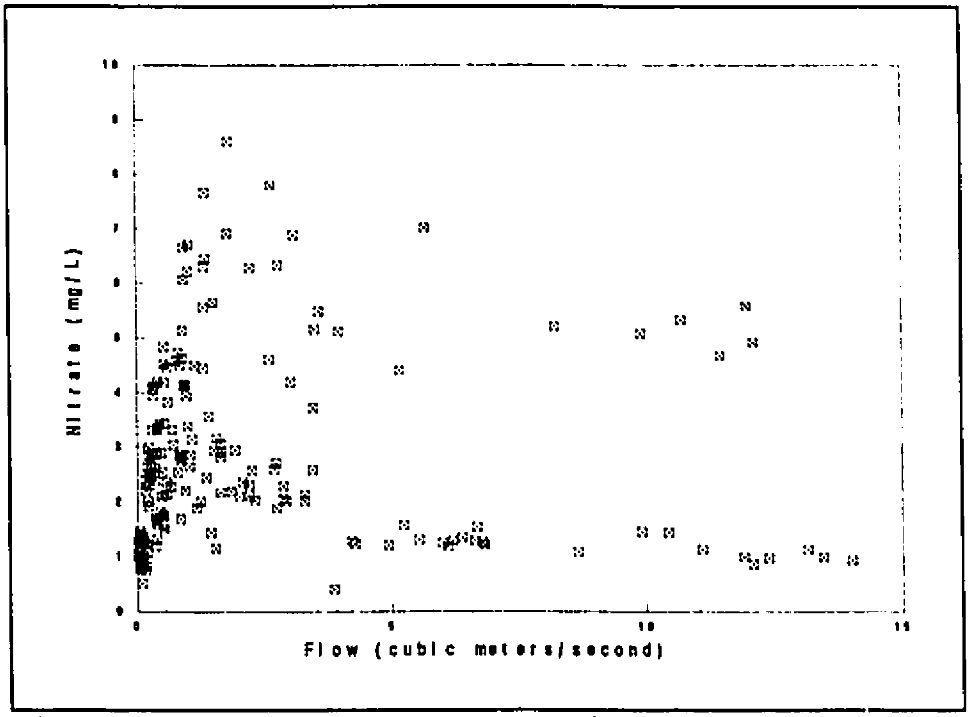

Figure 4.64 Nitrate concentration versus flow

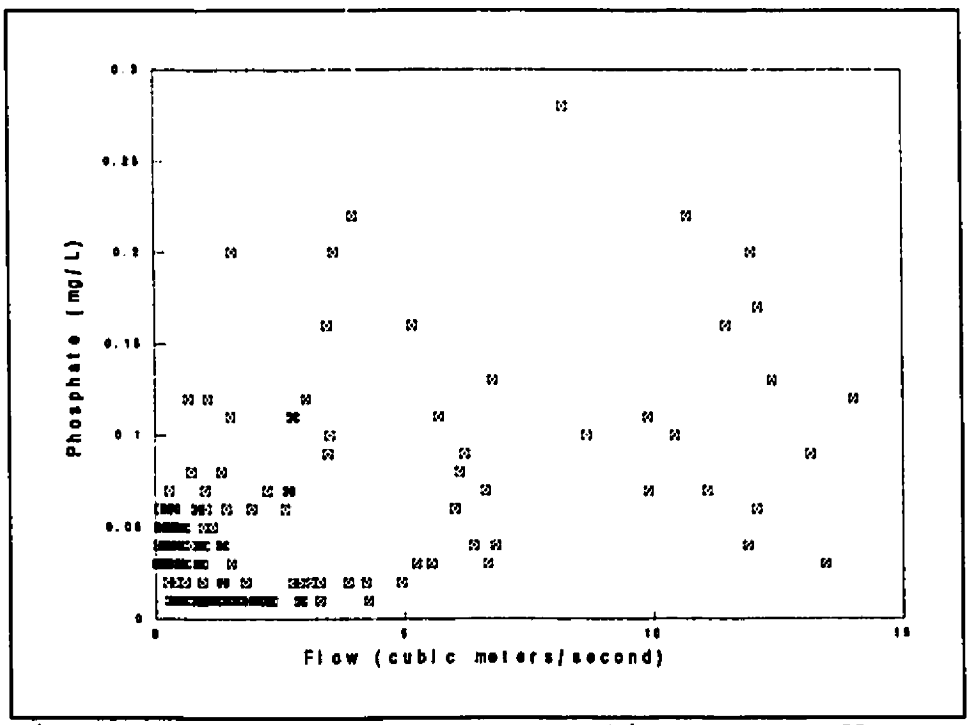

Figure 4.65 Phosphate concentration versus flow

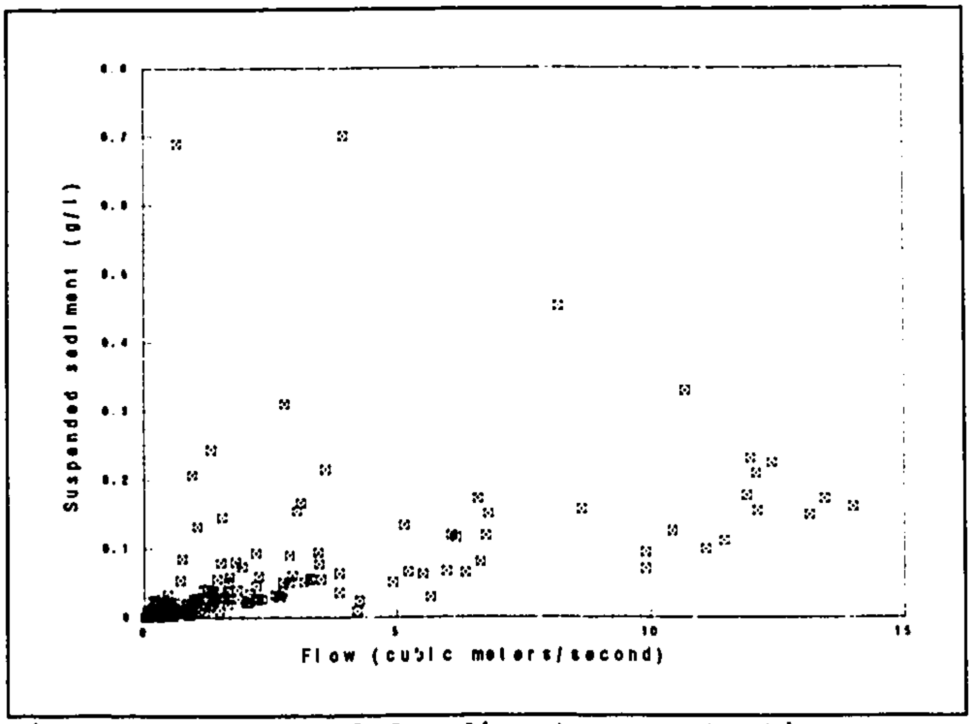

Figure 4.66 Suspended sediment concentration versus flow

concentrations of nitrate associated with the June storm are likely a result of fertilizer application during crop establishment on the watershed.

As shown in Figure 4.65, the relationship between phosphate concentration and flow appears to be random in nature. It has already been observed that phosphate likely moves by at least two paths to the watercourse so this type of relationship should be expected.

Figure 4.66 shows the relationship between suspended sediment concentration and flow. A satisfactory regression equation was not found for this relationship. This appears to be somewhat surprising given that other analyses on sediment data indicated that movement of sediment is associated with flow events. Peak suspended sediment concentrations are associated most strongly with moderate flow levels. The poor relationship shown in this plot can be explained by examining the concentration of suspended sediment during an event. As an example three measured suspended sediment concentrations for the event of June 27, 1994 will be examined. The event began at 2300 hr on June 27, 1994. At that time, the discharge was approximately 1 m^3/s. At 0221 hr on June 28, 1994, a sample was taken with a suspended sediment concentration of 0.701 g/l. At that time, the discharge was 3.98 m^3/s. At 0732 hr, a sample was taken with a suspended sediment concentration of 0.155 g/l. The flow at this time was 12.11 m^3/s. As the event receded, a sample was taken at 1540 hr with a suspended sediment concentration of 0.036 g/l. The flow at this time was 3.87 m^3/s. The profile of suspended sediment concentration given by these points indicates the reason why peak concentrations of suspended sediment do not appear to be associated with peak flows. Peak concentrations in suspended sediment appear to occur as the water level rises during an event. The first and third sampling points were at a period of equivalent flow, but the sample taken on the ascending portion of the hydrograph had a much higher concentration of suspended sediment than the one taken on the receding portion of the hydrograph. This pattern is repeated for most events on the basin. This accounts for the observation that peak concentrations of suspended sediment are associated with moderate flows rather than peak flows.

4.2.7 Load versus Runoff volume Relationships

Figures 4.67 to 4.69 show the relationship between the calculated load of material exported during a runoff event and the volume of surface runoff for nitrate, phosphate, and suspended sediment respectively.

Good fits were found for linear regressions describing these relationships. It should be noted however, that the flux of material was calculated by multiplying the interpolated concentration for a 15 minute interval by the volume of discharge for the 15 minute interval. Therefore, there is a certain amount of correlation in these plots between the volume of surface runoff and the volume of discharge for each interval. Attempts to make inferences regarding material export based on these plots should be done with caution.

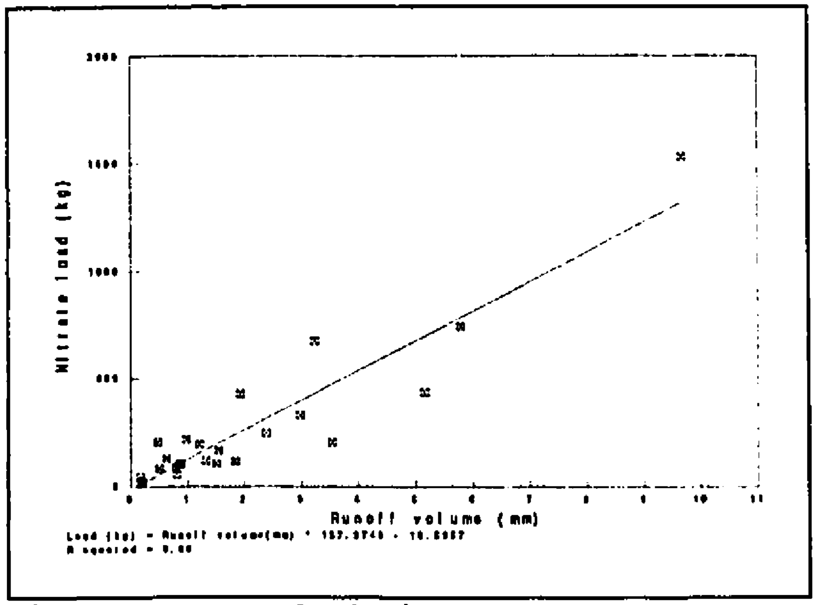

Figure 4.67 Load of nitrate exported versus runoff volume for observed events

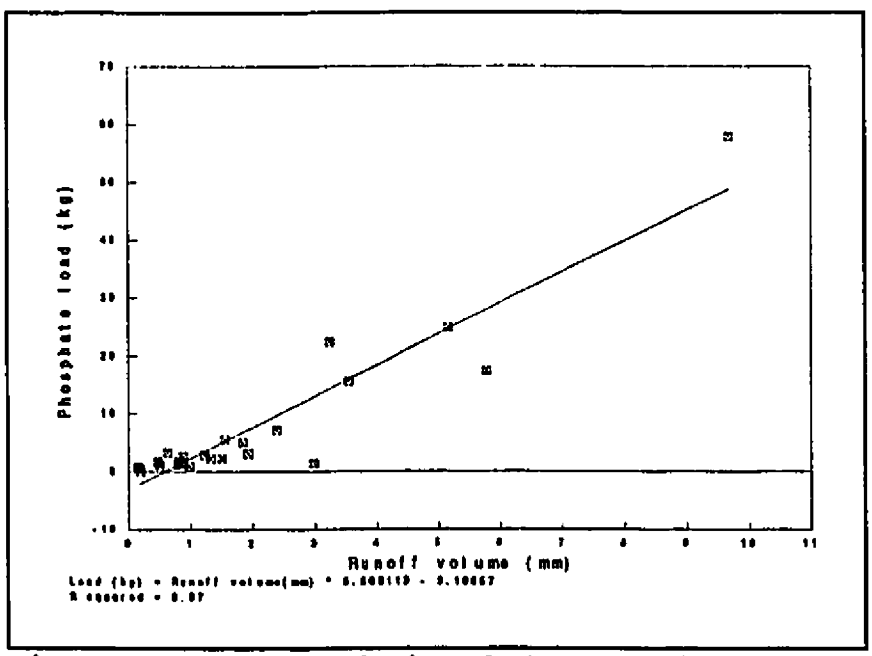

Figure 4.68 Load of phosphate exported versus volume of runoff for observed events

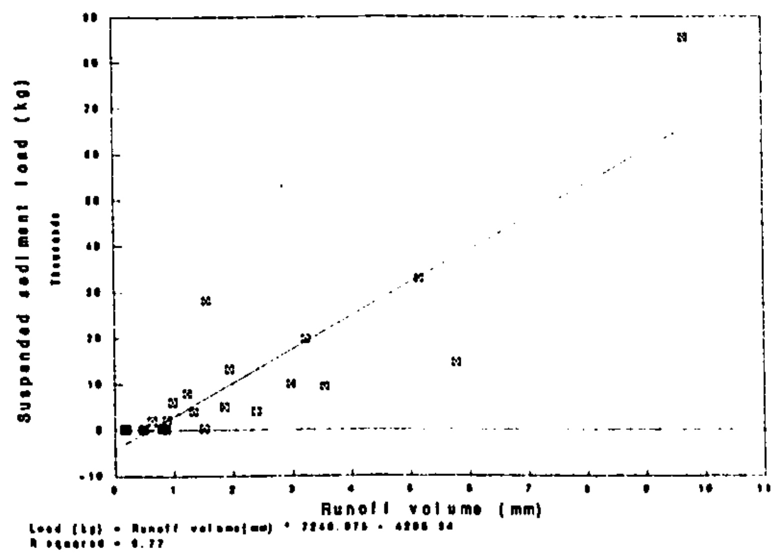

Figure 4.69 Load of suspended sediment exported versus runoff volume for observed events

5.0 Summary and Conclusions

5.1 Summary

A research project to study the hydrology and water quality of a 26 km^2 agricultural watershed in Quebec was undertaken from April 1994 to September 1995. Hydrologic data were derived from water level and precipitation readings taken from automated gauging stations. Water quality data were derived from an intensive event-based sampling program at the outlet of the watershed.

The hydrologic data were analyzed to determine standard hydrograph parameters, and to assess possible relationships between measured hydrologic parameters. The water quality data were analyzed to assess trends in pollutant concentration and load of nitrate, phosphate, suspended sediment, and atrazine in the watercourse. The observed water quality data were related to hydrologic parameters for the basin to assess the relationship between the observed water quality and the hydrology of the watershed.

5.2 Conclusions

The hydrograph time parameters, time of concentration (t_c), time to peak (t_p), and lag time (t_l) were calculated for 25 selected events. The mean time of concentration was found to be 6.89 hours with a standard deviation of 1.3 hours. The time of concentration was not correlated with storm intensity, volume or duration and could be considered as a constant for the 25 events that were studied.

The time to peak was found to be related to the storm duration by the relation:

$$t_p = 0.7468 * [d(hr)] + 5.83 \qquad (4.1)$$

The constant in the above equation can be taken to represent the wave travel time of an instantaneous storm and it thus represents the lag time. Measured values of the lag time (t_l) were found to be influenced by the causative storm. An estimate of the lag time was developed by only considering the measured lag time for storms with a duration less than the time of concentration. The mean of the lag time for these storms was 6.89 hours with a standard deviation of 0.94 hours.

Commonly used formulae for determining t_c were compared to the measured value. The Kirpich method was found to be inappropriate. The best result was derived from the SCS formula.

The recession characteristics of events on this watershed were identified. From the time of peak flow until the inflection point on the receding limb, the recession was found to follow the relation:

$$q_1 = 1.15*q_0 - 0.12*[\text{peak flow}(m^3/s)] - 0.04 \qquad (4.2)$$

From the inflection point on, the event recession was found to follow the relation:

$$q_1 = 0.97*q_0 \qquad (4.3)$$

An attempt was made to describe hydrologic processes on the basin through the use of empirical models and regression equations. The strongest relationship found was between the percentage of the rainfall from a storm appearing as surface runoff and the sum of the 72 hour antecedent precipitation plus the storm precipitation. The goodness of fit of this model as measured by the R^2 value was 0.52.

The results of the water quality data analysis indicated seasonal and within storm variation in the concentration and load of pollutant material in the watercourse. Loss of suspended sediment appears to be well correlated with high flow periods and times when fields are most susceptible to erosion.

Nitrate loss is believed to be primarily by subsurface flow to the watercourse. High concentrations of nitrate in the watercourse were found to be associated with periods of crop establishment in the spring. The path of movement of nitrate to the watercourse during these periods is not precisely known but the source of the nitrate is likely associated with fertilizer management practices.

Phosphate loading was found to be greatest during spring snowmelt periods and during crop establishment periods. It appears that most of the load of phosphate is associated with eroded sediment. High loads during crop establishment periods indicate that, as for nitrate, fertilizer management may be an important consideration. High sustained concentrations of phosphate were associated with low base flow periods. The source of these higher concentrations is not known. Natural geologic origin, leachate from septic systems, and deep percolation from fields are all possible sources.

Records for atrazine were only available for 1994. Atrazine was found to parallel suspended sediment in it's pattern of loss. High observed concentrations in the watercourse during the spring were associated with periods of atrazine application to crops. High observed concentrations in September and October cannot be explained in terms of standard agricultural practices. A spill or other point source cannot be ruled out as a possible source. Ditch cleaning operations which took place on the watershed in the Fall of 1994 may also provide a possible source of high atrazine levels if atrazine carrying sediment was disturbed.

The observed concentration of pollutant material was not well correlated with flow levels for any of the materials studied. Seasonal and within storm variation in concentration appears to be an important consideration in the lack of correlation.

Empirically modelling the flow and pollutant transport processes on this watershed is difficult with limited data. Instead of using data for the entire season to develop models, a more promising approach may be to develop seasonal models for the various processes under study. Such a procedure will require data from several more years on this watershed in order to build seasonally based data sets for hydrologic and water quality parameters. This study has shown that differences in material export processes can be considered in at least three general seasons and possibly more. The first is snowmelt, the second is the crop establishment period, and the third is the remainder of the growing season. Part of this seasonal variation is likely due to hydrologic conditions and part is likely due to land-use patterns and activities on the watershed. As data are analyzed from the following years of this study, the relative importance of each of these two components in influencing material export in each season may become more apparent.

The data set developed for this study will prove useful in developing, testing, and refining physically based models describing hydrologic and pollutant export processes. This route is likely the most promising in developing NPS pollution control strategies for use throughout the agricultural regions of Quebec.

6.0 Recommendations for future research

1. The land use and cropping practices on the watershed have not been quantified to the extent that would allow for a reliable estimate of basin characteristic coefficients (C) that are used in Snyder's formula, and those derived from it (Viessman et al. 1989; Sheridan 1994), for determining the time of concentration. The data on the land use has been tabulated but because of the size of the watershed, reliable estimates of C will likely require the use of computer software such as a GIS program. The use of more physically based models for estimating t_c may provide a better means of estimation.

2. Only two seasons of record were available for this study. It is believed that the lack of observed correlation between the hydrologic and water quality parameters was principally due to seasonal variations in these parameters which could not be adequately separated owing to the short period of record. It is recommended that as more data from this project are gathered, the hydrologic and water quality data be analyzed on a seasonal basis. Such an approach may reveal better correlations between the hydrologic and water quality parameters.

3. Because of the size of the watershed and the complexity of the interactions between land use, soils, and hydrology, physically based models capable of describing these processes may be the most reliable means of modelling hydrologic and water quality parameters. It is recommended that the data from this study be tabulated and organized into a form that would allow this type of model to be run.

7.0 List of References

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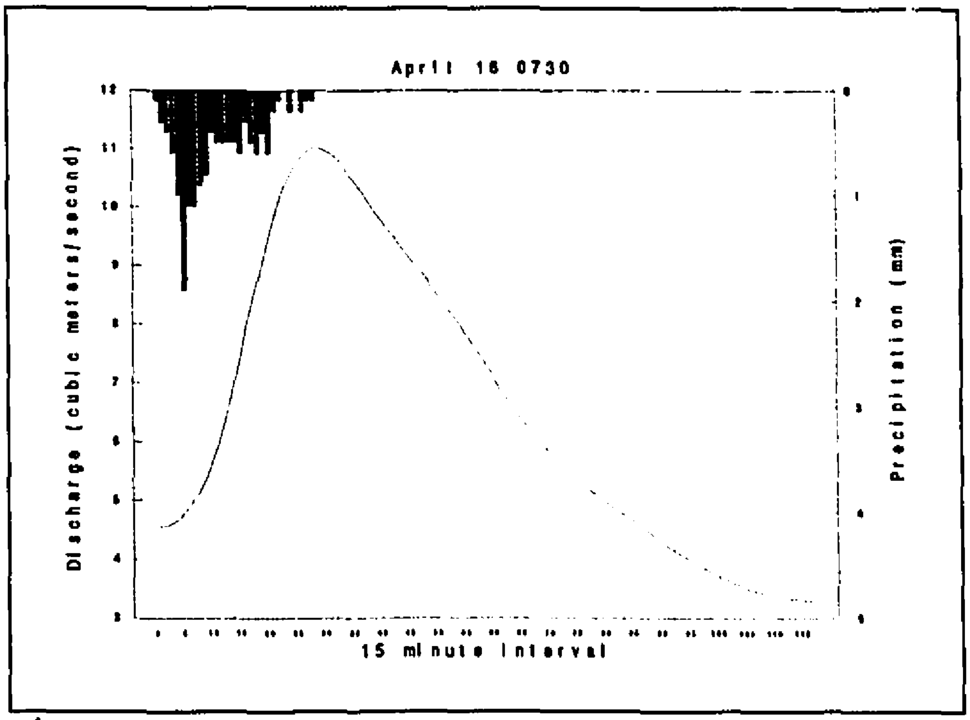
Appendix A

Rainfall and runoff hydrographs for

selected events in 1994

List of Figures in Appendix A



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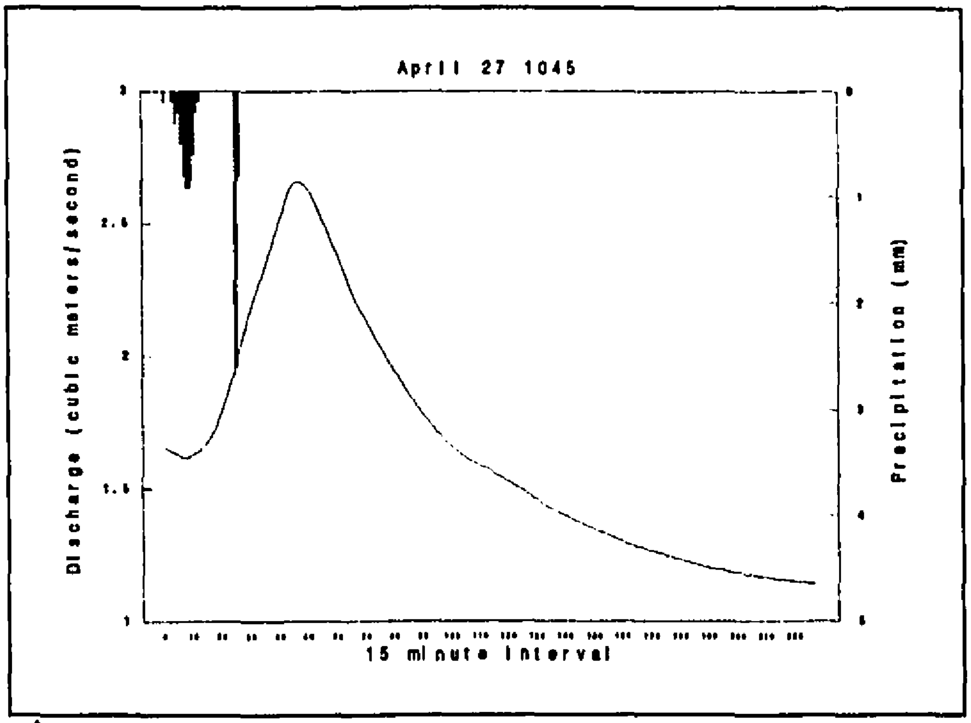

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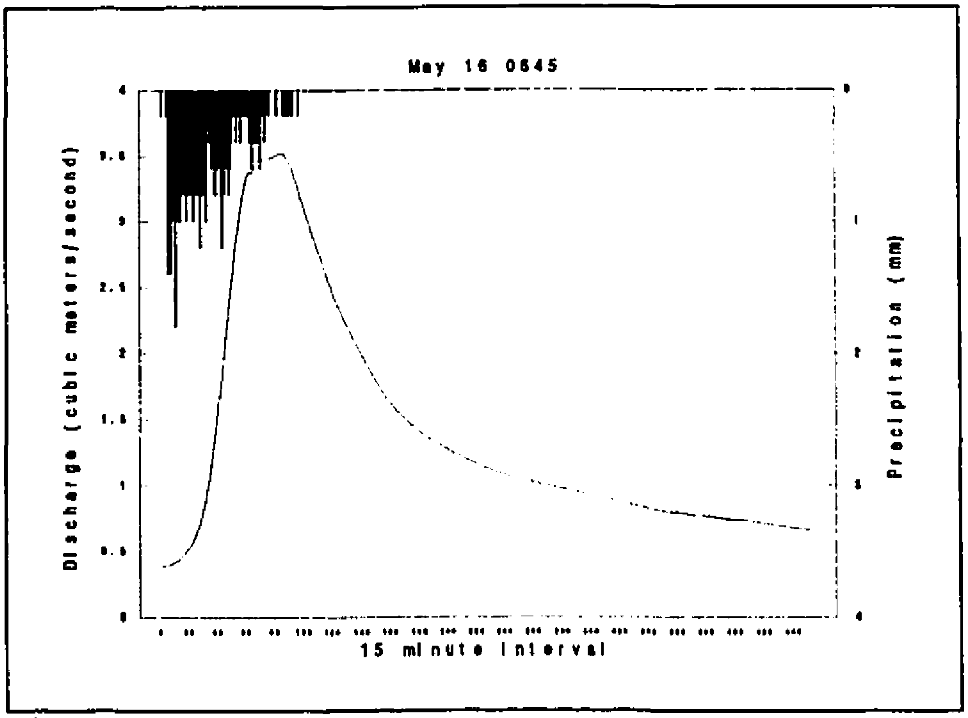

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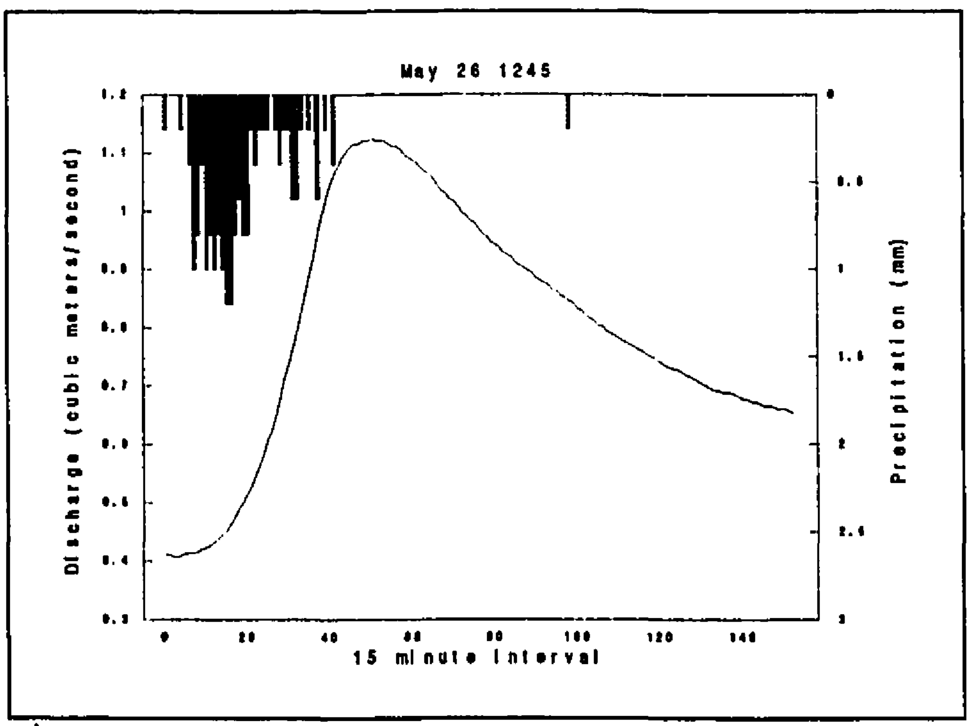

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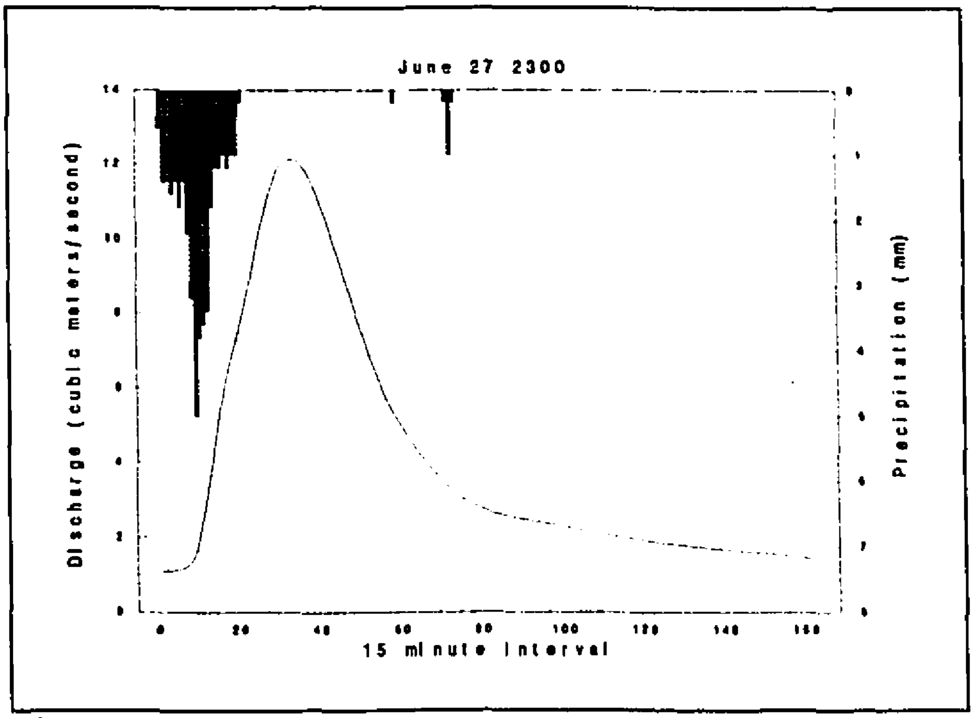

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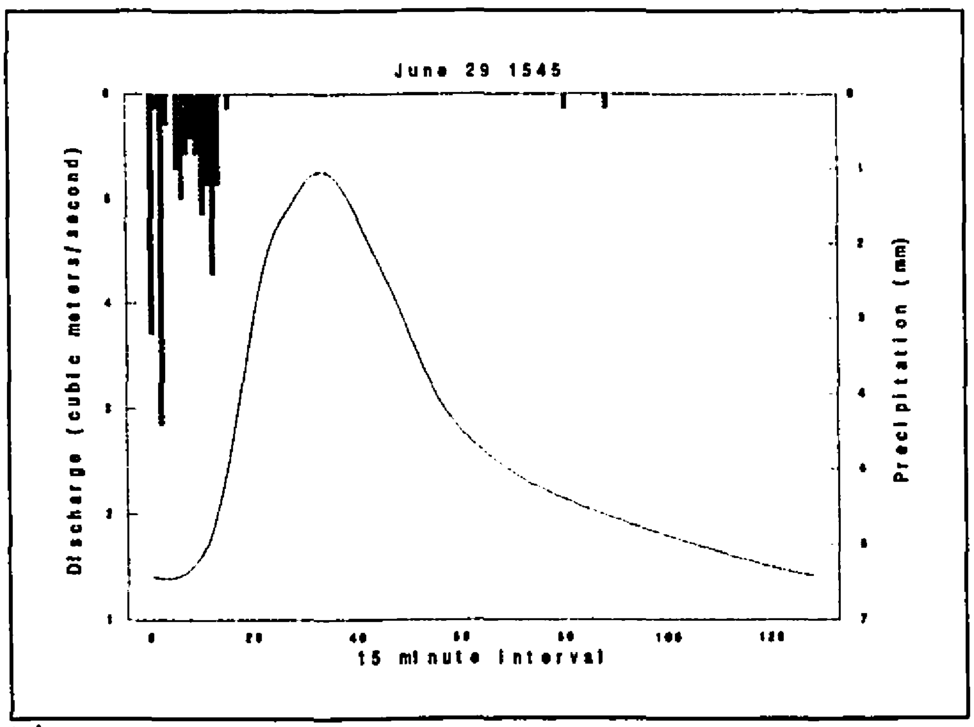

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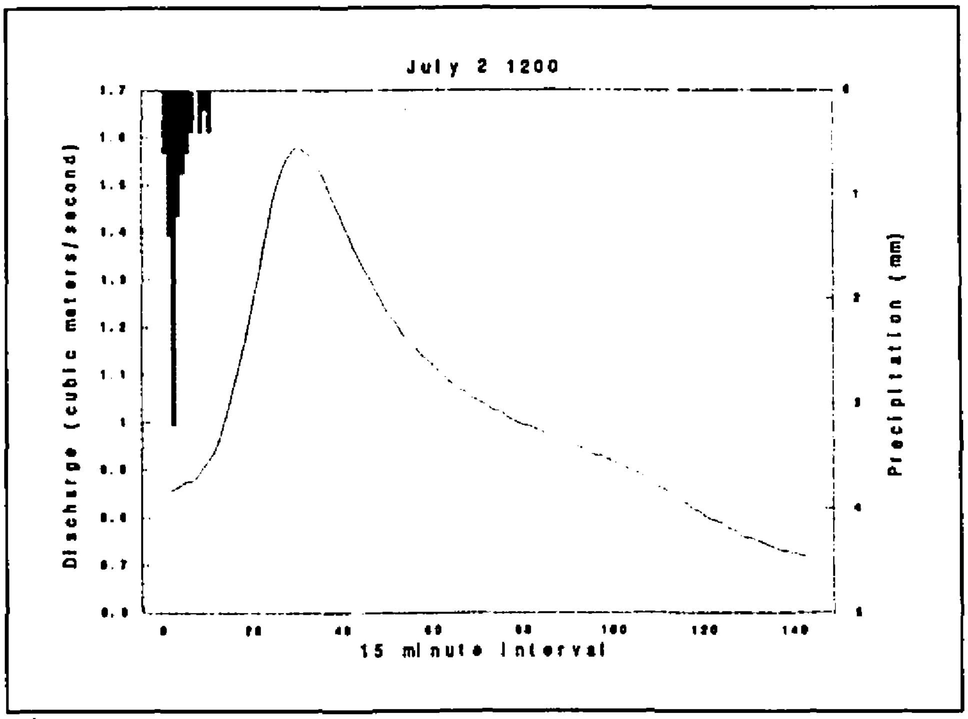

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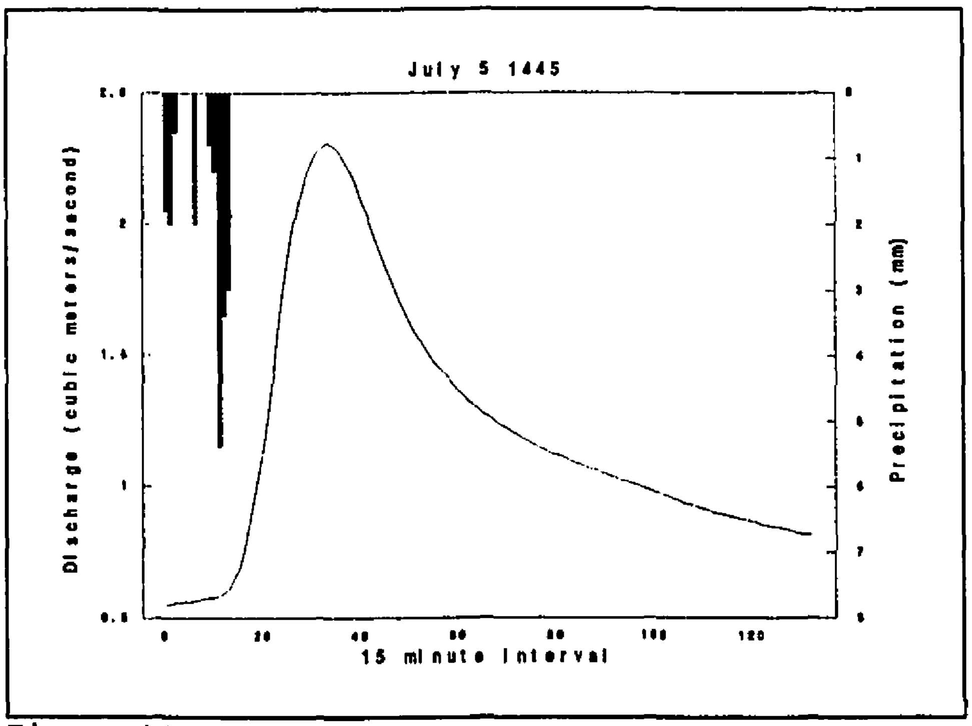

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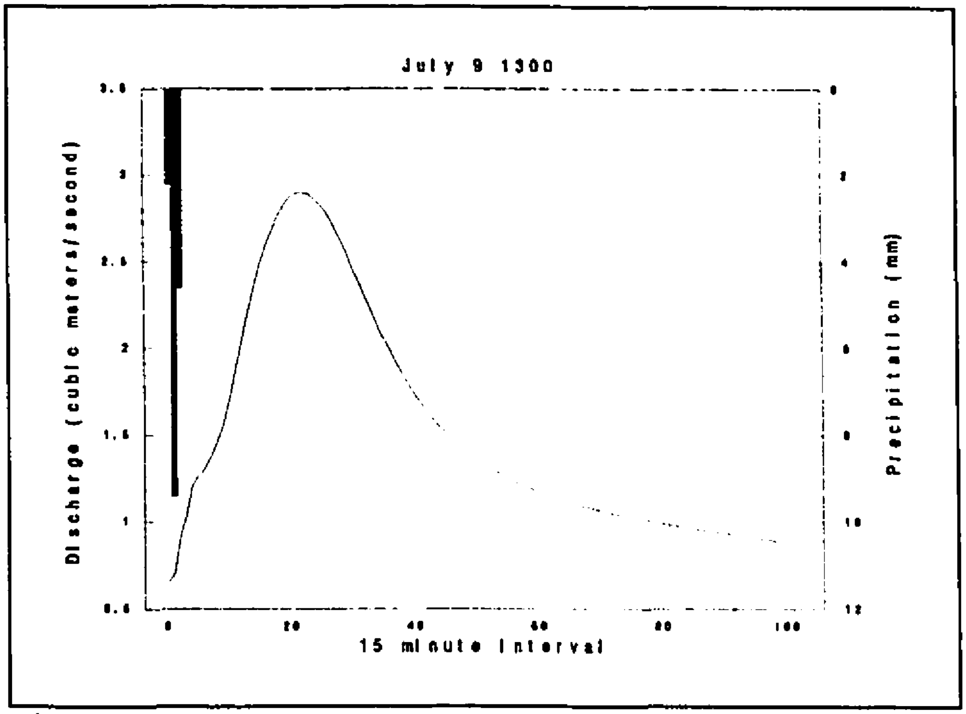

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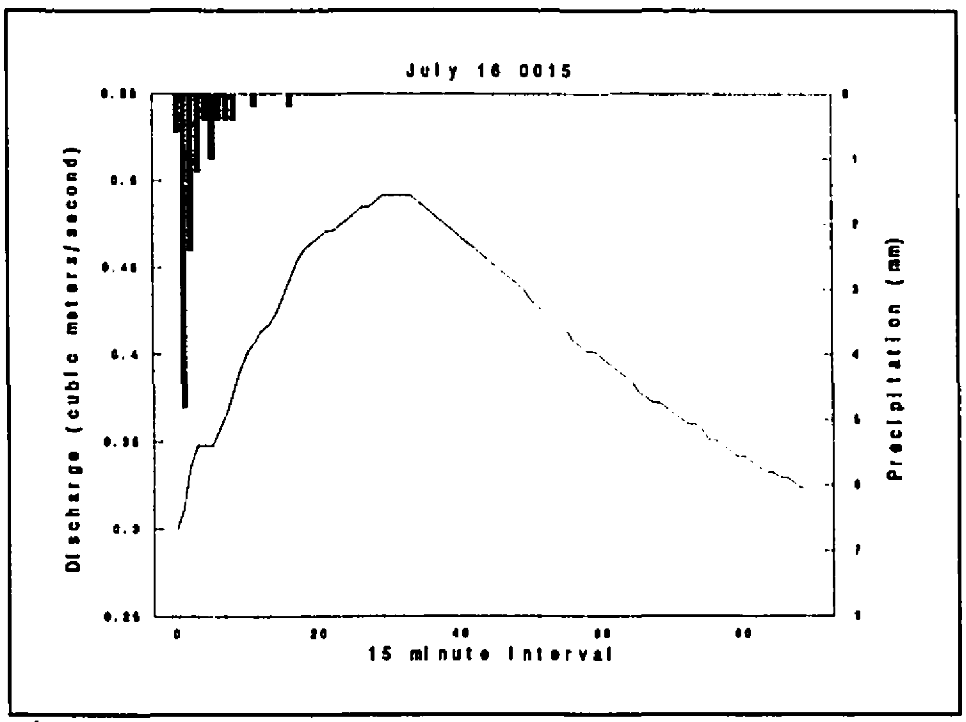

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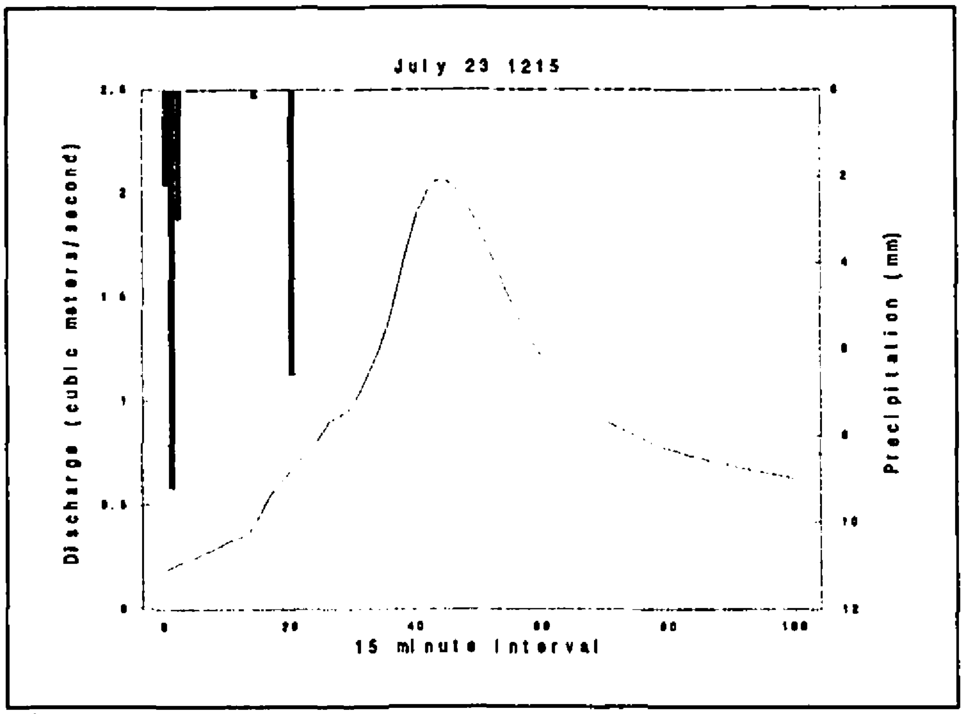

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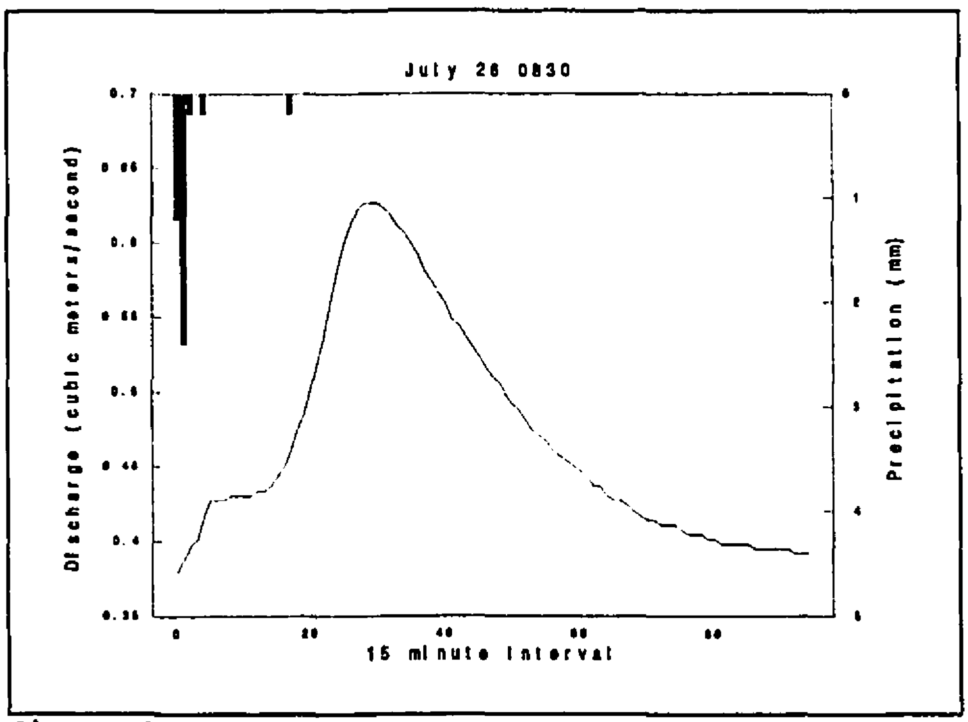

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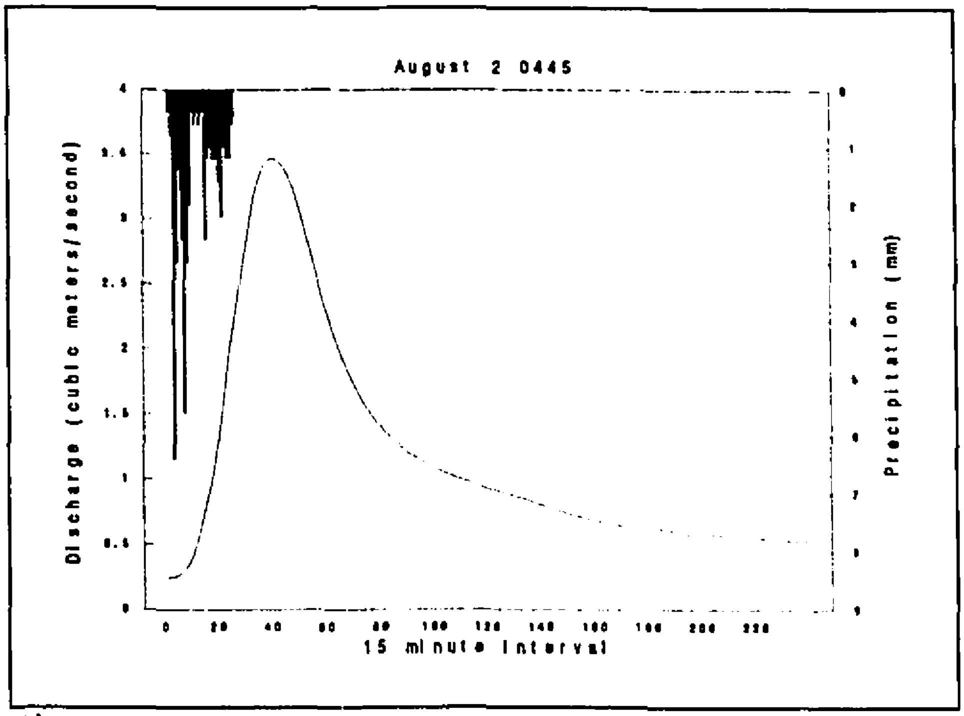

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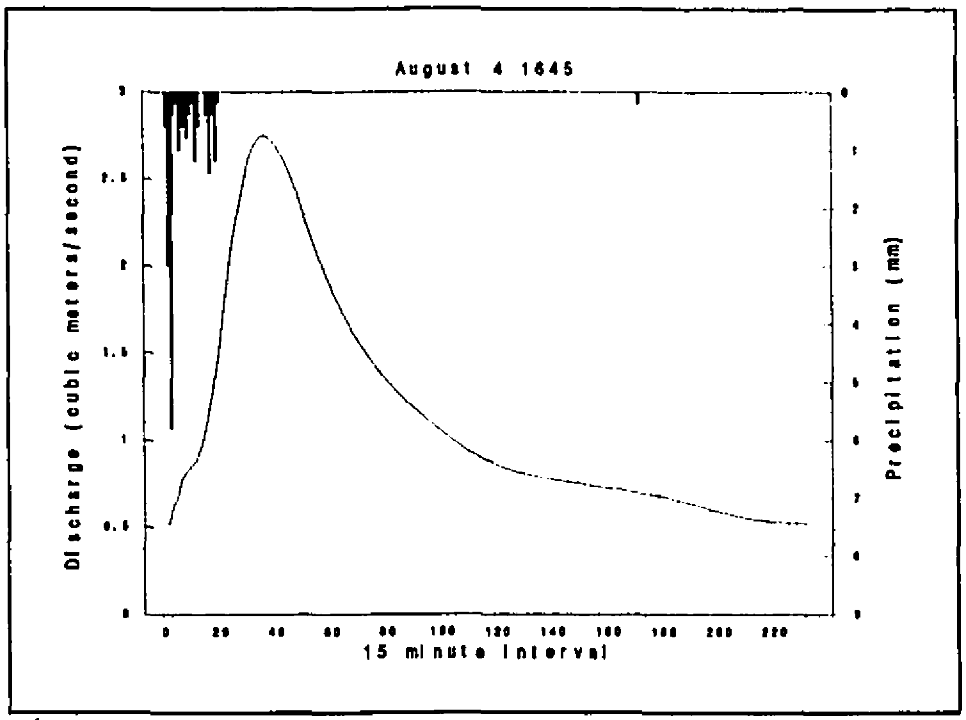

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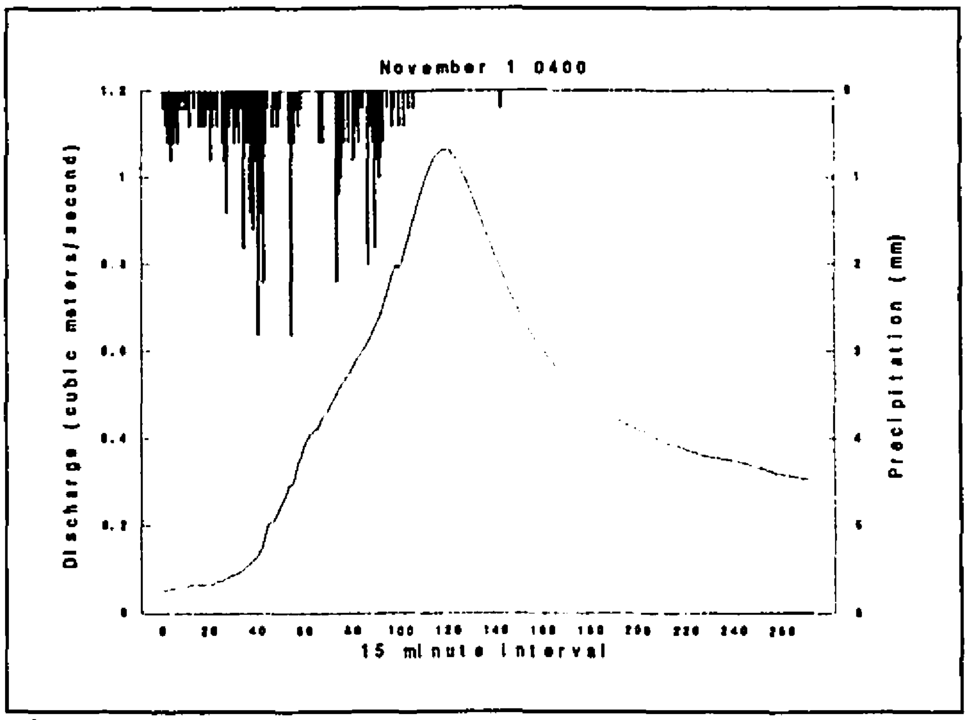

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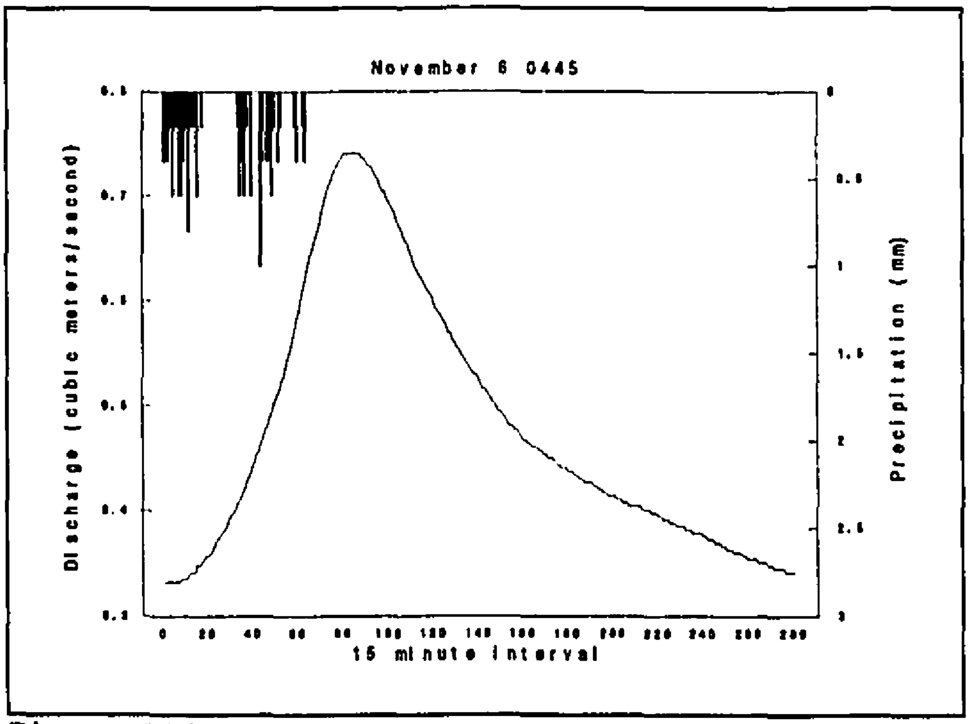


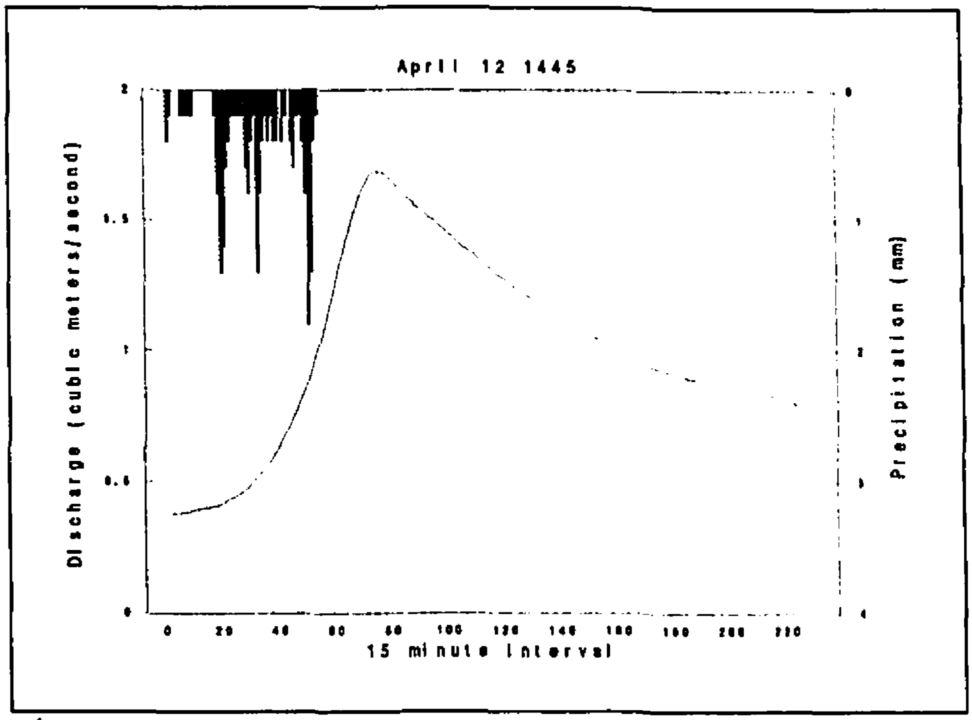
Figure A16

Appendix B

Rainfall and runoff hydrographs for

selected events in 1995

List of Figures in Appendix B



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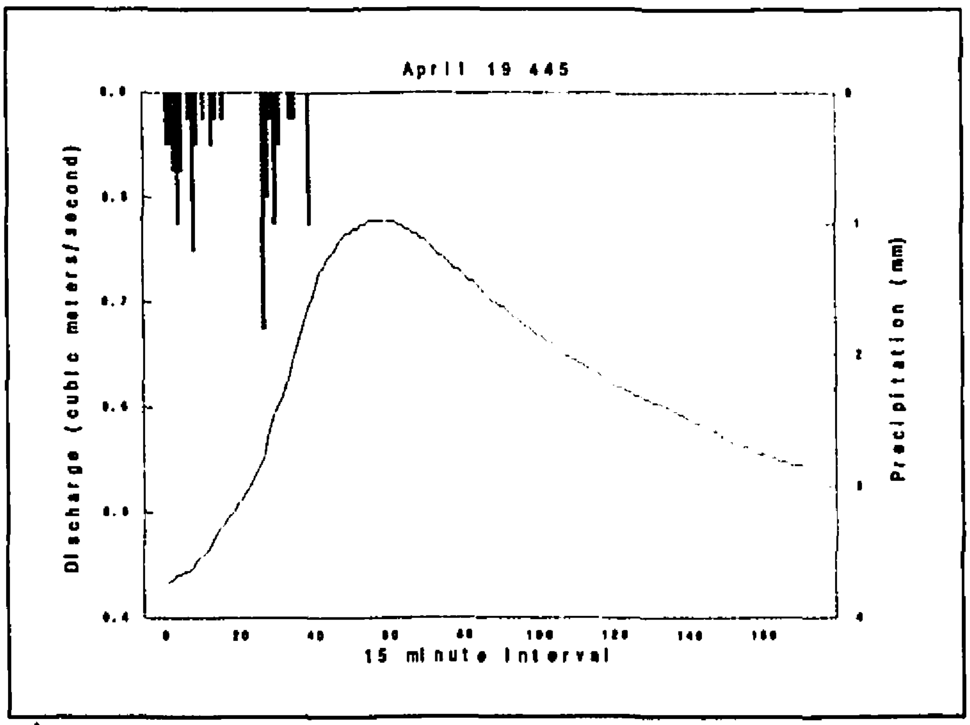

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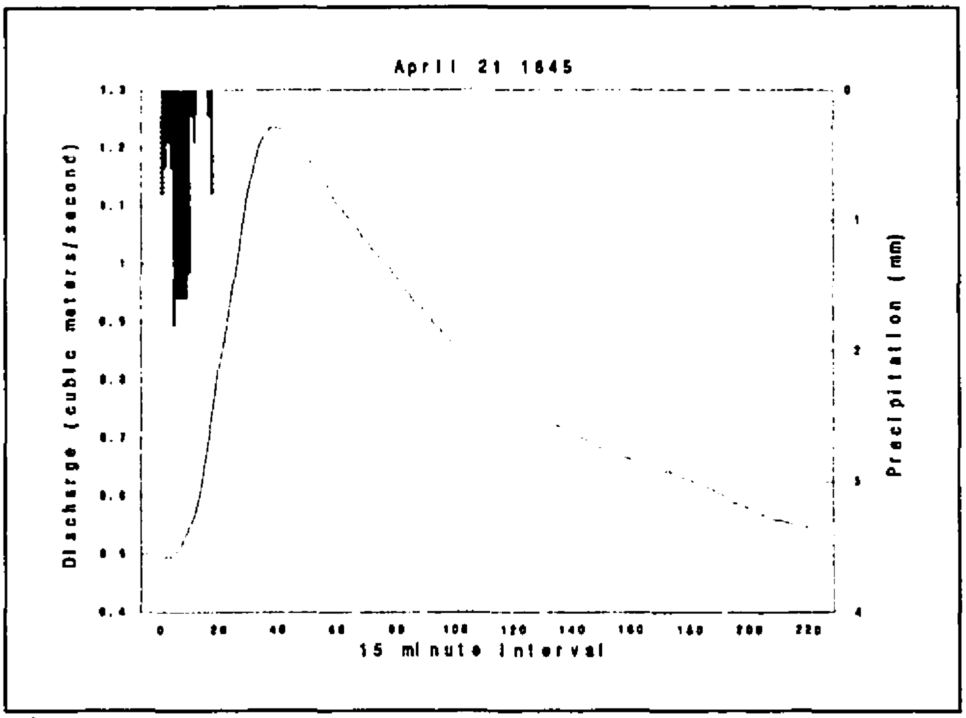

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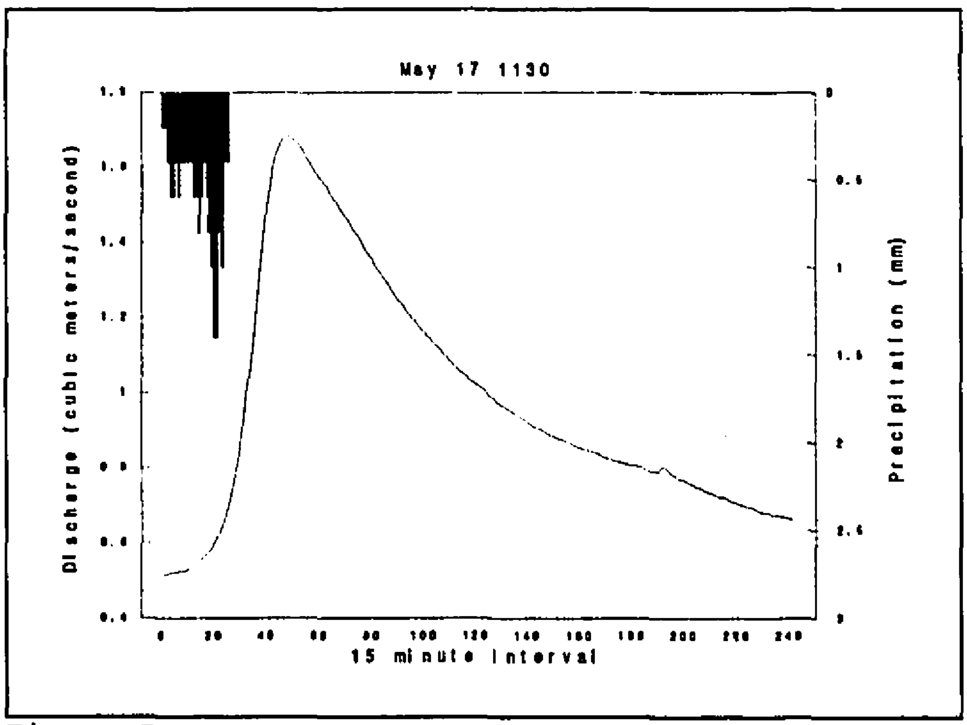

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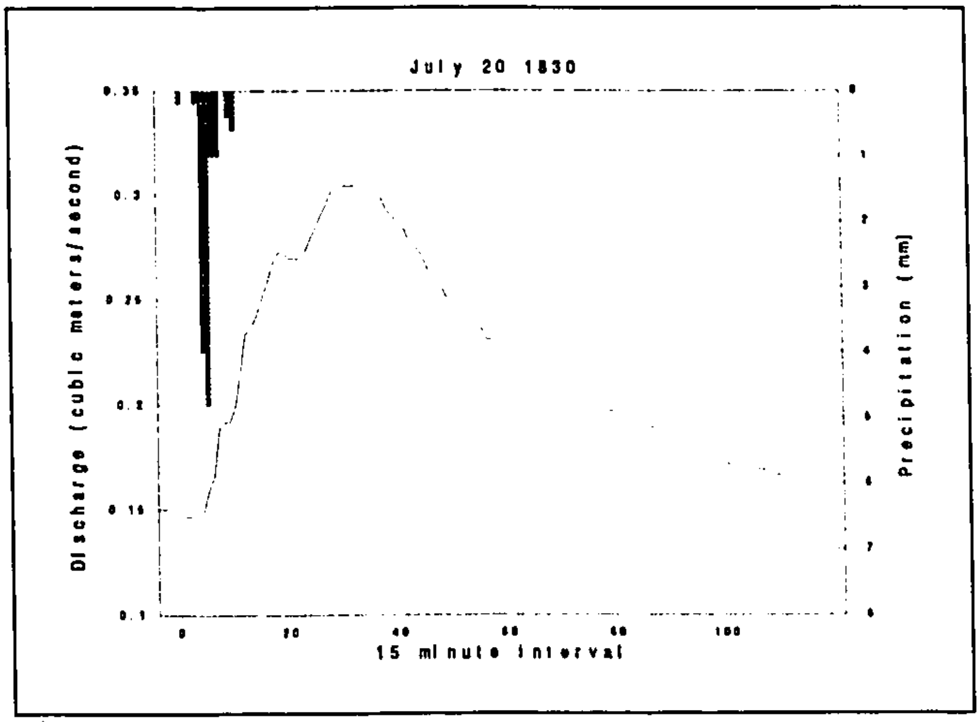

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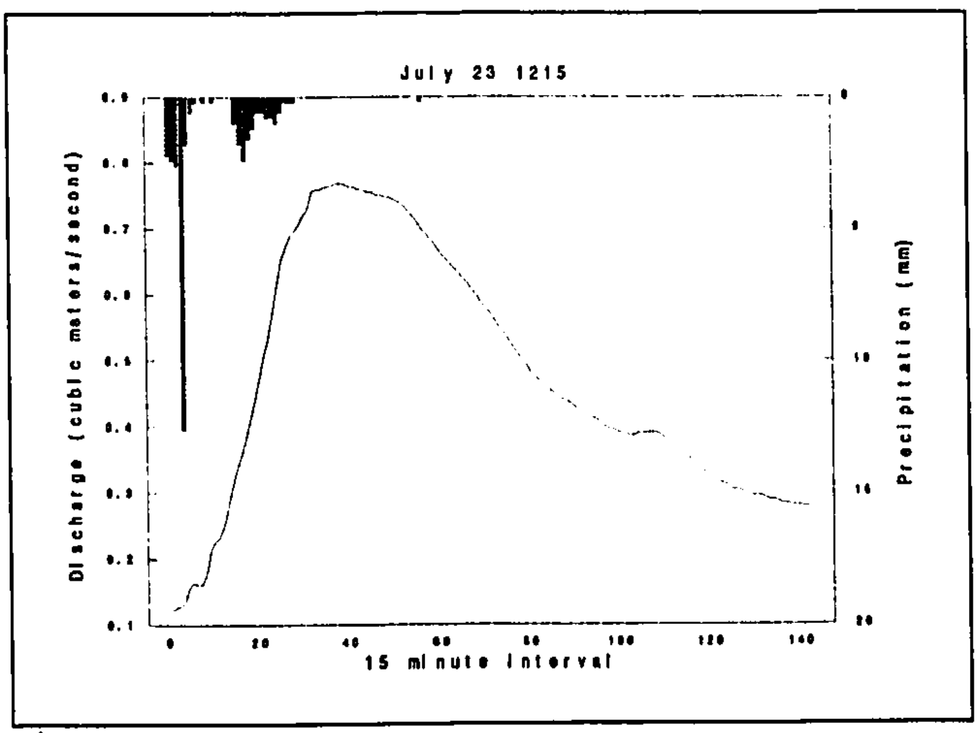

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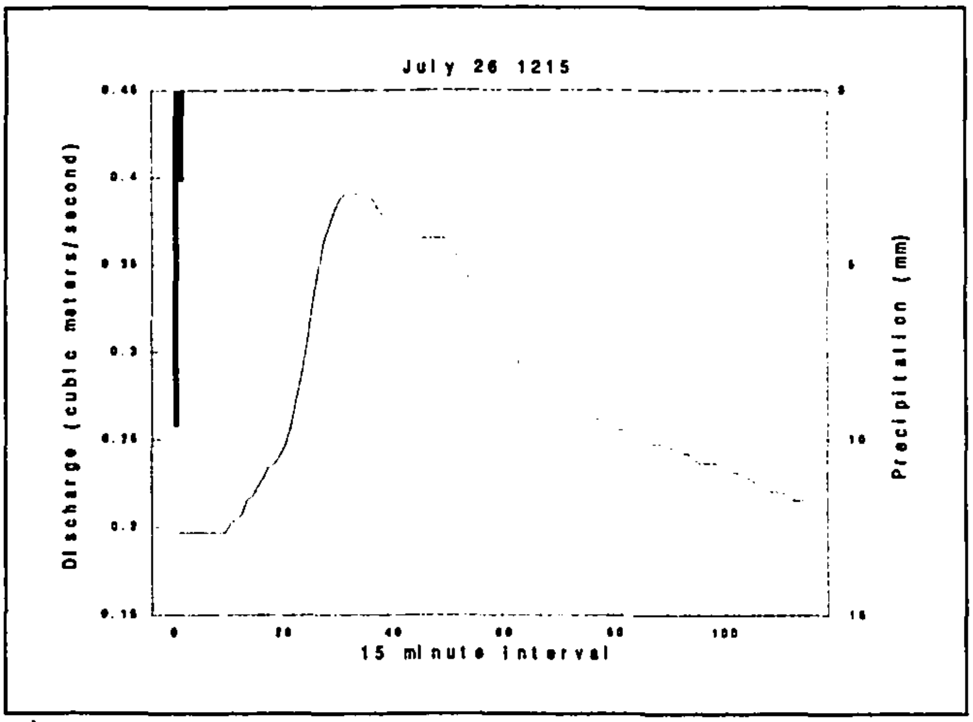

July 26 1215
Discharge (cubic meters/second)
Precipitation (mm)
15 minute interval

Figure B7