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**NWRI CONTRIBUTION NO. 96-158** 

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# THE LOSSES AND TRANSPORT OF ATRAZINE AND METOLACHLOR IN RUNOFF EVENTS FROM AN AGRICULTURAL WATERSHED

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#### MANAGEMENT PERSPECTIVE

This work evaluates the losses of atrazine and metolachlor in transient runoff events from an agricultural watershed. Twenty-five runoff events monitored in this watershed during 1990 and 1991 were used for the evaluations.

The evaluation identified that majority of the losses of atrazine and metolachlor occurred within 70 days of application and during a large storm event, shortly after a herbicide application. The surface runoff combined with interflow is a major pathway for the losses of the two herbicides.

The results of this work are useful for fine-tuning of agricultural practices and for watershed management considerations in the protection of water quality of the Great Lakes Basin.

This short paper is prepared for the Watershed Management Symposium to be held at the National Water Research Institute, Burlington, Ontario, December 6-8, 1995.

#### SOMMAIRE À L'INTENTION DE LA DIRECTION

Ce rapport évalue les pertes d'atrazine et de métolachlore lors d'événements d'écoulement passager des eaux de ruissellement d'un bassin hydrographique agricole. Vingt-cinq événements d'écoulement qui ont fait l'objet d'une surveillance dans ce bassin en 1990 et 1991 ont été utilisés pour les évaluations.

L'évaluation a permis d'établir que la plupart des pertes d'atrazine et de métolachlore ont eu lieu dans les 70 jours suivant l'application et durant un important événement pluvio-hydrologique, peu après l'application d'un herbicide. L'écoulement de surface combiné à l'écoulement divergent constitue la principale voie d'acheminement des pertes de ces deux herbicides.

Les résultats de ces travaux permettront d'améliorer les pratiques agricoles, et la gestion des bassins hydrographiques en tenant compte de la protection de la qualité de l'eau dans le bassin des Grands Lacs.

Ce court rapport a été préparé pour le Watershed Management Symposium qui devait se tenir à l'Institut national de recherche sur les eaux, à Burlington (Ontario), du 6 au 8 décembre 1995.

# **ABSTRACT**

Twenty-five runoff events monitored in an agricultural watershed in 1990 and 1991, were studied for losses of atrazine and metolachlor in the runoff components. The results showed that majority of losses of the applied herbicides occurred in surface runoff and interflow. The combined losses in surface runoff and interflow accounted for about 75% and 65% of the total loss of atrazine and metolachlor respectively. Majority of the losses occurred within 70 days of application and during a large storm event, shortly after a herbicide application. Herbicide concentrations showed a steady disappearance with pseudo first-order half-lives of 54 days for atrazine, and 50 days for metolachlor.

# RÉSUMÉ

Vingt-cinq événements d'écoulement des eaux de ruissellement qui ont fait l'objet d'une surveillance dans un bassin hydrographique agricole en 1990 et 1991 ont permis de faire l'étude des pertes d'atrazine et de métolachlore dans les divers composants de l'écoulement. Les résultats ont démontré que la plupart des pertes des herbicides appliqués avaient lieu dans l'écoulement de surface et dans l'écoulement divergent. Ces pertes combinées représentaient respectivement 75 et 65 % des pertes totales d'atrazine et de métolachlore. La majorité des pertes se produisaient dans les 70 jours suivant l'application et durant un événement pluvio-hydrologique important, peu après l'application d'un herbicide. Les concentrations d'herbicide révélaient une disparition constante, avec une pseudo-période de premier ordre de 54 jours pour l'atrazine et de 50 jours pour le métolachlore.

#### INTRODUCTION

Agricultural activities and chemicals used in crop productions are important sources of contaminants affecting the water quality of the Great Lakes. Atrazine (2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine) and metolachlor (2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy1-methylethyl)-acetamide) are major herbicides used in Ontario's agricultural cropland, representing about 75% of all pesticides used.

Watershed monitoring has been useful in identifying the magnitude and significance of a contaminant load from agricultural practices. Herbicide loss from an agricultural treated area is controlled by a complex of interactions among the herbicides, soil type, soil solutes and weather. Study on field plots and watershed scale indicates that losses of herbicides are approximately 1-4%, depending on the soil types, tillage practice and slope of the fields (Glotfelty et al., 1984). 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 applications (Wauchope, 1978).

The purpose of this communication is to assess the amount of herbicide loss and the magnitude of transport by a transient runoff event, after the herbicide application. The results of the study are useful for the fine-tuning of agricultural practices and for watershed management considerations in the protection of water quality of the Great Lakes.

### **METHODS**

Agricultural Watershed: The Nissouri Creek agricultural watershed, located in southwestern Ontario (Figure 1), contains 55 active farms. The cultivation practices were both conventional and no-till procedures, and crops were rotated. The active farm area is planted in corn (> 50%), and a 30% in hay, soybeans, cereals, cash crops and fruits. 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 is about 3,470 ha

measured upstream from the hydrometric station of the Water Survey of Canada (Figure 1).

The areas planted with corn and other crops during the study period, as determined by a questionnaire survey conducted in 1990, were 1,470 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. Both rates of application are within the ranges recommended (atrazine: 1.20-2.50 kg/ha, metolachlor: 1.92-2.64 kg/ha) by the Ontario Ministry of Agriculture and Food (1990).

Physiographical Characteristics: The soil types are classified as Guelph loam = 45%, Embro silt loam = 36%, and Honeywood Guelph Complex = 12%. The well-drained Guelph loam and Embro silt loam represent 81% of the area of the watershed. The overland slopes of the watershed area, ranging from 0.5 to 5%, represent more than 85% of the watershed. The remaining 10% and 4% of the watershed, respectively, have slopes >5% and < 0.5%. The large slope represents mostly noncultivated land and the smaller slope basically represents the wetland or depression areas.

Hydrometeorological Characteristics: The climate was characterized by the 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, and discharge of the Creek = 0.437 m<sup>3</sup>/s (Ontario Ministry of Environment, 1989). The maximum and minimum flows observed during the field seasons of 1990 and 1991 were 13.0 m<sup>3</sup>/s and 0.01 m<sup>3</sup>/s respectively. The average temperature of the Creek water from April to December is 14.5 °C.

Runoff Sampling and Streamflow Measurement: The runoff event samples were collected by an automatic sampler. The sampler was equipped with a sensor that connected to a stilling well to activate the sampler when the water level in the stilling well has risen to a reference level during a runoff event. The runoff samples were collected consecutively in 350 ml glass bottles at a fixed time interval. A total of 24 samples can be collected during a runoff event. Baseflow samples were also collected between rain events. The discharge of the Creek was measured by Water Survey of Canada.

Herbicide Extraction: The herbicide extractions from runoff samples were performed at the Provincial Pesticide Residue Testing Laboratory in Guelph, Ontario. The procedures of the herbicide extractions in runoff water have been described elsewhere (Ramsteiner et al., 1974). The detection limit is  $0.01 \mu g/L$ .

Decomposition of Runoff Components: Precipitation entering a watershed travels to a stream by three main components: surface runoff, interflow and baseflow. The discharge measured in a stream and plotted as a hydrograph combines all three components. The techniques proposed to separate baseflow, interflow and surface runoff in a hydrograph include (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 hydrograph under consideration. The measured areas are converted to volumes of the runoff components.

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

$$C_{j} = \sum_{i=1}^{m} C_{i}V_{i}/V$$

$$(1)$$

where  $C_j$  is the volume-weighted concentration for 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 0.01  $\mu$ g/L for the purpose of computational stability.

The losses of atrazine and metolachlor were calculated as a product of  $C_j$  and the volume. The following expression was applied to calculate the losses of atrazine and metolachlor for surface runoff, interflow, and base flow.

$$L_{i} = C_{i} V_{i,k} \tag{2}$$

where  $L_j$  is the loss (mg) of herbicides 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  $C_i$  was defined earlier.

#### **RESULTS AND DISCUSSIONS**

Normalized Time Period: Ten and fifteen runoff events were monitored in 1990 and 1991, respectively, in the study area. The number of days elapsed from the first to the last runoff events was 186 and 236 days for 1990 (from 21 April to 5 November) and 1991 (6 April to 8 November) respectively. The data series of herbicide concentrations and the volumes of runoff components in 1990 and 1991 were further reduced by means of averaging. The procedures of averaging were based on matching the normalized time scales on the x-axis.

Dissipation Rate of Atrazine and Metolachlor: The concentrations of the studied herbicides declined during the growing season after they attained the probable maximum, for both years (Figure 2). The disappearance follows the first-order half-lives of 54 days for atrazine, and 50 days for metolachlor. The key point of obtaining the half-lives information is to calculate the amount of herbicide migration in the water phase, potentially reaching a nearby aquatic system. There is an uncertainty in the losses of the herbicide as shown in Figure 2. The uncertainties of losses of atrazine and metolachlor are 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.

Losses of Atrazine and Metolachlor in the Runoff Components: Within the context of a systematic study of the watershed, it is desirable to express the cumulative losses of atrazine and metolachlor in the runoff components (Figure 3 (a), (b) and (c)), so that the mass balance shows which component pays the major role for the loss of herbicide during the transient processes of a runoff event. It follows that the loss of atrazine in the combined surface runoff and interflow accounted for up to 75%, whereas the loss of metolachlor in the combined surface runoff and interflow accounted for about 65% of the total loss.

## **SUMMARY**

The losses of atrazine and metolachlor through surface runoff and interflow occurred mostly within 70 days, or during the first large storm event, after herbicide application. The loss of atrazine in the combined surface runoff and interflow transported up to 75% and the loss of metolachlor in the combined surface runoff and interflow accounted for about 65%.

The disappearance rate of half-live for atrazine is 54 days and for metolachlor is 50 days.

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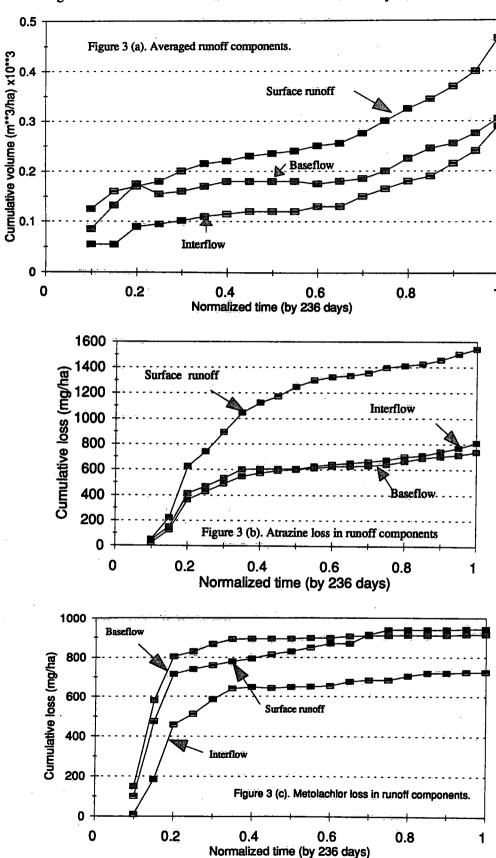
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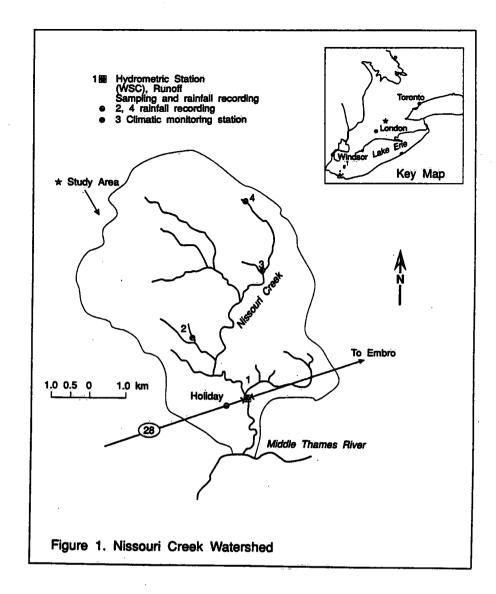
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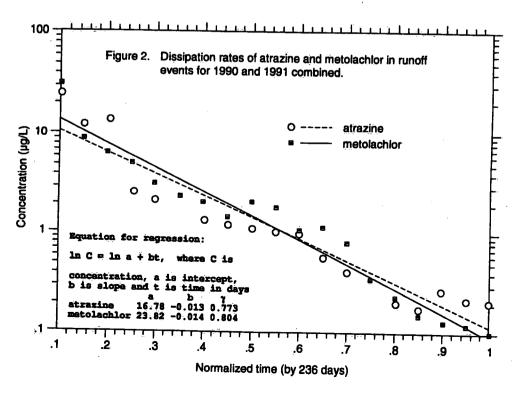
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Figure 3. Atrazine and Metolachlor losses in the Runoff Components.











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