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AGRICULTURAL SOURCES IMPACTING ON STREAM WATER QUALITY: INVESTIGATIONS AND CHARACTERIZATIONS

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NWRI CONTRIBUTION NO. 96-166

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ABSTRACT

Fifteen runoff events were monitored in each of the 1991 and 1992 field years and twenty-five sample collection periods of baseflow from an agricultural watershed were realized in 1992. The runoff events monitored in 1991 were assessed for losses of atrazine and metolachlor in runoff. The runoff events monitored and baseflow samples collected in 1992 were assessed for losses of phosphorus, ammonia, nitrate, nitrite, and potassium in event flow and baseflow. Majority of the losses of atrazine and metolachlor occurred within 48 days after application and most of the losses were associated with surface runoff during event flow. The losses of atrazine and metolachlor in surface runoff were, respectively,1522 mg/ha and 1800 mg/ha. The cumulative losses of phosphorus, ammonia, nitrate, nitrite and potassium in baseflow were substantially higher than in event flow. The fractions of losses of nutrients in baseflow ranged from 83% of ammonia to 94% of phosphorus with respect to its combined event flow and baseflow. The losses of phosphorus, ammonia, nitrate, nitrite and potassium in event flow, were respectively 0.217, 0.443, 4.364, 0.028 and 4.331 kg/ha. Similarly, the cumulative losses of phosphorus, ammonia, nitrate, nitrite, and potassium in baseflow, were respectively 3.557, 2.214, 32.433, 0.247 and 33.151 kg/ha.

RÉSUMÉ

Quinze épisodes de ruissellement ont fait l'objet de mesures pendant les campagnes 1991 et 1992 sur le terrain, et on a procédé en 1992 à des périodes de collecte de 25 échantillons de l'écoulement (débit) de base produit par un bassin hydrographique agricole. Les épisodes de ruissellement ayant fait l'objet d'échantillonnages en 1991 ont été évalués pour déterminer les pertes d'atrazine et de métolachlore dans les eaux de ruissellement. Les épisodes de ruissellement et les échantillons d'écoulement de base examinés en 1992 ont été évalués pour déterminer les pertes de phosphore, d'ammoniac, de nitrate, de nitrite et de potassium lors d'un épisode de ruissellement et dans le cas du débit de base. La majeure partie des pertes d'atrazine et de métolachlore se sont produites moins de 48 jours après l'application, et la plupart des pertes étaient attribuables au ruissellement de surface pendant l'épisode. Les pertes d'atrazine et de métolachlore dans le ruissellement de surface étaient respectivement de 1 522 et 1 800 mg/ha. Les pertes cumulatives de phosphore, d'ammoniac, de nitrate, de nitrite et de potassium correspondant au débit de base étaient sensiblement plus élevées que lors d'un épisode. Les pertes de nutriments variaient de 83 % d'ammoniac pour le débit de base à 94 % de phosphore pour le débit épisodique et celui de base combinés. Les pertes de phosphore, d'ammoniac, de nitrate, de nitrite et de potassium dans le cas d'un débit épisodique étaient respectivement de 0,217, 0,443, 4,364, 0,028 et 4,331 kg/ha. De même, les pertes cumulatives de phosphore, d'ammoniac, de nitrate, de nitrite et de potassium correspondant au débit de base étaient respectivement de 3,557, 2,214, 32,433, 0,247 et 33,151 kg/ha.

MANAGEMENT PERSPECTIVE

This report presents the results of evaluation of the magnitudes of losses of five nutrients (phosphorus, ammonia, nitrate, nitrite, and potassium), and two herbicides (atrazine and metolachlor) from an agricultural watershed during the runoff event flow and baseflow. The study identified that the losses of nutrients were substantially higher (up to 94%) in baseflow as compared to the runoff event flow. Conversely, exported herbicides were mainly transported by surface runoff and interflow (up to 72%) rather than by the baseflow.

The results of this work will be presented at the Canadian Water Resources Association Conference addressing those involved in watercourse management and design which links their practices with an ecosystem, (Watercourses - Getting on Stream with Current Thinking Conference to be held at the Hyatt Regency, Vancouver, B.C. October 22-25, 1996).

SOMMAIRE À L'INTENTION DE LA DIRECTION

Le présent rapport présente les résultats de l'évaluation de l'importance des pertes de cinq nutriments (phosphore, ammoniac, nitrate, nitrite et potassium) et de deux herbicides (atrazine et métolachlore) par le ruissellement provenant d'un bassin hydrographique agricole, correspondant à un débit épisodique ou au débit de base. L'étude a montré que les pertes de nutriments étaient sensiblement plus élevées (jusqu'à 94 %) pour le débit de base, comparativement au débit épisodique. Inversement, les herbicides étaient surtout transportés par le ruissellement de surface et par l'écoulement hypodermique (jusqu'à 72 %), plutôt que par l'écoulement de base.

Les résultats de ces travaux seront présentés à la Conférence de l'Association canadienne des ressources en eau, qui intéressera tous ceux concernés par la gestion et le développement des cours d'eau, en relation avec un écosystème («Watercourses - Getting on Stream with Current Thinking», conférence qui se tiendra au Hyatt Regency à Vancouver, C.-B., du 22 au 25 octobre 1996).

INTRODUCTION

Increased public awareness of environmental issues has led to a heightened concern for our river systems and the impact of agricultural sources of contaminants upon them. Such concerns include those for the health, aquatic life and water quality in the watercourses. Wastewater disposal from agricultural area has become a water resource's management issue and prompted an urgency in obtaining information on the impacts upon watercourses for those involved in watercourse management and design which link their practices in an ecosystem. In Ontario, the concern began in the 1970's because of the deterioration of water quality in Lake Erie. Studies under the Pollution from Land Use Activities Reference Group (PLUARG) of the International Joint Commission (PLUARG, 1978) identified that phosphorus associated with sediment in runoff from agricultural land was one of the significant contributors to the eutrophication of Lake Erie. More recently, concerns have expanded to include nitrate contamination of groundwater from fertilizer and manure use (Ontario Water Management Research and Service Committee, 1992), pesticides in surface and groundwater and bacterial contamination of water supplies from land application of livestock manure (Centre for Soil and Water Conservation, 1991). Contaminants in many watercourses within the Great Lakes basin originate from all kinds of human activities. Such activities can be depicted in Figure 1. As depicted in Figure 1, the impacts of contaminants upon a watercourse are complex. The contaminants can originate from a point or non-point source. To minimize agricultural sources of impacts upon a watercourse, remediations of agricultural water quality require targeting at watershed level to work with the critical source areas (Sharpley and Meyer, 1994; Harris et al., 1995).

This work assesses the amount of losses and the magnitude of transport of seven major agricultural chemicals to the watercourse by event flow and baseflow related to the temporal distribution of a cropping cycle. The terminologies of event flow and baseflow used in this report as wet-weather flow = event flow and dry-weather flow = baseflow.

The study area

The agricultural watershed: The characteristics of the studied agricultural watershed have been described elsewhere (Ng et al., 1993). They are briefly repeated here for convenience.

The Nissouri Creek agricultural watershed has an area of about 3470 ha measured upstream from the hydrometric station (Figure 2) of the Water Survey of Canada (WSC). This watershed located in southwestern Ontario 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 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, and the area-weighted application rates of nitrogen, phosphorus and potassium were respectively, 83 kg/ha, 42 kg/ha and 46 kg/ha. The rate of application of manure (usually liquid hog manure) was 34,810 kg/ha.

Physiographic characteristics: The 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.

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 (0-15 cm) 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 values calculated from the 1991 and

1992 runoff samples and rainwater samples were, respectively 7.8 and 5.2. The mean value of pH calculated from the 1992 baseflow samples was 7.6.

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).

Hydrometeorological characteristics: 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 m^3/s (Ontario Ministry of Environment, 1989). The maximum and minimum flows observed during the field seasons of 1991 and 1992 were 26.2 m^3/s and 0.01 m^3/s respectively. The average temperature of the Creek from April to December is 14.5 ^{o}C.

Methods and procedures

Measurements of discharge and collection of runoff event and baseflow samples: To monitor stream discharge and collect storm runoff samples, a hydrometric station was installed at the outlet of the watershed (Figure 2). The storm runoff samples were collected by an automatic sampler, the Sigma Model Series 702. The sampler was equipped with a water level sensor that connected to a stilling well to activate the sampler when water level in the stilling well has risen to a referenced level during a runoff event. The runoff samples were collected consecutively in a 350-mL glass bottle at a fixed time interval. A total of 24 sequential samples can be collected during a runoff event. Baseflow samples were manually collected. The discharge of the Creek was measured by Water Survey of Canada.

Analysis of runoff and baseflow samples for chemical concentrations: The analysis of runoff and baseflow samples for chemical concentration comprised atrazine ((2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine) and metolachlor (2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-

methoxy1-methylethyl)-acetamide), ammonia (NH_4-N), nitrate (NO_3-N), nitrite (NO_2 -N), total phosphorus (P), and potassium (K).

The extractions of runoff and baseflow samples for concentrations of atrazine and metolachlor were performed at the Provincial Pesticide Residue Testing Laboratory in Guelph, Ontario. The procedures of the herbicide extractions in runoff water can be found Ramsteiner et al., 1974, and Frank et al., 1990.

The analysis of samples of runoff and baseflow for concentrations of ammonia, nitrate, nitrites, total phosphorus, and potassium were conducted at the National Laboratory for Environmental Testing, Burlington, Ontario using the National Water Quality Laboratory Protocol (Water Quality Branch, IWD, 1979).

Calculation of volumes of surface runoff and baseflow and runoff events: Precipitation entering a watershed travels to a stream by three main components: surface runoff, interflow and baseflow. The discharge measured in a stream during a storm event and plotted as a hydrograph combines all three components. Several techniques (Pilgrim et al., 1979; Starosolszky, 1987; Sklash, 1990; Caissie et al., 1996) have been proposed for separation of a hydrograph components. The traditional technique was used because it is simple to apply. The technique includes (a) the straight line method, (b) fixed base length method, and (c) the variable slope method (Starosolszky, 1987). The straight line method was used in this study. The partitioned streamflow hydrographs with the time base length facilitate estimation of volumes of baseflow, interflow, and surface runoff. A planimeter was used to measure the area between the curves of the partitioned hydrograph under consideration. The areas measured by a planimeter were converted into volumes of each component. For practical reasons, the volume of interflow has been included in the surface runoff.

Calculations of mean concentration of a chemical in a runoff event: The mean concentration of a chemical was calculated for each runoff event by using the following expression:

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

where C_j is the volume-weighted concentration of a runoff event, C_i is the concentration in the 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 happens to be under a detection limit, the concentration of that sample is assumed to be the detection limit for the purpose of computational stability. All the runoff samples for nutrients have concentrations above the detection limit; a few runoff examples have herbicide concentrations below the detection limit. The detection limit of herbicides (atrazine and metolachlor) is 0.01 μg/L.

Calculation of losses of a chemical in surface runoff and in baseflow: The losses of nutrients (ammonia, nitrate, nitrite, total phosphorus, and potassium) and herbicides (atrazine and metolachlor) were calculated as a product of C_j and the volume. The loss of each chemical in surface runoff and in baseflow was calculated by the following expression:

$$L_j = C_j V_{j,k} \qquad (2)$$

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

Calculation of volume of baseflow and loss of a constituent in baseflow: The volume of baseflow during dry periods was calculated by using the mean daily discharge (antecedent period) measured at the gauging station (Figure 2) multiplied by the number of antecedent days. Thus,

$$V_b = q_b d \qquad (3)$$

where V_b is the volume of baseflow during an antecedent period, in m^3, q_b is the mean daily discharge (m^3/s) of the antecedent period and d is the number of antecedent day (days). It follows that the loss of a constituent in baseflow, L_i, is calculated by

$$L_i = V_b C_b \tag{4}$$

where C_b is the mean concentration of a constituent in baseflow.

Total of loss of chemical in baseflow: The total loss of a constituent, L_b, in baseflow is the sum of the loss of a constituent in both dry weather and wet weather flows:

$$L_b = C_j V_{j,k} + L_i \tag{5}$$

where $C_j V_{j,k}$ has been given in equation (2).

Results

Analytical results of herbicides and nutrients in runoff event and baseflow samples: The herbicide data set was collected in 1991. A total of 15 runoff events was monitored. The number of days elapsed from the first to last runoff events were 236 days (from 6 April to 8 November, 1991). Metolachlor was below the detection limit in all the baseflow samples. Consequently, the baseflow data set of 1991 was not evaluated for herbicide losses. The nutrient data set was collected in 1992. A total of 15 runoff events was monitored. The number of days elapsed from the first to the last events was 200 days (16 April to 13 November, 1992). The nutrient data for baseflow were collected in 1992. A total of 25 collection periods was realized. The number of days elapsed from the first to the last periods was 205 days.

Statistical descriptions of concentrations of constituents: The characteristics of the concentrations of each constituent in runoff events and in baseflow periods are statistically summarized in Table 1. Included in Table 1 are total rainfall, unit volumes of runoff and baseflow.

Table 1. Characteristics of rainfall, streamflow and water chemistry of runoff events and baseflow of the Nissouri Creek watershed (1991 and 1992)

(Wet weather flow)					
Parameter	Minimum	Maximum	Median	Mean	SD
1991					
Rainfall (mm)	7.90	64.00	28.40	28.76	13.26
Runoff (m^3/ha)	2.88	246.69	12.68	39.54	62.58
Baseflow (m^3/ha)	1.44	79.83	6.63	15.93	21.24
Atrazine (μg/L)	0.18	24.90	0.35	2.19	6.10
Metolachlor (μg/L)	0.01*	31.27	0.33	3.02	7.72
1992Rainfall (mm)	8.63	55.12	33.28	33.73	13.27
Runoff (m^3/ha)	2.53	125.62	19.18	45.84	41.81
Baseflow (m^3/ha)	0.71	64.44	9.06	15.75	17.02
Phosphorus (mg/L)	0.04	0.49	0.19	0.22	0.13
Ammonia (mg/L)	0.18	1.82	0.23	0.39	0.42
Nitrate (mg/L)	3.32	13.45	5.49	6.46	2.62
Nitrite (mg/L)	0.02	0.06	0.04	0.04	0.01
Potassium (mg/L)	2.37	9.80	4.90	5.14	1.92
(Baseflow)					
Parameter	Minimum	Maximum	Median	Mean	SD
1992					
Baseflow (m^3/ha)	5.00	2629.00	45.00	231.08	562.09
Phosphorus (mg/L)	0.01	0.68	0.11	0.21	
0.22Ammonia (mg/L)	0.07	0.42	0.18	0.23	0.11
Nitrate (mg/L)	3.08	7.63	6.10	6.00	1.13
Nitrite (mg/L)	0.03	0.08	0.05	0.05	0.01
Potassium (mg/L)	2.80	6.50	3.60	4.32	1.33

* Minimum corresponds to a detection limit.

Concentration of herbicide in transient runoff event: The transient runoff samples were collected for a range of runoff flow rates from 2.88 to 246.69 m^3/ha and a range of baseflow from 1.44 to 79.83 m^3/ha during the 1991 field year. The highest concentrations of atrazine and metolachlor both occurred in the May 25 event. After May 25 event, the concentrations of both herbicides declined during the growing season after they attained the probable maximum. The disappearance rates were reported in an earlier study (Ng, 1996). The disappearance rates of herbicides were calculated in terms of half-lives. The first-order half-lives of54 days for atrazine and 50 days for metolachlor were given in the earlier report (Ng, 1996). The maximum concentration of atrazine and metolachlor exceeded the interim maximum acceptable concentrations (IMAC) of 5 μg/L for atrazine and 50 μg/L for metolachlor of drinking water quality guidelines (Water Quality Branch, 1995). The average concentrations for atrazine and metolachlor were 2.19 μg/L and 3.02 μg/L, respectively. The baseflow samples collected in 1991 showed small concentrations of atrazine. The highest concentration of atrazine observed in May 1 was 0.37 μg/L and the lowest concentration (0.16 μg/L) of atrazine observed was on August 7. From September onward, all the baseflow samples for concentration of atrazine were under detection limits

Concentrations of nutrient in a transient runoff event: The transient runoff event samples were also collected for a range of runoff flow (surface runoff + interflow) rates from 3.73 to 125.62 m^3/ha and a range of baseflow rates from 0.71 to 64.44 m^3 /ha during the 1992 field year. All five nutrients (Table 1) had concentrations above a detection limit. Nitrate had the highest concentration among the five studied nutrients. The minimum and maximum concentrations of nitrate were 3.32 mg/L and 13.45 mg/L, respectively. This may suggest that nitrate leaches from soil into ground water, especially when soils have a naturally high water table (1.10 m for Nissouri Creek watershed). The concentration of potassium ranked second highest among the five constituents. This may be interpreted as potassium moves in soil more than phosphorus, but less than nitrate. The potassium ion is very soluble in water and can leach. Nitrite had the lowest concentration among studied nutrients (Table 1).

Concentration of nutrients in baseflow: The baseflow samples were collected for a wide range of flow rates from 5 to 2629 m^3/ha during the 1992 field program. Nitrate followed by potassium had the highest concentrations. The ratios of mean concentrations between runoff events and baseflow for phosphorus, ammonia, nitrate, nitrite and potassium are 0.96, 0.58, 0.92, 1.20 and 0.84 respectively. The values of this ratio are useful to identify the source of farm nutrients transported in event flow or in baseflow. For example, the ratio of ammonia (0.58) suggested that the transport of ammonia was mainly in runoff phase. Conversely, the transport of nitrite (1.20) was in baseflow. The transport of atrazine and metolachlor were mainly by runoff. Low concentration of atrazine was observed at the beginning of the cropping season in baseflow (Table 1).

Cumulative losses and normalized time period: Within the context of systematic study of the watershed with multiple water chemistry parameters, it is desirable to express the cumulative losses of each parameter in both runoff and in baseflow on a normalized time scale on the x-axis (Figures 3, 4, 5 and 6), so that the mass balance shows which parameter pays the major role on the watercourse. It follows that ammonia, nitrate, nitrite, phosphorus and potassium were transported in both event flow and baseflow (Figures 3, 4, and 5). Atrazine and metolachlor were transported mostly in event flow. Figure 6 showed that most of the losses of atrazine and metolachlor occurred within the first 48 days. Subsequently, the cumulative losses of atrazine, metolachlor, phosphorus, ammonia, nitrate, nitrite and potassium in runoff and in baseflow were calculated as a fraction of their sum. The fractions of losses in runoff and in baseflow expressed as a percentage of their sums are presented in Table 2.

Table 2. Fractions of losses of water chemistry in runoff and in baseflow

	Runoff (%)	Baseflow (%)
Phosphorus	6	94
Ammonia	17	83
Nitrate	12	88
Nitrite	10	86
Potassium	12	88
Atrazine	71	29
Metolachlor	71	29

Summary

The losses of atrazine and metolachlor in runoff occurred mostly within 48 days, or during the first large runoff event, after herbicide application. The cumulative losses of atrazine and metolachlor in runoff events, were respectively 1522 mg/ha and 1800 mg/ha. Metolachlor in baseflow was under the detection limit. Low concentration of atrazine in baseflow samples was detected at the beginning of the growing season with an average concentration of 0.23 μg/L.

The cumulative losses of phosphorus, ammonia, nitrate, nitrite and potassium in runoff, were respectively 0.217, 0.443, 4.364, 0.028 and 4.331 kg/ha. The cumulative losses of phosphorus, ammonia, nitrate, nitrite and potassium in baseflow (including baseflow from the event flow component), were respectively, 3.557, 2.214, 32.433, 0.247 and 33.151 kg/ha.

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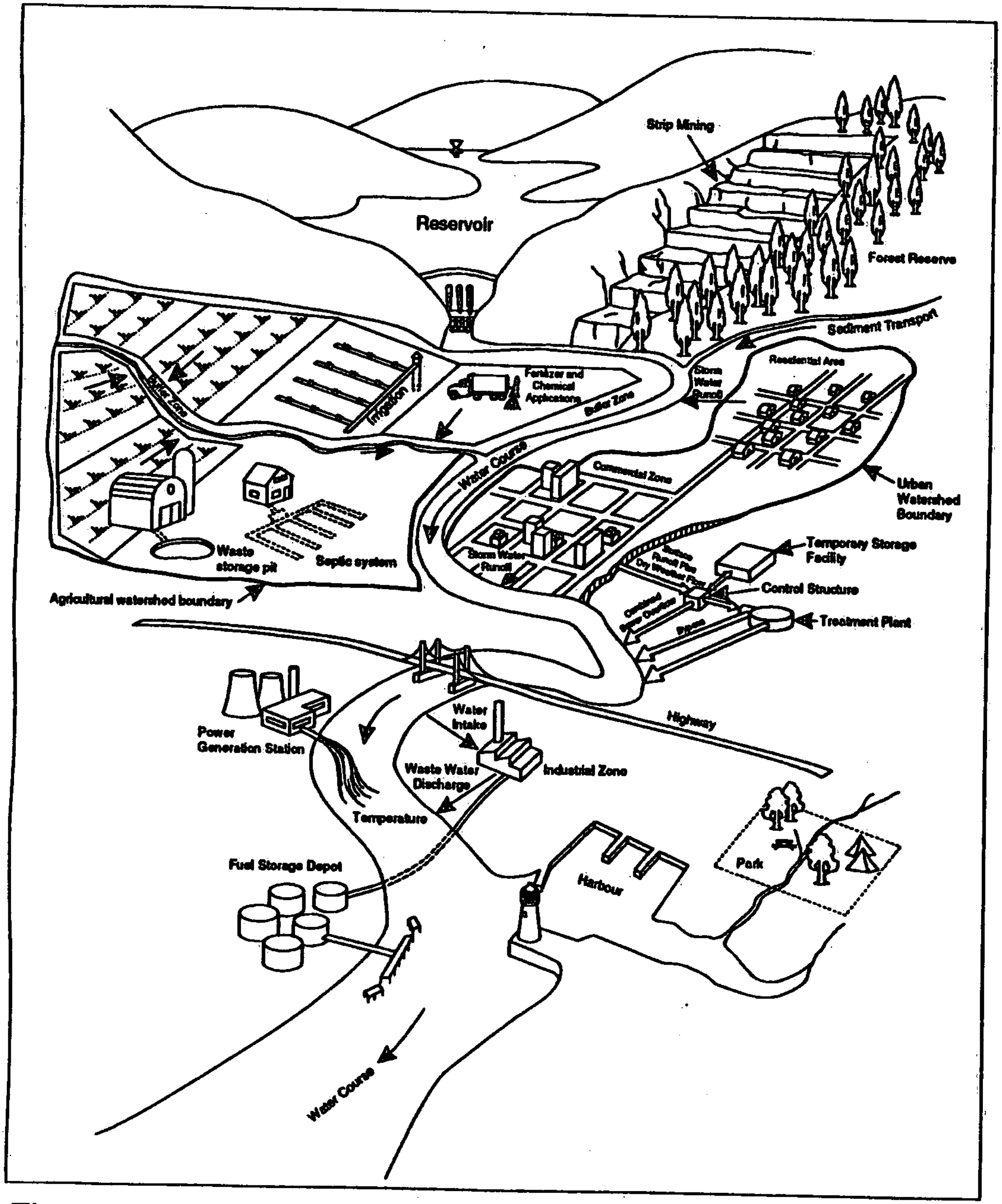


Figure 1. Schematic of Major Sources of Contaminant Contributed to Watercourse Water Quality

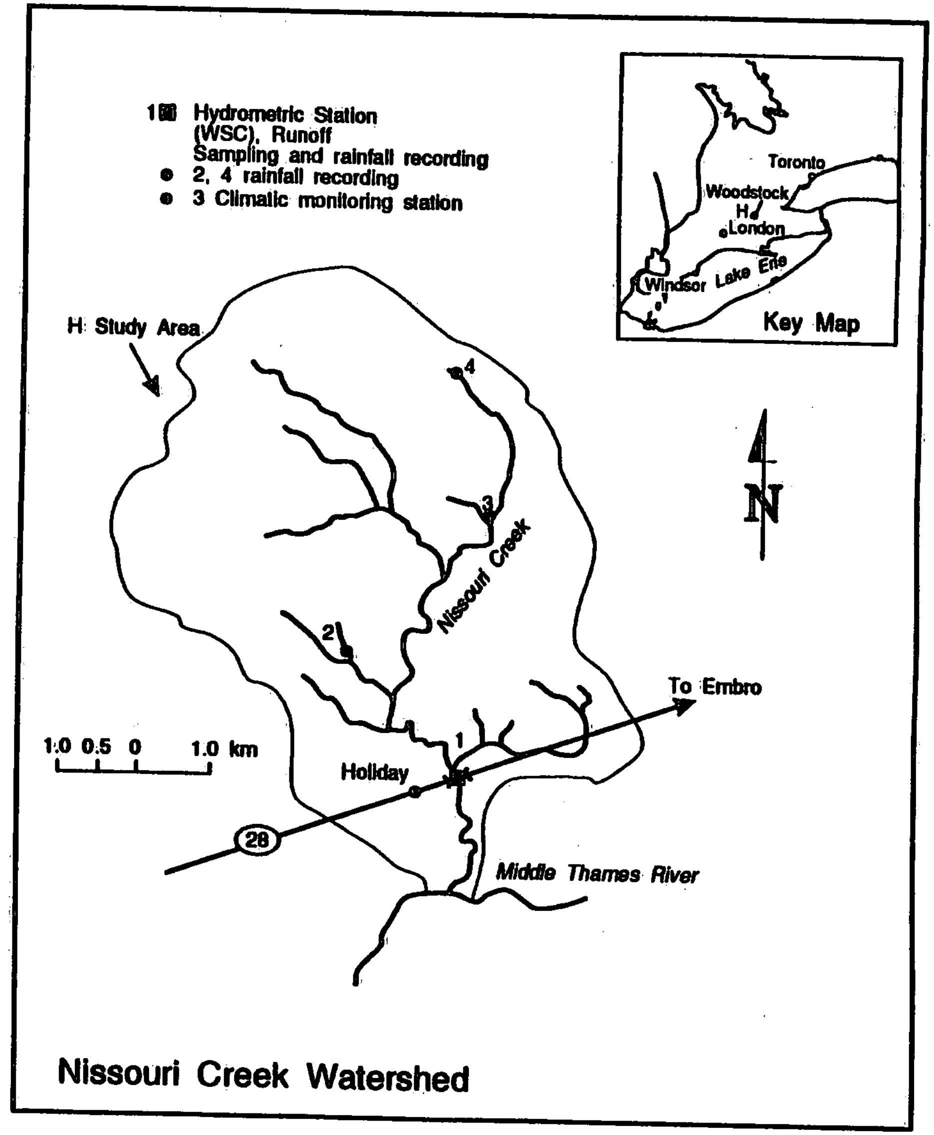


Figure 2. Studied Agricultural Watershed

Figure 3. Cumulative losses of ammonia, nitrate, nitrite, phosphorus and potassium in baseflow

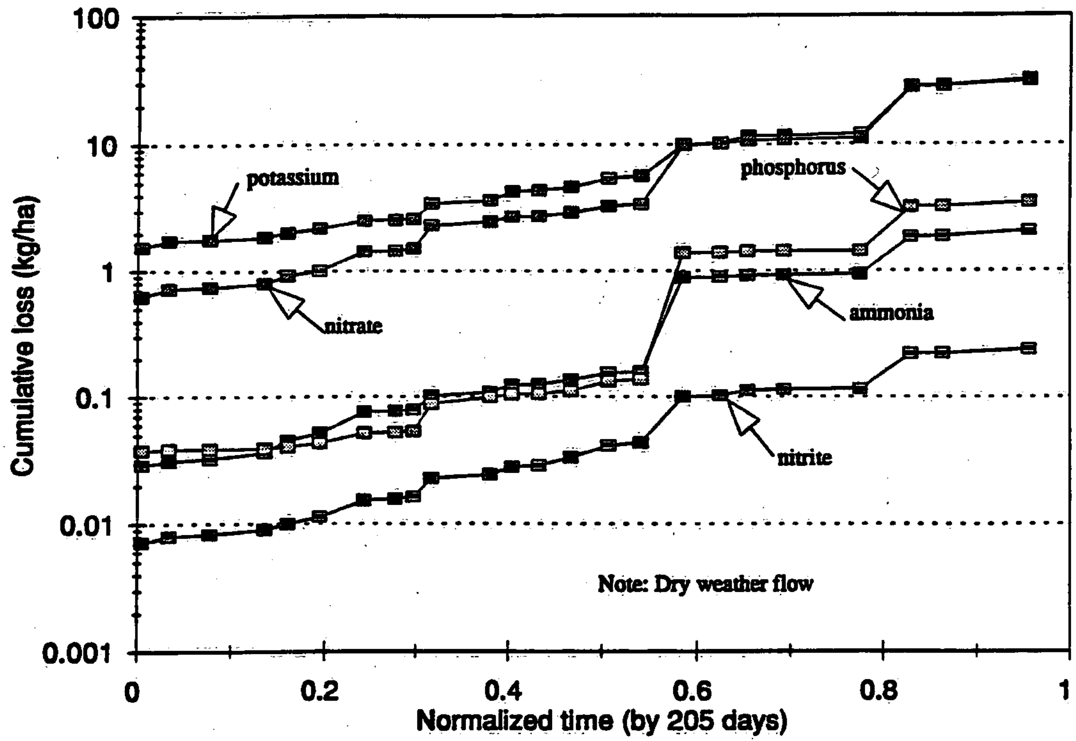


Figure 4. Cumulative losses of ammonia, nitrate, nitrite, phosphorus and potassium in surface runoff

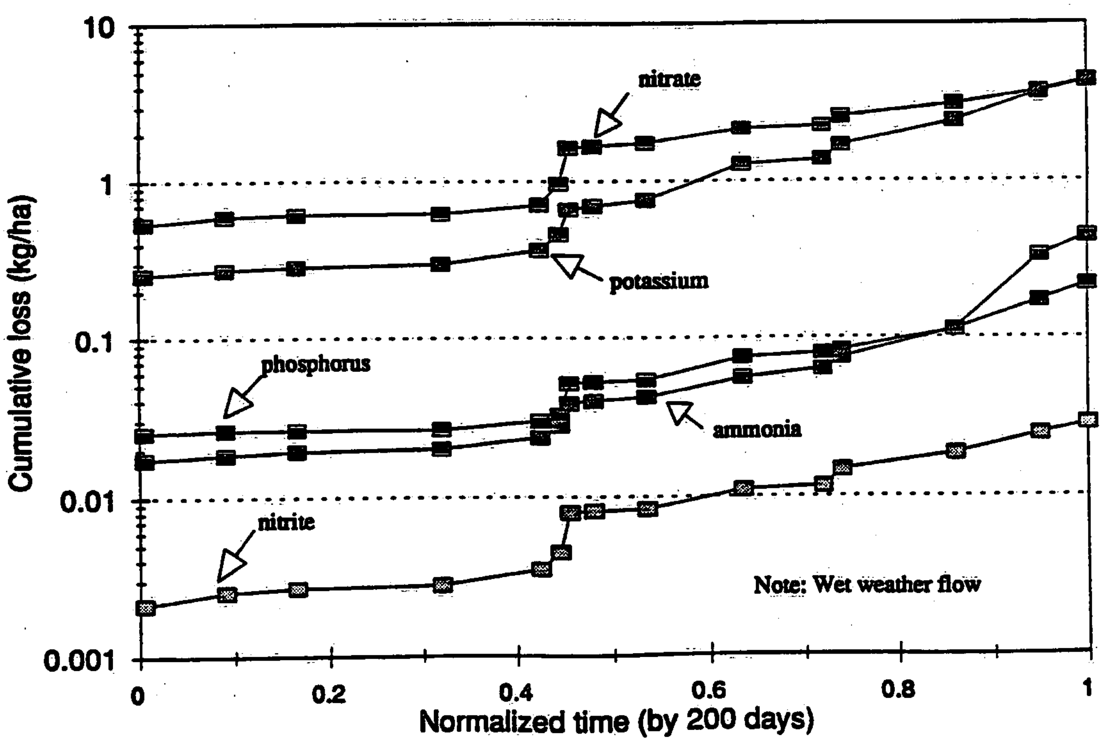


Figure 5. Cumulative losses of ammonia, nitrate, nitrite, phosphorus and potassium in baseflow

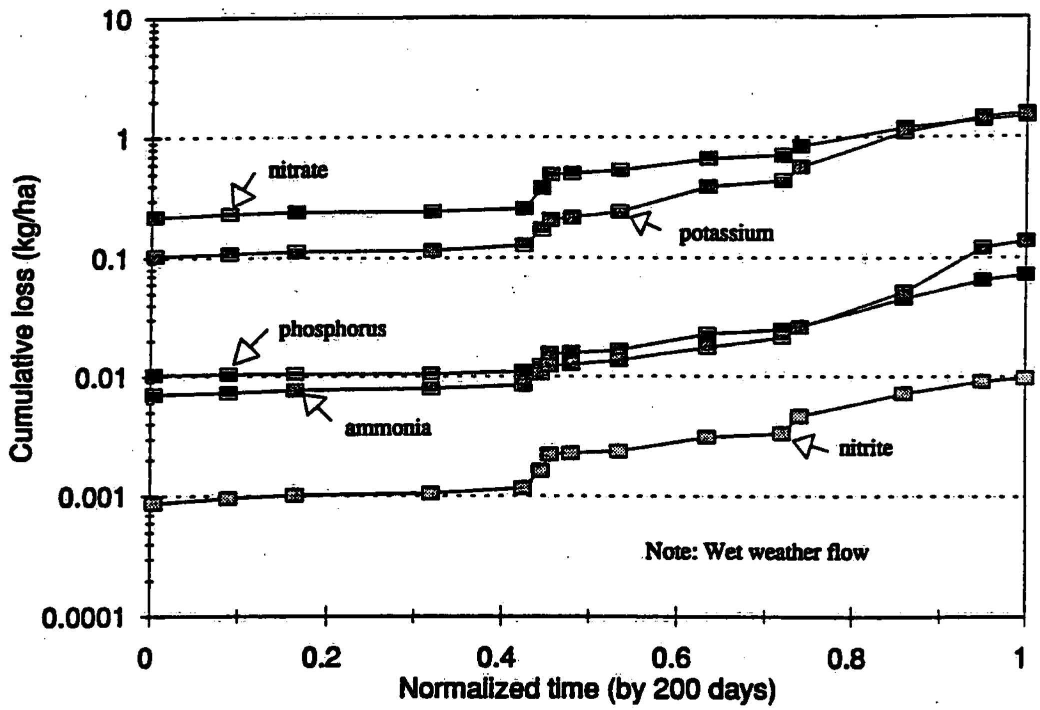
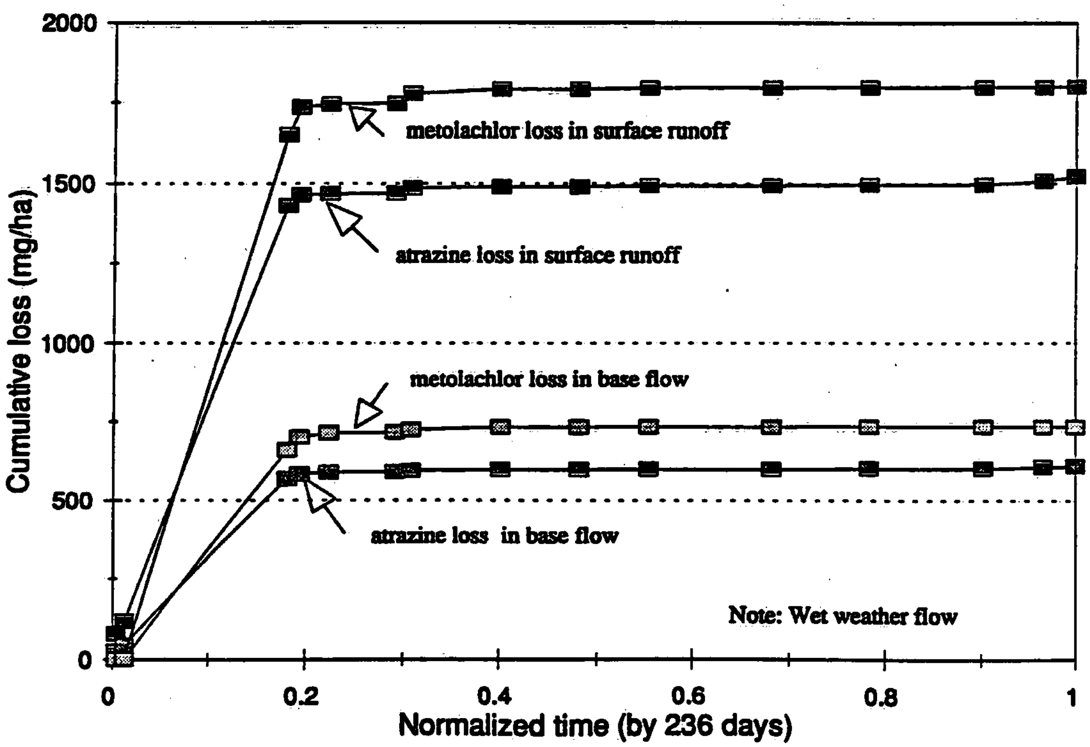


Figure 6. Cumulative losses of atrazine and metolachlor in surface runoff and in baseflow



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