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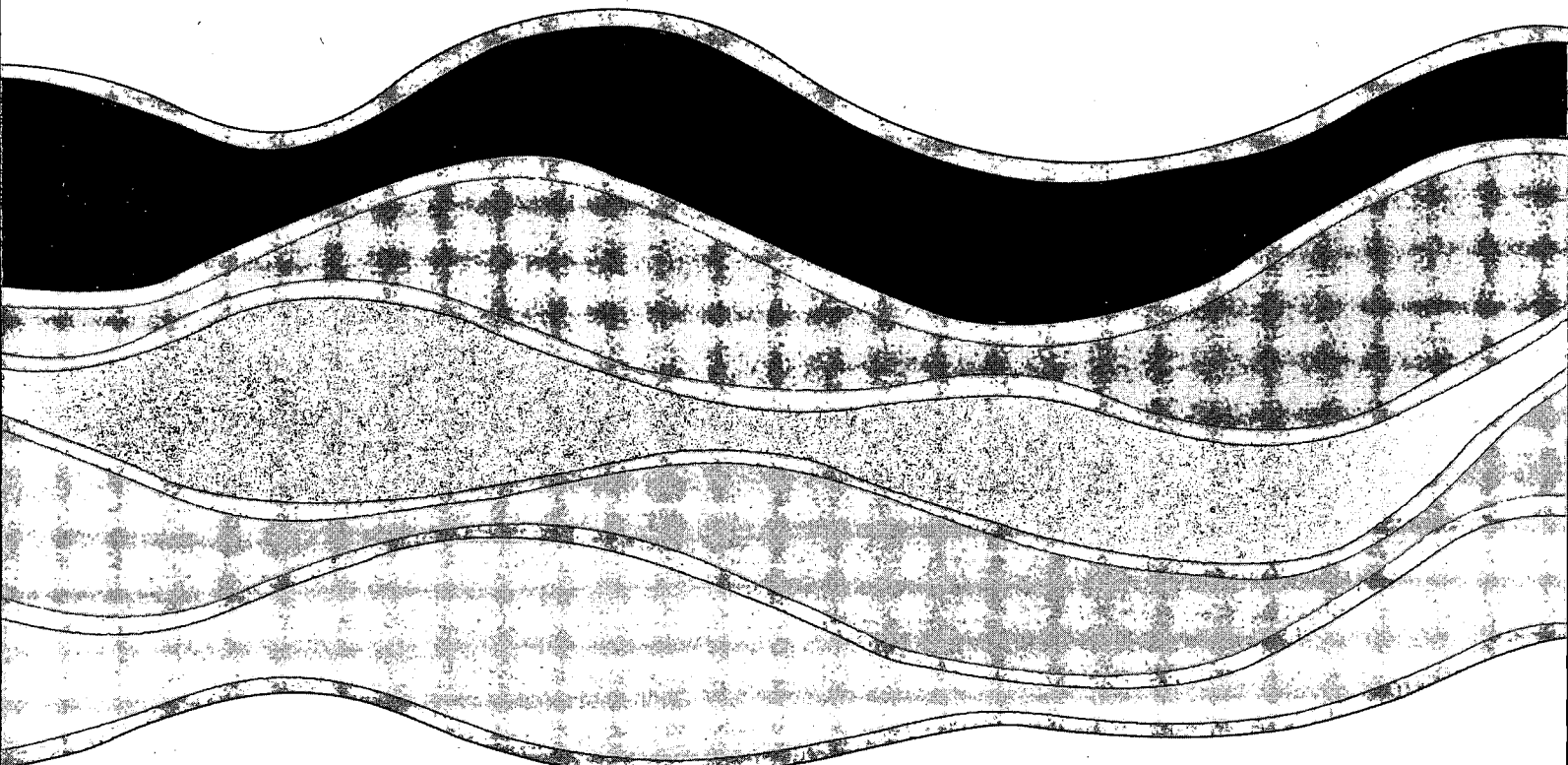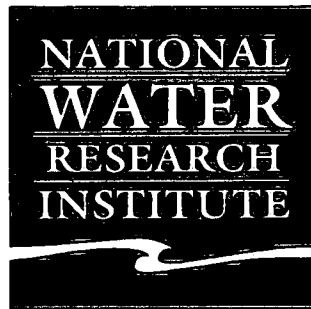WATER
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ATRAZINE AND METOLACHLOR LOSSES IN
TRANSIENT RUNOFF
EVENTS FROM AN AGRICULTURAL
WATERSHED

H.Y.F. Ng, and S.B. Clegg

NWRI Contribution No. 95-68

MANAGEMENT PERSPECTIVE

The decomposition of the runoff event hydrograph is useful for evaluation of the significance and magnitude of pesticide transport in transient runoff events.

Twenty five transient runoff events, monitored in an agricultural watershed, were analysed for losses of atrazine and metolachlor in the surface runoff, interflow, and baseflow. The majority of the losses of the applied herbicides occurred in surface runoff and interflow.

Atrazine loadings are consistently higher than metolachlor loadings even though metolachlor has a higher application rate.

This paper is prepared at the invitation of the chairman of the IAWQ Inter-Disciplinary International Symposium - July 1995 on Uncertainty, Risk and Transient Pollution Events: Acute Risks to the Aquatic Environment.

Atrazine and Metolachlor Losses in Transient Runoff Events from an Agricultural Watershed

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ABSTRACT

Losses of atrazine and metolachlor were monitored in transient runoff events at the outlet of an agricultural watershed. The streamflow hydrographs were decomposed into surface runoff, interflow, and baseflow. The majority of losses of the applied herbicides occurred in surface runoff and interflow. The combined losses in surface runoff and interflow accounted for up to 75% of atrazine and 65% of metolachlor, of the total loss. Vast majority of the losses occurred within 70 days of the application and during a large storm event, shortly after herbicide application. Herbicide concentrations showed a steady disappearance with pseudo first-order half-lives 54 days for atrazine, and 50 days for metolachlor.

The depletion ratios determined from the transient runoff events, respectively, were 0.989, 0.943, and 0.939 for baseflow, interflow, and surface runoff. The high depletion ratios of the runoff components characterized slow withdrawal of water from the watershed storage. The slow withdrawal of water from the storage allowed time necessary for herbicide adsorption-desorption processes.

KEYWORDS

Atrazine; metolachlor; surface runoff; interflow; baseflow; organic carbon; hydrograph

INTRODUCTION

Whenever herbicides are used, a portion of the applied dose will reach the soil. An important aspect of subsequent behaviour is a) the length of time during which herbicide residues persist and remain active in the soil, and b) herbicide loss to surface and subsurface water. Herbicide loss is controlled by a complex of interactions among the herbicide, soil type, soil solutes and weather. Studies on field plots and watershed scales indicate that losses of herbicides are approximately 1-4%, depending on the soil types, tillage practice and slope of the fields (Hall, 1974; Glotfelty et al., 1984; Buttle, 1990). Furthermore, herbicide transport in surface runoff occurs within a critical period of 2-6 weeks after application and may be maximized when intense rain storms closely follow application (Wauchope, 1978; Weber et al., 1980; Glotfelty et al., 1984).

Although surface runoff is a dominant pathway for herbicide losses, some chemicals are also lost in subsurface flow. Information on subsurface flow provides threshold values required for on farm practice and water resource management issues such as ground water quality and streamflow quality. The subsurface tile flows combined with baseflow from the watershed are critical to the maintenance of aquatic life and the quality of the stream system. The present report describes the losses of atrazine and metolachlor in transient runoff components that comprise surface runoff, interflow and baseflow from an agricultural watershed. The overall objectives of this

work are to estimate the losses of atrazine (2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine) and metolachlor (2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy1-methylethyl)-acetamide) in each of the runoff components.

DESCRIPTION OF THE STUDY AREA

Land Use

The Nissouri Creek agricultural watershed, located in southwestern Ontario (Figure 1), contains 55 active farms (Ontario Ministry of Environment, 1989). The cultivation practices were both conventional and no-till procedures, and crops were rotated. The active farm area is planted in corn (> 50%), and in hay, soybeans, cereals, cash crops and fruits (30%). The remaining areas are forested, feed lots, country roads and residences. More than 90% of the cultivated area has a subsurface tile drainage system (Ontario Ministry of Environment, 1989).

The watershed area is about 3470 ha measured upstream from the hydrometric station (Figure 1) of the Water Survey of Canada (WSC).

The areas planted with corn and other crops, as determined by a questionnaire survey conducted in 1990, were 1470 ha and 850 ha, respectively. The area-weighted application rates of atrazine and metolachlor were respectively, 2.11 kg/ha and 2.48 kg/ha.

Soil Type

The most predominant soil types in the study area are Guelph loam (50%), Embro silt loam (36%) and Honeywood-Guelph complex (12%) (Ontario Ministry of Agriculture and Food, 1989) . Particle size distributions are in the range from 0.98 to 44.20 microns.

Physiographical Characteristics

The overland slopes of the area, ranging from 0.5 to 5%, represent 85% of the watershed. The remaining 10% and 5% of the land areas, respectively, have slopes greater than 5% and smaller than .5%. The soil organic carbon fraction is 2.66%.

The soil surface is stone free to slightly stony, and the surface soil reaction is neutral (Soil Map, Canada Department of Agriculture, 1987). The mean pH value calculated from the 1990 and 1991 runoff samples was 7.8 (range 7.0-8.8). The mean pH value of rainwater samples was 5.2 (range 4.3-6.1). Thus buffering capacity of the soils in the watershed is about 33%.

The hydraulic conductivity of the soil is 0.36 m/day and the mean water table depth is 1.1 m (Ontario Ministry of Environment, 1989).

Climate and Streamflow

The long-term meteorological records from the London and Woodstock meteorological stations, located approximately 10 km from the study area, were assumed to be representative for the Nissouri Creek watershed, due to their proximity and location in similar topography. The climate was characterized by the following annual mean values: air temperature = 7.3 °C, precipitation = 909 mm/yr, sunshine = 1896 hr/yr, relative humidity =

77%, wind speed = 16 km/hr all directions. The long term annual mean discharge of the Creek is 0.437 m³/s (Ontario Ministry of Environment, 1989). The maximum and minimum flows observed during the field seasons of 1990 and 1991 were 13.0 m³/s and 0.01 m³/s respectively. The average temperature of the Creek from April to December is 14.5 °C.

METHODS AND MATERIALS

Runoff Sampling and Streamflow Measurement

The runoff event samples were collected by an automatic sampler, the Sigma Model Series 702. The sampler is equipped with a water level sensor to activate the sampler when water level has risen to a referenced level during runoff event. The sensor was housed in a stilling well. The stilling well was used by the Water Survey of Canada to measure the stage and derive the discharge. In addition, the sampler was equipped with a programable device to control sampling modes and to purge the sample intake line to prevent cross-contamination between samples. The sampler collected up to 24 sequential samples. Because of seasonal variations in storm characteristics in summer (high intensity short duration of storm), spring and fall (moderate intensity, long duration of storm), runoff sample collection was set at a 15-minute interval for summer months and at a 30-minute interval for spring and fall. The runoff samples were collected in 350 ml glass bottles. Subsequently, the samples were consecutively composited into an hourly sample. Baseflow samples were also collected during dry periods or between rain events. All the runoff event samples were brought back from the field within 36 hours and stored at 4°C cold room until extraction was performed.

The streamflow was measured by a Stevens Leupold water level strip chart recorder which was operated by Water Survey of Canada.

Herbicide Extraction

The herbicide extractions in runoff samples were performed at the Provincial Pesticide Residue Testing Laboratory in Guelph, Ontario. One litre of unfiltered runoff sample was adjusted to a pH 9.0 with NH_4OH : H_2O (1 : 2.5) and extracted twice with 100 mL of chloroform ($CHCl_3$). The extract was dried with anhydrous Na_2SO_4, and evaporated to dryness (50-60°C). The residue was redissolved in 5 mL of methanol for gas chromatograph (GC) analysis. Recoveries of triazine and acetanilide herbicides from samples ranged from 92-98% at fortification level above .25 μg/L and 72-88% for residues below this level. The detection limit for the studied herbicides was 0.01 μg/L. Further details regarding the herbicide extraction can be found in Ramsteiner et al., 1974, and Frank et al., 1990.

RUNOFF AND HERBICIDE DATA ANALYSIS PROCEDURES

Event Runoff

During the field years of 1990 and 1991, there were 25 event runoff records and runoff samples collected at the WSC gauging station in the Nissouri Creek watershed (Figure 1). The records for both field years covered the periods from early spring to late fall. The streamflow event hydrographs were plotted in Figure 2. The runoff event samples were analysed for concentrations of atrazine and metolachlor.

Hydrograph Separation Techniques

Precipitation entering a watershed travels to a stream by three main pathways: surface runoff, interflow (or subsurface storm flow), and groundwater flow (or baseflow). The amount of water contributed to the stream by each of the three processes is reflected in the shape of the stream hydrographs (Figure 2). The hydrograph for a single or multiple, short duration precipitation events, occuring over the entire watershed, shows a period of rising limb, or increasing discharge, that culminates in a peak. Following the peak discharge, the hydrograph shows a period of decreasing discharge, referred to as the falling limb.

Hydrograph separation begins with the baseflow. Several techniques have been proposed for separating baseflow and direct runoff. They are (a) the straight line method, (b) fixed base length method, and (c) the variable slope method. Detailed discussion of these methods can be found in Chow, 1964, and Starosolszky, 1987. The straight line method was used in this study. The separation of baseflow from the combined runoff for each of the 25 runoff event hydrographs is shown graphically in Figure 2. The residues ordinates above the baseflow (dash line) represent the combined surface runoff and interflow. This combined hydrograph is replotted on semilogarithmic scale and a straight line was fitted to the interflow recession CD (details are given under Recession Curves and Recession Constants of Runoff Components) as shown in the example (Figure 3a, Event #10, November 11, 1990). The separation of the interflow from the combined runoff for the rest of the events was not shown, because this was deemed to be unnecessary. Further discussions on hydrograph separation techniques are given in the Results and Discussion.

Determination of Volume of Runoff Components

The partitioned streamflow hydrographs with time base length facilitate estimation of volumes of baseflow, interflow, and surface runoff. There are two ways to estimate the volume of each of the runoff components. The first way is by means of trapezoidal approximation:

$$V = \sum_{n=1}^{n} \{(q_n + q_{n+1})/2\}*(t_{n+1} - t_n) \qquad (1)$$

where V is the volume in m^3, q_n and q_{n+1} are successive discharges (m^3/s) at respective times (seconds) t_n and t_{n+1}.

The second way is to measure the area between curves of the hydrograph under consideration by a planimeter. The planimetered areas are then converted into volume. This method was employed here, because of its ease-of-use.

Herbicide Mean Concentration

Mean concentrations of atrazine and metolachlor were calculated for each runoff event by using the following expression:

$$C_j = \sum_{i=1}^{m} C_i V_i /V \qquad (2)$$

where C_j is the volume-weighted concentration for a runoff event, C_i is the concentration in i-th sample, V_i is the flow volume during the periods from $(t_{i-1} + t_i)/2$ to $(t_i + t_{i+1})/2$, t is the time of sampling measured from

the onset of sampling, m is the total number of samples and V is the sum of V_i's. If the concentration of the sample falls below the detection limit, the concentration of that sample is assumed to equal the detection limit (0.01 μg/L) for the purpose of computational stability.

The losses of atrazine and metolachlor were calculated by using the C_j times the volume. The following expression was applied to calculate the losses of atrazine and metolachlor for surface runoff, interflow, and baseflow.

$$L_j = C_j \, V_{j,k} \tag{3}$$

where L_j is the losses (mg) for herbicides in the j-th event, $V_{j,k}$ is the volume designated by k, as surface runoff, interflow, or baseflow of the j runoff event, and C_j was defined earlier.

RESULTS AND DISCUSSION

The antecedent days, rainfall depth, volumes of surface runoff, interflow, baseflow, concentrations and losses of atrazine and metolachlor are presented in Table 1.

Limitations of Hydrograph Separation Techniques

Theoretically, it should be straightforward to separate the recession limb of a streamflow hydrograph into three segments of different slopes from which the quantity of water contributed to the stream by surface runoff, interflow, and the baseflow can be determined. In practice, separating the recession limb of a stream hydrograph into three segments of different slope is a somewhat arbitrary process (Hall, 1968; Nutbrown and Downing, 1976; Anderson and Burt, 1980; Starosolszky, 1987). Often no clear-cut change in slope exists. Given that precipitation events are not often of constant intensity or evenly distributed, and considering the heterogeneity of a typical watershed, this is not surprising. Additionally, the effects of bank storage and the subsurface tile drainage (typical to southern Ontario grain crop production areas) will make separation difficult. The accuracy of the techniques also has been questioned by several authors. Sklash and Farvolden (1979) reported that ground water plays a much more active, responsive and significant role in the generation of storm and snow-melt runoff in streams than hydrograph separations may predict. Although numerous solutions have been sought on hydrograph separation (Pilgrim et al., 1979, Sklash, 1990), the current state of the art of hydrograph separation still poses many methodical questions. Therefore, if the purpose of the application of hydrograph separation techniques is to establish means of predicting the basin as a whole for forecasting, design or management tool, an extremely refined hydrograph separation may be unnecessary, since any water omitted from one component is also included in the others.

Statistical Inference of Losses of Atrazine and Metolachlor in the Runoff Components

The normal and lognormal distributions of the event means of losses of atrazine and metolachlor were computed for each of the runoff components in Nissouri Creek for 1990 & 1991, and are presented in Table 2. The variability of a distribution of the losses of atrazine and metolachlor is described by its standard deviations (Table 2). The standard deviations of the losses of atrazine and metolachlor are from one to more than three times greater than the mean, with the sample being positively skewed (left skewed, mean > median), for both years. Both the losses of atrazine and metolachlor in the event runoff components were better described by the lognormal distributions (median closes to the mean) than the normal distributions (Table 2). The lognormal distribution is a normal distribution of the logarithms of the data. Thus, the logarithmic transformation of the data implies that the observed losses of atrazine and metolachlor in the runoff components can vary significantly

from one event to the other. The variations of losses of the herbicides in the runoff components are mainly influenced by the magnitude of the rainfall and the time of occurence of the rain. As shown in Table 1, 57.2 mm of rainfall occurred on July 9 and produced a loss of 7534 mg of atrazine and a loss of 2972 mg of metolachlor. Similarly, a loss of 6374 mg of atrazine and a loss of 8005 mg of metolachlor to a rainfall of 33.3 mm occurred on May 25, 1991. It is noted that this event occurred soon after the herbicide application. Similar results were reported by Leonard, et al., (1979).

The variations of losses of atrazine and metolachlor are also influenced by many factors including pesticide properties, application rates and methods, soil characteristics, crop management, tillage (Isensee and Sadeghi, 1995), antecedent precipitation and the partition of the pesticide into dissolved and adsorbed components. Dissolved and solid-phase pesticide concentrations in runoff are related to comparable concentrations in surface soil during a storm. The latter are determined by the proximity of the storm to the application date.

Recession Curves and Recession Constants of Runoff Components

Within the context of a systematic study of the watershed, it is desirable to characterize the interflow, baseflow, and surface runoff by a flow depletion constant. The flow depletion constant reflects the catchment processes which is represented by the stream discharge and recharge.

To derive the flow depletion constant for each of the runoff components, all the 25 runoff hydrographs were utilized to produce a synthesized master recession curve. A traditional matching strip method (Hall, 1968; Starosolszky, 1987; Nathan and McMahon, 1990) was used to synthesize the master recession curve. This method involved plotting individual recessions on transparent paper in semilogarithmic scale, the recessions are then superimposed and adjusted horizontally until the main recessions overlap to form a set of common lines. The master recession curve combined from the 25 hydrographs is shown in Figure 3b.

Once the master recession curve (Figure 3b,(XB)) is defined, the baseflow can be approximated by a straight line (Chow, 1964; Starosolszky, 1987), extended back under the hydrograph to point A, which is arbitrarily located directly below the point of inflection X on the hydrograph. The points H and A are connected arbitrarily by a straight line. The areas under the curve HXB and above the curve HAB are considered to represent the combined surface runoff and the interflow. This combined surface runoff and interflow is replotted and a straight line CD can be fitted to the recession curve below the point of inflection Y of the YD curve. A straight line is connected between C and I. Thus, the curve ICD divides the replotted hydrograph into surface runoff above the ICD, and the interflow below the ICD. The surface runoff is replotted. A straight line EF is extended back below the point of Z and a straight line is connected to J, for the purpose to determine the recession constant of the surface runoff. Further separation of the surface runoff curve is possible, but produces no useful information.

The interflow itself may consist of a number of components, each representing the discharge-time function for a particular layer of soil and the subsurface tile drain. Further separation of the interflow components (e.g bank storage, and mixtures of soil type in the vadose zone) would be difficult. Thus no attempt was made to separate the interflow components.

All three curves XB, YD, and ZF, shown in Figure 3b, represent withdrawal of water from storage with no further inflow. It is often possible to represent such curves by means of exponential equations (Hall, 1968; Starosolszky, 1987) of the type :

$$q_t = q_0 \, K_r^{\,t} \qquad\qquad\qquad (4)$$

where q_t is discharge at time t, q_0 is discharge at time 0, and K_r is a constant known as the depletion ratio.

The depletion ratio, K_r, depends on the time units, t, in which it is expressed. In this study, it is referred to as the hourly depletion ratio. The different values of depletion ratio are represented by different storage characteristics for the particular catchment applicable to baseflow, interflow, and surface runoff. The depletion ratio, determined for the baseflow is 0.989, for interflow is 0.943, and for surface runoff is 0.939. These values are higher than the values reported by Klaasen and Pilgrim (1975). The range of daily recession constants found in Klaasen and Pilgrim (1975) are 0.93-0.995 for baseflow, 0.7-0.94 for interflow, and 0.2-0.8 for surface runoff.

The difference of the depletion ratios between the baseflow and the interflow is 4.7%, and between baseflow and the surface runoff is 5.1%. The small difference of the depletion ratios of surface runoff and interflow may suggest that the soil of the watershed is very well drained. Water supply to the surface soil is rapidly transmitted to the subsurface zone. Combined with the subsurface tile drain, the water removed from the subsurface zone re-emerged back to the stream. Thus, this may reflect the greater losses of the atrazine and metolachlor during large runoff event.

Dissipation Rate of Atrazine and Metolachlor

The concentrations of the studied herbicides declined during the growing season after they attained the probable maximum (Table 1) for both years. Similar results were reported by Pantone et al., (1992); Isensee and Sadeghi, (1995). The concentrations of the two studied herbicides also exhibited similar characteristics in time regardless of their application rates. The dissipation follows the first-order rate function (Triplett et al., 1978; Walker, 1987; Pantone et al., 1992) as shown below:

$$C = a \, e^{bt} \tag{5}$$

where C is the herbicide concentration, in $\mu g/L$, a is an intercept, b is the slope and t is time in days. To estimate the values of a and b, the mean concentrations of the herbicides listed under column V-mean (Table 1), in time sequence, were utilized for determination of a and b by a linear regression method. In order to maximize the value of the intercept, a procedure was used to eliminate some of the smaller values at the beginning of the data series as well as those with concentrations below the detection limit. As a result, the event concentrations of 1.03, 0.60 and 0.59 $\mu g/L$ corresponding to ID #1 to #3 of atrazine of 1990 data series, and event concentrations of 0.32 and 0.39 $\mu g/L$ corresponding to ID #1 and ID #2 of atrazine of 1991 data series, were not entered into the regressional analysis.

Event concentrations of <0.01 $\mu g/L$ of metolachlor for both 1990 and 1991 data series were dropped from regressional analysis. These included the first two events of ID #1 and ID #2 of 1990 and 1991 data series (Table 1).

Characterization of the Losses of Atrazine and Metolachlor in the Watershed

The event mean concentrations of the studied two herbicides varied from one year to another (Table 1). The herbicides also showed declination during the growing season. To characterize the transitions of the herbicide transport in steady state, the event mean concentrations of the 1990 and 1991 data series were further reduced into one data series for each of the studied herbicides, by means of averaging. The procedures of averaging were based on the match of the normalized time scales on the x-axis. The match of the normalized time scales was done by plotting the event mean concentrations of the herbicide corresponding to its normalized time values on a graph, for example, the event mean concentrations of atrazine of 1990 and 1991 were plotted against its normalized time scales (days from the first event divided by number of days of last event (Table 1)) on a graph.

The same procedures were repeated for metolachlor as applied for atrazine. Finally, the corresponding values of the event mean concentrations of the herbicide of 1990 and 1991, for a given time scale, can be obtained directly from the graph of common time scale. The sum of the two values taken from 1990 and 1991 curves was divided by 2. The combined 1990 and 1991 data series of atrazine and metolachlor were regressed and plotted in Figure 4.

The dissipation rates of atrazine and metolachlor depicted in Figure 4 represent all three runoff components derived for the watershed. It follows that half-life for atrazine is 54 days and for metolachlor is 50 days. The atrazine has longer half-life than metolachlor. The longer half-life of atrazine reflects its slower dissipation rate. The dissipation rate is related to the sorption coefficient, K_D, by the following relationships:

$$K_{oc} = K_D / f_{oc} \tag{6}$$

where K_{oc} (mL/g) is the organic carbon partitioning coefficient, and f_{oc}(%) is the organic carbon soil fraction. Thus, if the measured organic carbon soil fraction f_{oc} = 2.66%, the K_{oc} for atrazine is 150 mL/g (Laskowski et al., 1982) and K_{oc} for metolachlor is 1140 mL/g (Karickhoff, 1981; Hassett et al., 1983), the K_D may be evaluated for the whole watershed as

K_D (atrazine)   = 150 x 0.0266 = 3.99 mL/g

K_D (metolachlor) =1140 x 0.0266 = 30.32 mL/g

The greater K_D may influence the dissipation rate of metolachlor ($t_{1/2}$ = 50 days) as compared to the dissipation rate of atrazine ($t_{1/2}$ = 54 days) .

CONCLUSION

The bulk of the atrazine and metolachlor losses through surface runoff and interflow occurred mostly within 70 days, or during the first large storm event, after herbicide application.

The depletion ratios, determined for the baseflow, interflow and surface runoff are respectively, 0.989, 0.943, and 0.939. The differences between the baseflow and interflow (4.7%) and between the baseflow and surface runoff (5.1%), are very small. The small difference of the depletion ratio between runoff components implies that the soils of the watershed have good moisture holding capacity. Thus it prolonged the withdrawal of water from the watershed storage and subsequently allowed the time necessary for herbicide adsorption-desorption processes.

The loss of atrazine in the combined surface runoff and interflow accounted for up to 75% (Table 3), whereas the loss of metolachlor in the combined surface runoff and interflow accounted for about 65% (Table 3), of the total loss.

ACKNOWLEDGEMENTS

REFERENCES

Anderson, M.G. and Burt, T.P. (1980). Interpretation of recession flow. *J. Hydro.*, **46**: 89-101.

Buttle, J.M. (1990). Metolachlor transport in surface runoff. *J. Environ. Qual.* **19**: 531-538.

Canada Department of Agriculture. (1987). Soil Survey by Ontario Agricultural College. Guelph and Environmental Farm Services, Reprinted 1987.

Chow , V.T. (1964). Handbook of Applied Hydrology. McGraw-Hill Book Company, New York.

Glotfelty, D.E., Taylor, A.W., Isensee, A.R., Jersey, J. and Glenn, S. (1983). Atrazine and simazine movement to Wye River Estuary. *J. Environ. Qual.* **13**: 115-121.

Frank, R., Clegg, B.S., Sherman, C. and Chapman, N.D. 1990. Triazine and chloroacetamide herbicides in Sydenham River Water and Municipal Drinking Water, Dresden, Ontario, Canada 1981-1987. *Arch. Environ. Contam. Toxicol.* **19**: 319-324.

Hall, F.R. (1968). Base-flow recessions - A review. *Water Resour. Res.* 4(5): 973-983.

Hall, J.K. (1974). Erosional losses of S-triazine herbicides. *J. Environ. Qual.* **3**: 174-180.

Hassett, J.J., Banwart, W.L. and Griffin, R.A. (1983). Correlation of compound properties with sorption characteristics on nonpolar compounds by soils and sediments: Concepts and Limitation. p. 161-178 in C.W. Francis and S.I. Auerbach, eds. Environment and Soild Wastes: Characterization, Treatment, Disposal. Butterworth, Woburn, MA.

Isensee, A.R., Sadeghi, A.M. (1995). Long-term effect of tillage and rainfall on herbicide leaching to shallow groundwater. *Chemosphere.* 30(4): 671-685.

Klaasen, B. and Pilgrim, D.H. (1975). Hydrograph recession constants for New South Wales streams. Inst. Eng. Civ. Trans. CE17: 43-49.

Karickhoff, S. (1981). Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils. *Chemosphere* 10: 833-846.

Laskowski, D.A., Goring, C.A.I., McCall, P.J. and Swann, R.L. (1982). Terrestrial environment. In Environmental Risk Analysis for Chemicals, ed. R.A. Conway, Van Nostrand Reinhol Co., New York, 558p .

Leonard, R.A., Langdale, G.W. and Fleming, W.G. (1979). Herbicide runoff from Upland Piedmont Watersheds - data and implications for modeling of pesticide transport. *J. Environ. Qual.* **8**: 223-229.

Nathan, R.J. and McMahon, T.A. (1990). Evaluation of automated techniques for base flow and recession analyses. *Water Resour. Res.* **26** (7): 1465-1473.

Nutbrown, D.A. and Downing, R.A. (1976). Normal-mode analysis of the structure of baseflow-recession curves, *J. Hydrol.* **30**: 327-340.

Ontario Ministry of Agriculture and Food, (1989). The soil survey of Oxford County. Report No. 28 of the Ontario Soil Survey.

Ontario Ministry of Environment, (1989). Modelling of the loss of phosphorus in a southern Ontario agricultural watershed. A report prepared by Beak Consultants Limited for Ontario Ministry of Environment.

Pantone, D.J., Young, R.A., Buhler, D.D., Eberlein, C.V., Koskinen W.C. and Forcella, F. (1992). Water quality impacts associated with pre-and postemergency application of atrazine in maize. *J. Environ. Qual.* **21**: 267-273.

Pilgrim, D.H., Huff, D.D. and Steele, T.D. (1979). Use of specific conductance and contact time relations for separating flow components in storm runoff. *Water Resour. Res.* 15(2): 329-339.

Ramsteiner K., Hormann W.D. and Eberle D.O. (1974). Multi-residue method for determination of triazine herbicides in field grown agricultural crops, water and soil. *J. Assoc. Offic anal Chem.* 57: 192-201.

Starosolszky, Ö. (1987). Applied Surface Hydrology. Water Resources Publications, P. O. Box 2841, Littleton, Colorado 80161, U.S.A.

Sklash, M.G. and Farvolden, R.N. (1979). The role of groundwater in storm runoff. *J. Hydro.* 43: 45-65.

Sklash, M.G. (1990). Environmental isotope studies of storm and snow-melt runoff generation. In: M.G.

Anderson and T.P. Burt (editors), Process Studies in Hillslope Hydrology. Wiley, Chichester, 401-435.

Triplett, G.B., Conner, B.J. and Edwards, W.M. (1978). Transport of atrazine and simazine in runoff from conventional and no-tillage corn. *J. Environ. Qual.* 7(1): 77-84.

Wauchope, C. W. (1978). The pesticide content of surface water draining from agricultural field - A review. *J. Environ. Qual.* 7(4): 459-472.

Walker, A. (1987). Herbicide persistence in soil. *Rev. Weed Sci.* 3: 1-17.

Weber, J.B., Shea, P.J. and Strek, H.J. (1980). An evaluation of nonpoint sources of pesticide pollution in runoff. p. 69-98. In M.R. Overcash and J. M. Davidson (ed.) Environmental impact of nonpoint source pollution. Ann Arbor Science Publishers, Ann Arbor. MI.
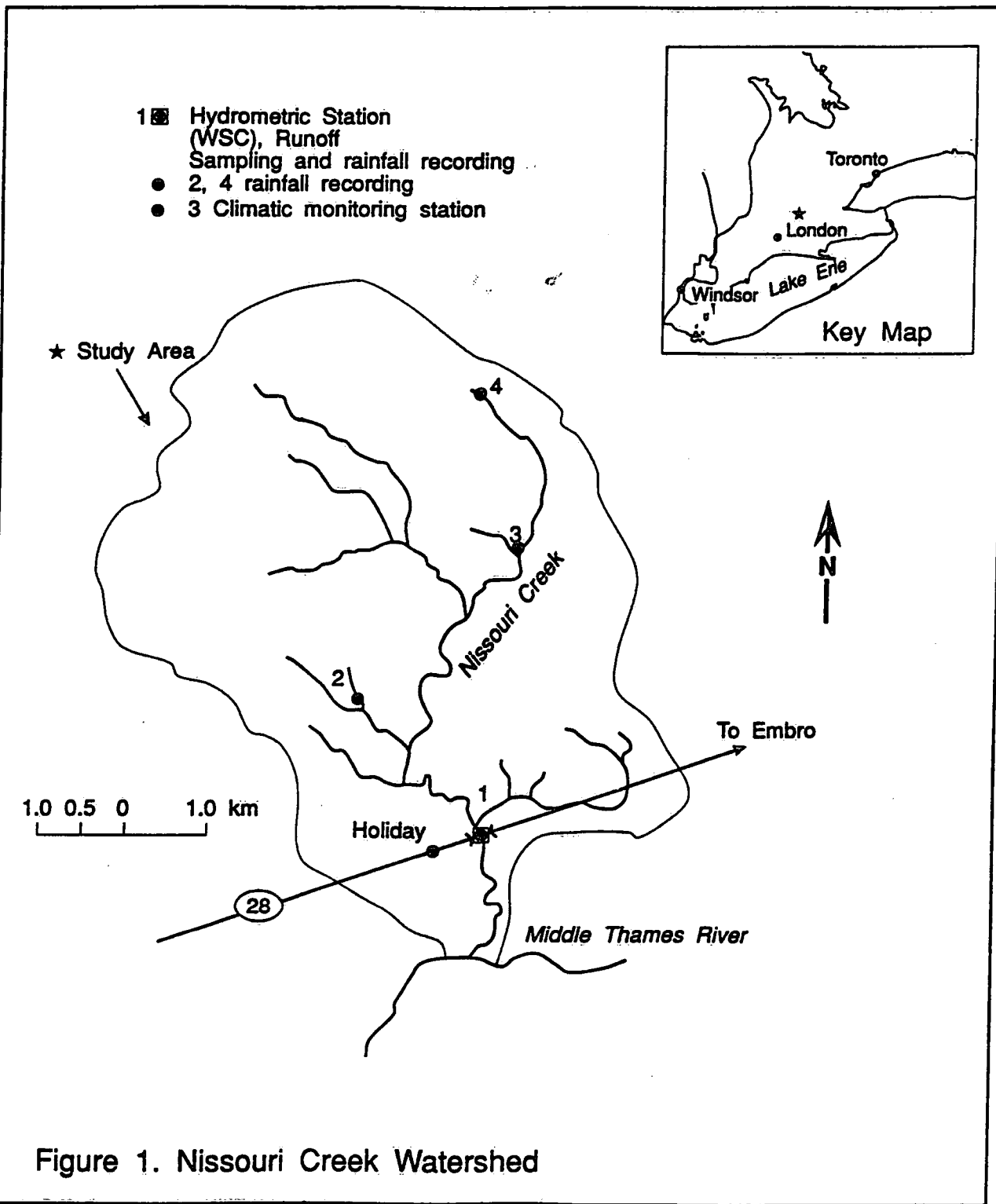
Figure 1. Nissouri Creek Watershed
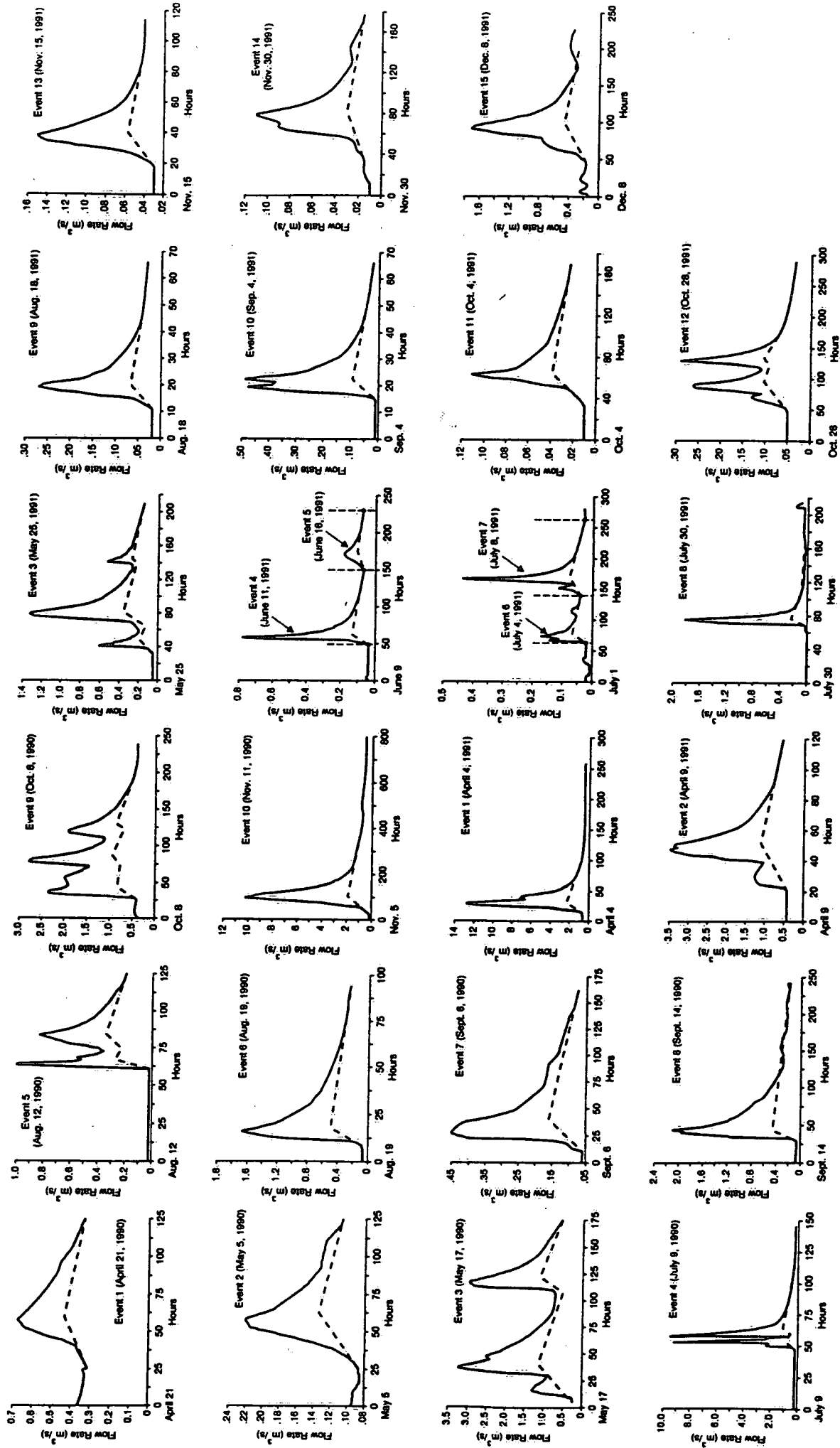
Figure 2. Hydrographs of Runoff Events from Nissouri Creek Watershed.
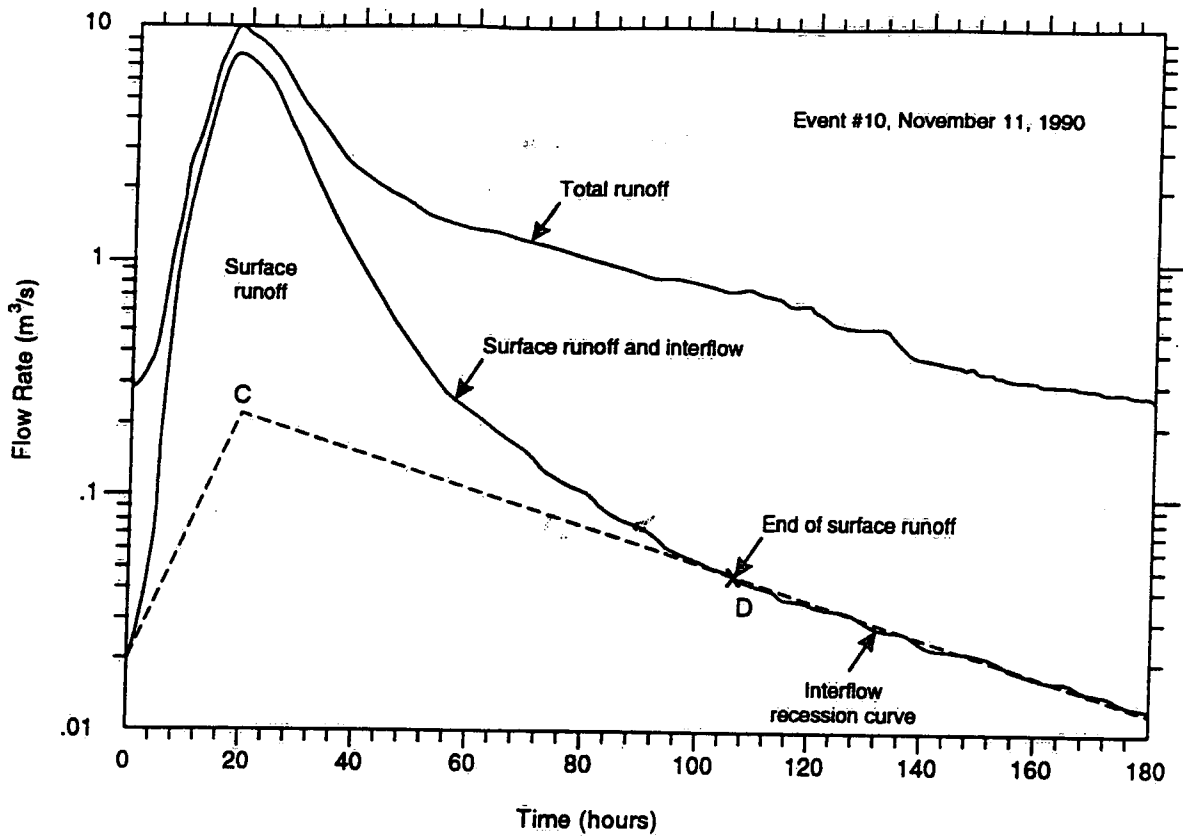
Figure 3a. Separation of Interflow from Combined Surface runoff and Interflow
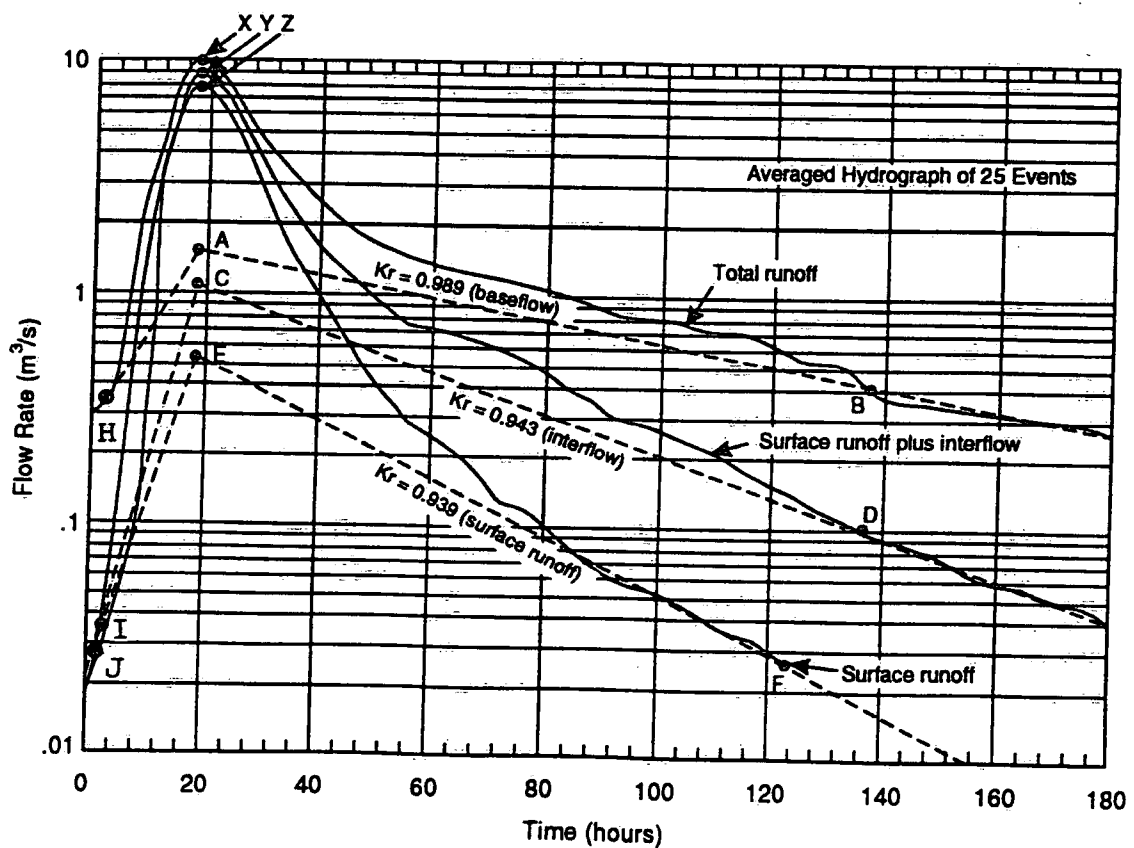
Figure 3b. Separation of Hydrograph Components.

Figure 4. Dissipation rates of atrazine and metolachlor in runoff events for 1990 and 1991 combined.

○ ----- atrazine

■ ———— metolachlor

Equation for regression:

ln C = ln a + bt, where C is

concentration, a is intercept,
b is slope and t is time in days

	a	b	γ
atrazine	16.78	-0.013	0.773
metolachlor	23.82	-0.014	0.804

Concentration (μg/L)

Normalized time (by 236 days)

Table 1. Antecedent days, Rainfall depth, Volume of runoff components, Concentrations and Loadings of Atrazine and Metolachlor

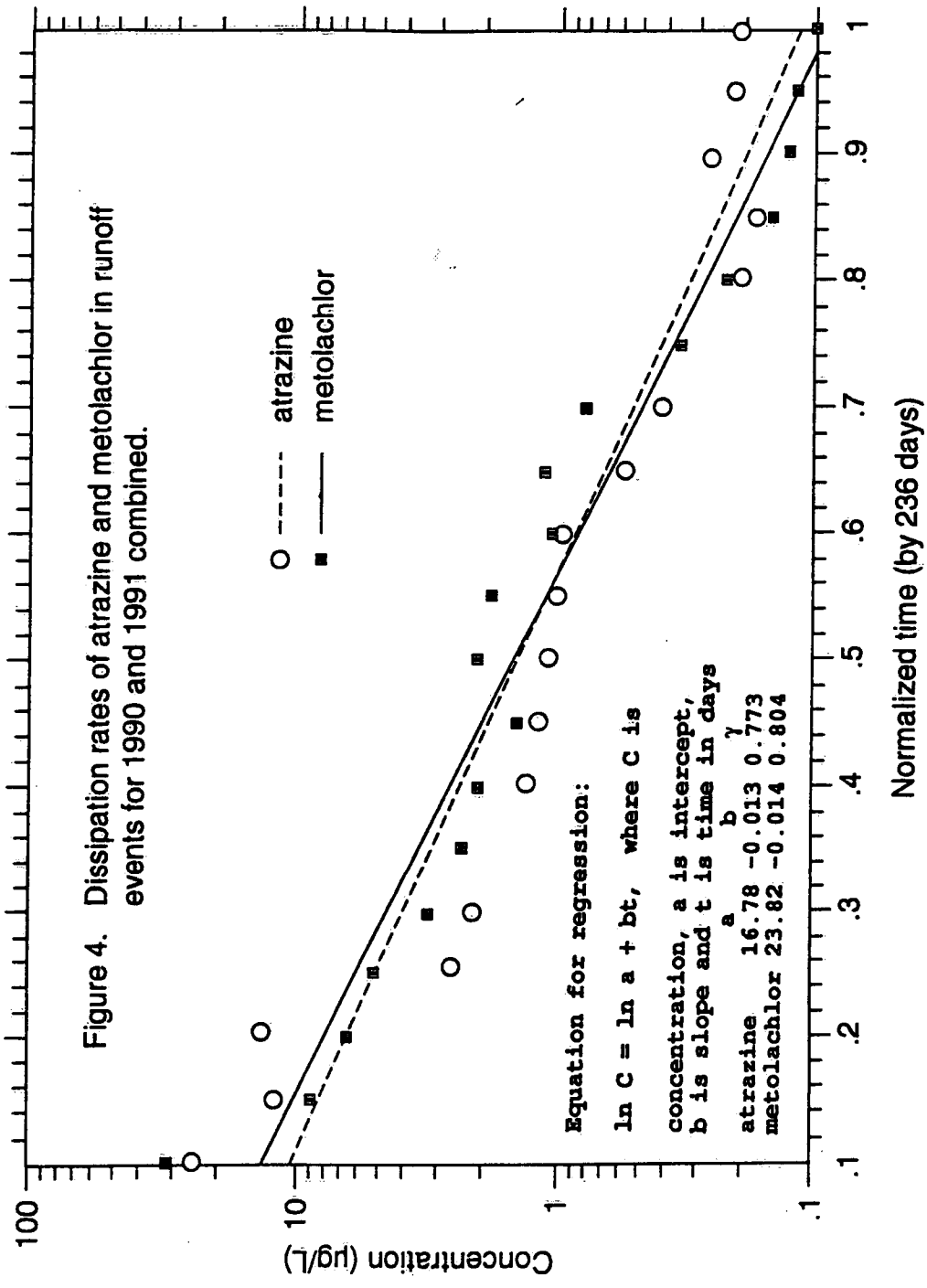| ID	1990 dd/m	Day from 1st. event (days)	Antecedent (days)	Rainfall (mm)	Runoff volume x 10^3 m^3 Total Q	Intfw. q1	Basefw. q2	Surfc. q3	Atrazine Concentr. (ug/L) V-mean	Range	loadings (mg) q1	q2	q3	Metolachlor Concentr. (ug/L) V-mean	Range	loadings (mg) q1	q2	q3
1	21/04	1	2	13.1	167	30	105	32	1.03	1.0-1.2	30.9	108.2	33.0	<.01	<.01	3.0	10.5	3.2
2	05/05	15	12	10.3	35	10	9	16	0.6	0.51-0.59	6.0	5.4	9.6	<.01	<.01	1.0	0.9	1.6
3	17/05	27	2	21.6	511	142	342	27	0.59	1.00-21.0	83.8	201.8	15.9	8.74	0.67-13.0	1241.1	2989.1	236.0
4	09/07	66	8	57.2	614	133	142	338	12.29	12.00-18.	1634.8	1745.2	4154.0	4.84	4.10-6.10	643.7	687.3	1640.8
5	12/08	100	4	32.5	155	34	8	113	13.94	1.60-2.50	474.0	115.5	1575.2	2.98	0.68-5.10	101.3	23.8	336.7
6	19/08	107	4	31.1	186	59	22	105	2.13	0.45-2.60	125.7	46.9	223.7	1.96	<.01-2.10	115.6	43.1	205.8
7	06/09	126	5	16.7	82	29	10	42	2.27	0.50-2.00	65.8	22.7	95.3	1.38	<.01-1.90	40.0	13.8	59.3
8	14/09	134	6	33.9	407	136	21	250	1.18	0.72-1.60	160.5	24.8	295.0	1.75	<.01-2.20	238.0	36.8	437.5
9	09/10	159	2	24.8	931	227	377	327	1.11	0.88-1.80	252.0	418.5	363.0	<.01	<.01	2.3	3.8	3.3
10	05/11	186	7	51.5	1286	495	229	562	1.38	0.94-1.40	683.1	316.0	775.6	<.01	<.01	5.0	2.3	5.6
	1991																	
1	06/04	1	5	7.9	1133	238	277	618	0.32	0.27-0.39	76.2	88.6	197.8	<.01	<.01	2.4	2.8	6.2
2	09/04	3	1	15.2	521	68	171	282	0.39	0.31-0.53	26.5	66.7	110.0	<.01	<.01	0.7	1.7	2.8
3	25/05	43	6	33.3	256	74	73	109	24.9	0.94-40.0	1842.6	1817.7	2714.1	31.27	29.0-54.0	2314.0	2282.7	3408.4
4	11/06	46	10	28.4	69	32	23	14	2.5	0.57-4.00	80.0	57.5	35.0	6.37	0.1-11.0	203.8	146.5	89.2
5	18/06	53	3	41.4	33	7	20	6	1.02	1.00-1.10	7.1	20.4	6.1	2.26	1.10-1.30	15.8	45.2	13.6
6	04/07	69	2	31.8	19	8	9	2	0.41	0.43-0.60	3.3	3.7	0.8	1.03	0.38-1.10	8.2	9.3	2.1
7	08/07	73	2	30.0	68	17	14	37	1.00	0.30-1.40	17.0	14.0	37.0	1.95	1.52-2.22	33.2	27.3	72.2
8	30/07	95	5	64.0	79	43	25	11	0.35	0.22-0.70	15.1	8.8	3.9	1.1	1.09-2.22	47.3	27.5	12.1
9	18/08	114	10	26.2	15	4	5	6	0.25	0.10-0.25	1.0	1.3	1.5	<.01	<.01	0.0	0.1	0.1
10	04/09	131	14	42.7	23	7	5	11	0.56	0.34-0.69	3.9	2.8	6.2	0.78	0.15-1.05	5.5	3.9	8.6
11	04/10	161	9	18.8	16	6	5	5	0.21	<.01-0.21	1.3	1.1	1.1	0.33	<.01-0.33	2.0	1.7	1.7
12	28/10	185	3	29.7	77	17	39	21	0.18	<.01-0.18	3.1	8.2	4.4	0.1	<.01-0.10	1.7	3.9	2.1
13	15/11	213	8	15.0	16	4	5	7	0.28	<.01-0.34	1.1	1.4	2.0	<.01	<.01	0.0	0.1	0.1
14	30/11	228	1	27.9	228	59	74	94	0.22	<.01-0.25	13.0	16.3	20.7	<.01	<.01	0.6	0.7	1.0
15	08/12	236	2	19.1	345	104	84	157	0.21	<.01-0.25	21.8	17.6	33.0	<.01	<.01	1.0	0.8	1.6

Q = combined runoff, Intfw. = Interflow, Basefw. = baseflow, Surfc. = surface runoff.

q1, q2, and q3 refer to, respectively, Interflow, baseflow and surface runoff.

V-mean = volume weighted mean concentration, Concentn. = concentration.

< = below detection limit and assumed to be = 0.01 ug/L for the purpose of calculating the runoff loadings.

Table 2. Descriptive statistics of volumes of interflow, baseflow and surface runoff, and mean losses of atrazine and metolachlor in each of the runoff components.

1990 - 10 events	1000 x m**3			Atrazine (mg)			Metolachlor (mg)		
Normal dist.	q1	q2	q3	q1	q2	q3	q1	q2	q3
Event mean	130	127	181	351	301	754	239	381	293
Std. deviation	146	142	182	499	526	1222	404	940	499
Std. error	46	45	58	158	166	407	128	297	158
Median	96	64	109	143	112	259	71	19	133
Skewness	2.00	0.93	1.09	2.25	2.79	2.48	2.13	2.90	2.62
Lognormal dist.									
Event mean	1.87	1.72	2.00	2.15	1.99	2.28	1.55	1.40	1.68
Std. deviation	0.51	0.68	0.54	0.70	0.73	0.86	1.09	1.08	1.09
Std. error	0.16	0.22	0.17	0.22	0.23	0.27	0.35	0.34	0.34
Median	1.95	1.68	2.04	2.16	2.05	2.41	1.81	1.26	2.04
Skewness	-0.10	0.05	-0.10	-0.47	-0.05	-0.09	-0.07	0.80	-0.18
1991 - 15 events Normal dist.									
Event mean	46	55	92	141	142	212	202	170	242
Std. deviation	62	76	165	471	464	694	697	585	877
Std. error	16	20	43	122	120	179	180	151	226
Median	17	23	14	13	14	6.2	2.4	3.9	2.8
Skewness	2.43	2.17	2.69	3.85	3.85	3.83	3.84	3.85	3.89
Lognormal dist.									
Event mean	1.34	1.39	1.40	1.06	1.13	1.13	0.55	0.72	0.72
Std. deviation	0.57	0.58	0.73	0.86	0.85	0.97	1.42	1.17	1.15
Std. error	0.15	0.15	0.19	0.22	0.22	0.25	0.37	0.30	0.30
Median	1.23	1.36	1.15	1.10	1.15	0.79	0.38	0.59	0.45
Skewness	0.25	0.29	0.50	1.09	0.95	0.89	-0.11	0.58	0.80

q1 = interflow, q2 = baseflow, q3 = surface runoff.
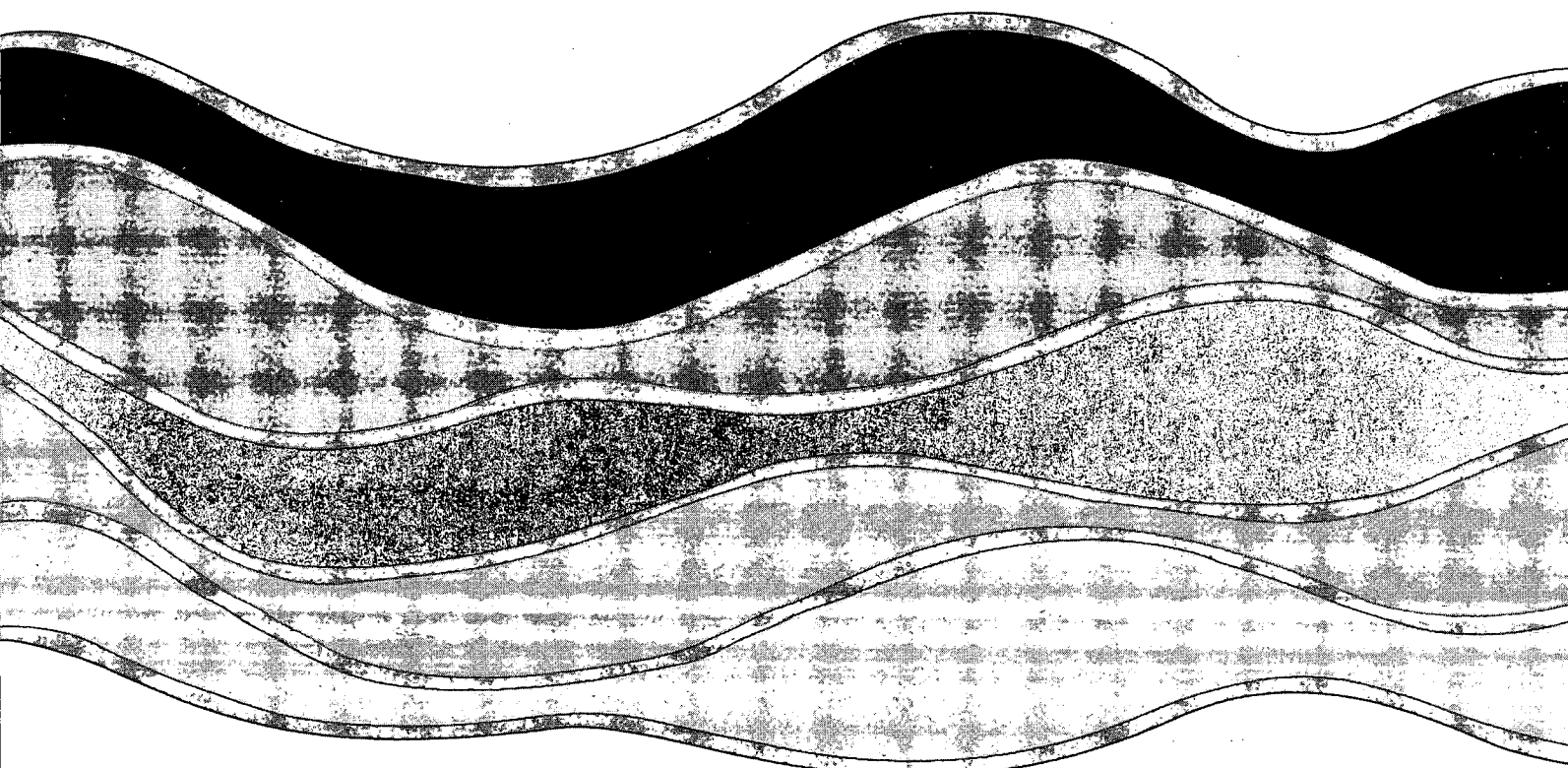
Std. = standard, dev. = deviation.

dist. = distribution.

Note: Values of skewness are dimensionless.

Table 3. The losses of atrazine and metolachlor in transient runoff components

Year	sum of event volume	atrazine				metolachlor			
		total (mg)	q1	q2	q3	total (mg)	q1	q2	q3
			percent of total				percent of total		
1990	4370	14061	25	21	54	9132	26	41	32
1991	2898	7412	29	29	42	8812	30	29	41

q1 = interflow, q2 = baseflow, q3 = surface runoff.

sum of event volume x 1000 m**3.