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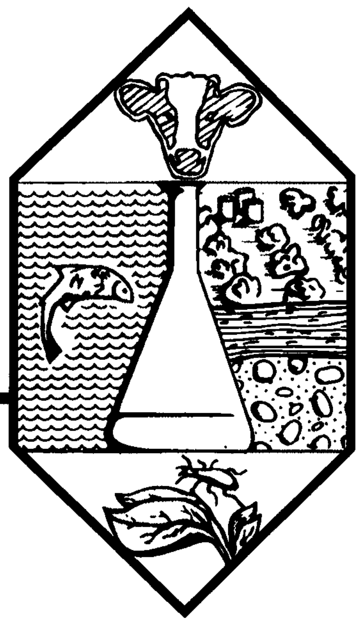

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STORM FLOW EXPORT OF METOLACHLOR FROM A COASTAL PLAIN WATERSHED

Key Words: Metolachlor, tropical cyclones, storm flow, surface water

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ABSTRACT

During an 18-month (1994-1995) survey of the surface water in an Atlantic Coastal Plain watershed, metolachlor was most frequently detected during storm flow events. Therefore, a sampling procedure, focused on storm flow, was implemented in June of 1996. During 1996, three tropical cyclones made landfall within 150 km of the watershed. These storms, as well as several summer thunderstorms, produced six distinct storm flow events within the watershed. Metolachlor was detected leaving the watershed during each event. In early September, Hurricane Fran produced the largest storm flow event and accounted for the majority of the metolachlor exports. During the storm event triggered by Hurricane Fran, the highest daily average flow (7.5 m^2 s^{-1}) and highest concentration (5.1 μg L^{-1}) ever measured at the watershed outlet were recorded. Storm flow exports leaving the watershed represented 0.1 g ha^{-1} or about 0.04% of active ingredient applied.

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INTRODUCTION

Over the past 10 years, numerous studies of the nation's surface waters have been initiated to monitor the occurrence and level of pesticides. Studies have been conducted at various scales from entire river basins (Anderson et al., 1997; Berndt et al., 1998; Spruill et al., 1998) to small agricultural watersheds (Novak et al., 1996; Donald et al., 1998; Jaynes et al., 1999). In these studies, metolachlor (2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide) has been one of the most frequently detected pesticides. Surface runoff and subsurface drainage are the major transport mechanisms for pesticides entering surface waters from agricultural areas (Larson et al., 1997). Ground water studies conducted in diverse agricultural areas (Blanchard et al., 1995; Novak et al., 1998; Wade et al., 1998) have reported infrequent detections and low concentrations of metolachlor in monitoring and domestic drinking wells. However, higher concentration have been detected in soil and water at shallows depths (1 to 2 m) in areas that have received metolachlor application (Huang and Frink, 1989; Watts and Hall, 1996). Therefore, while one could predict that most of the metolachlor was entering the streams via surface runoff, it would not be unreasonable to assume that some metolachlor could be transport into streams near the point of application through ground water recharge.

Metolachlor is a chloroacetamide herbicide extensively used for weed control in corn (*Zea mays* L.), grain sorghum (*Sorghum vulgare* L. Moench), and soybeans (*Gylcine max* (L.) Merr.). During the 1997 crop year, metolachlor was the second most commonly used herbicide in corn production with 20 million kg of active ingredient being applied in the United States (NASS, 1998). Even though metolachlor is frequently detected in surface water studies, the detections are usually seasonal, occurring most often immediately following application in the spring. Few reported detections (Ferrari et al., 1997) approach the EPA's adult Health Advisory Level (HAL) of 70 $\mu g\ L^{-1}$.

During an 18-month (June 1994-Jan. 1996) survey of pesticide exports from an Atlantic Coastal Plain watershed, metolachlor was only detected on seven separate days (unpublished data). The majority (71%) of the detections were noted during a 14-day summer storm period in 1995 (Watts et al., 1996). These results indicate that storm flow exports of metolachlor from this watershed may be very prominent. Therefore, a sampling protocol was established for the summer of 1996 that concentrated sampling efforts on storm flow periods. The summer of 1996 proved to be a good year for such a study because it experienced a 40% increase from the yearly average (40-year mean) in the number of named Atlantic tropical cyclones (collectively, tropical storms and hurricanes). During the 1996 tropical cyclone season, five of 13 named storms threatened or made landfall along the southeastern coast of the United States (Gray et al., 1996). The objective of this study was to evaluate the frequency and amount of metolachlor exported from a Coastal Plain watershed during summer storm events.

MATERIALS AND METHODS

Watershed Description

In 1990, the 2044-ha Herrings Marsh Run watershed was selected as part of a USDA water quality demonstration project area. This agricultural watershed is located in the southeastern Coastal Plain region of North Carolina and is part of the Cape Fear River basin. The geology and landscape of the watershed are presented in Novak et al. (1998). Agricultural practices implemented within the watershed are typical of the southeastern Coastal Plains with approximately 50% of the land area planted to row crops (Stone et al., 1995).

Sample Collection and Flow Determination

A Streamline 800 SL refrigerated autosampler (America Sigma, Medina, NY) equipped with an integral flow monitor was installed at the watershed outlet. The sampler was programmed to begin sample collection when stream flow exceeded 0.198 $m^3 s^{-1}$. This flow (designated as storm flow) represented approximately two times normal summer base flow. The integral flow meter consisted of a pressure transducer that measured the pressure (or head) of water. The measure head was calibrated with a discharge rating table developed for this site by the US

Geological Survey. After the discharge rating table was programed into the sampler, flow was automatically determined for any given pressure reading. The flow readings were recorded to correspond with each bottle collected during a sampling period. After the sample collection had begun, a 90-mL subsample was collected for every 353.8 m^3 of flow. A composite sample of 10 subsamples was collected in each sample bottle. Sample temperature was maintained at 7°C inside the refrigerator unit, and sample sets (up to 8 bottles) were collected within 24 hours. The samples were transported to the laboratory on ice and stored frozen until sample extraction could commence.

Sample Extraction and Determination

The extraction and determination of metolachlor were performed using the method outlined by Novak and Watts (1996). Briefly, 50 g of water were filtered (0.7 μm) and passed through a conditioned tC-18 Sep-Pak (Waters Co., Milford, MA) solid phase extraction cartridge. Metolachlor was eluted with ethyl acetate achieving a 50:1 concentration. The extracts were analyzed using a 3600CX gas chromatograph (Varian Co., Walnut Creek, CA) fitted with a nitrogen and phosphorus detector. The extraction procedure had an average efficiency of 85%, and the minimum detection limit for metolachlor was established at 0.30 $\mu g\ L^{-1}$ (Novak and Watts, 1996).

Weather Data

Precipitation data were measured and recorded with an automated weather station and data logger (Campbell Scientific, Logan, UT) located approximately 8 km from the watershed outlet. This station was utilized until it was damaged (Sept. 5th) by weather related to Hurricane Fran. Data from a North Carolina State University weather station located approximately 25 km away were recorded for the remaining three weeks of the study.

RESULTS AND DISCUSSION

Tropical Cyclone Season

The summer of 1996 was the most active tropical cyclone season in North Carolina since 1955 (Schneider, 1998). In North Carolina, the 1996 season was punctuated by one tropical storm and two hurricanes that made landfall along its coast. The two hurricanes (Bertha and Fran) both came ashore approximately 100 km due south of the Herrings Marsh Watershed while Tropical Storm Arthur made landfall approximately 150 km southeast of the watershed. Due to the amount of tropical cyclone activity along the North Carolina coast during this summer, the number of storm events within the watershed and the magnitude of these events were greater than the past two summers in which the watershed outlet had been monitored.

The occurrence of the tropical cyclones produced above average rainfall in both July and September. During the four-month summer period (June through Sept.), the total rainfall exceeded the 28-year average for that period by 208 mm. The 158 mm of rainfall that preceded Hurricane Fran on September 5th contributed to a total of 320 mm of rainfall for the month of September. September's rainfall was nearly three times the average monthly rainfall and was the greatest amount recorded during the month of September in the last 28 years.

The dramatic increase in rainfall contributed to the mean daily flow exceeding storm flow criteria (greater than 198 L sec) almost half of the days (49%) during the four summer months. Most storm flow days occurred in conjunction with Hurricanes Bertha and Fran making landfall. During September, the 1st and 2nd were the only days that flow at the watershed outlet was not at or above storm flow conditions.

Metolachlor Exports in Storm Flow

For the month of June, the watershed received slightly less rainfall (93.6 mm) than the 28-year average (112.3 mm). Thunderstorms on June 8th and 10th produced the first storm flow events of the summer (Table 1). Samples were collected daily from the 9th through the 12th. During the last two days of this storm event, the first concentrations of metolachlor were detected (Fig. 1). A total of 29.3 g of metolachlor was exported from the watershed during these two days. The occurrence of early season losses was not entirely unexpected since several watershed-scale monitoring studies (Thurman et al., 1991; Jaynes et al., 1999) also have reported that the highest frequency of metolachlor detections occurred during the post-application period.

TABLE 1
Timing of Major Storm Events and Their Associated Rainfall.

Distinct Storm Event	Date of impact on watershed[1]	Associated Rainfall (mm)
Summer thunder storm	June 8th-12th	47.0
Tropical Storm Arthur	June 19th-20th	25.8
Hurricane Bertha	July 10th-18th	176.7
Summer thunder storm	July 23rd-August 1st	52.8
Summer thunder storm	August 12th-16th	50.0
Hurricane Fran	September 5th-October 1st	296.1

[1] Start of rainfall until stream flow drops below storm flow conditions.

A substantial amount (28%) of June's rainfall occurred on the 19th due to the close proximity of Tropical Storm Arthur (Table 1). Dry conditions throughout the watershed limited storm flow at the outlet to a few hours on the 20th. The one sample that was collected during this event was found to be exporting a measurable amount (7.2 g) of metolachlor (Fig. 1).

After Tropical Storm Arthur, no storm events were recorded until July 12th when Hurricane Bertha made landfall approximately 100 km from the watershed (Table 1). The rainfall associated with this hurricane elevated the watershed's discharge above storm level for seven days (Fig. 1). Samples collected during this time contained metolachlor only on the first day of the storm event (Fig. 1). In addition to the increased flow produced by Hurricane Bertha, flooding and high winds caused substantial damage throughout the riparian forests surrounding the ephemeral streams and to the stream banks themselves. The resulting damage was severe enough to justify a 1997 initiative by the Natural Resource and Conservation Service to reestablish the flowpath of several streams within the watershed. This damage may have contributed to increases in stream discharge in subsequent rainfall events. Riparian buffer zones have been found effective in

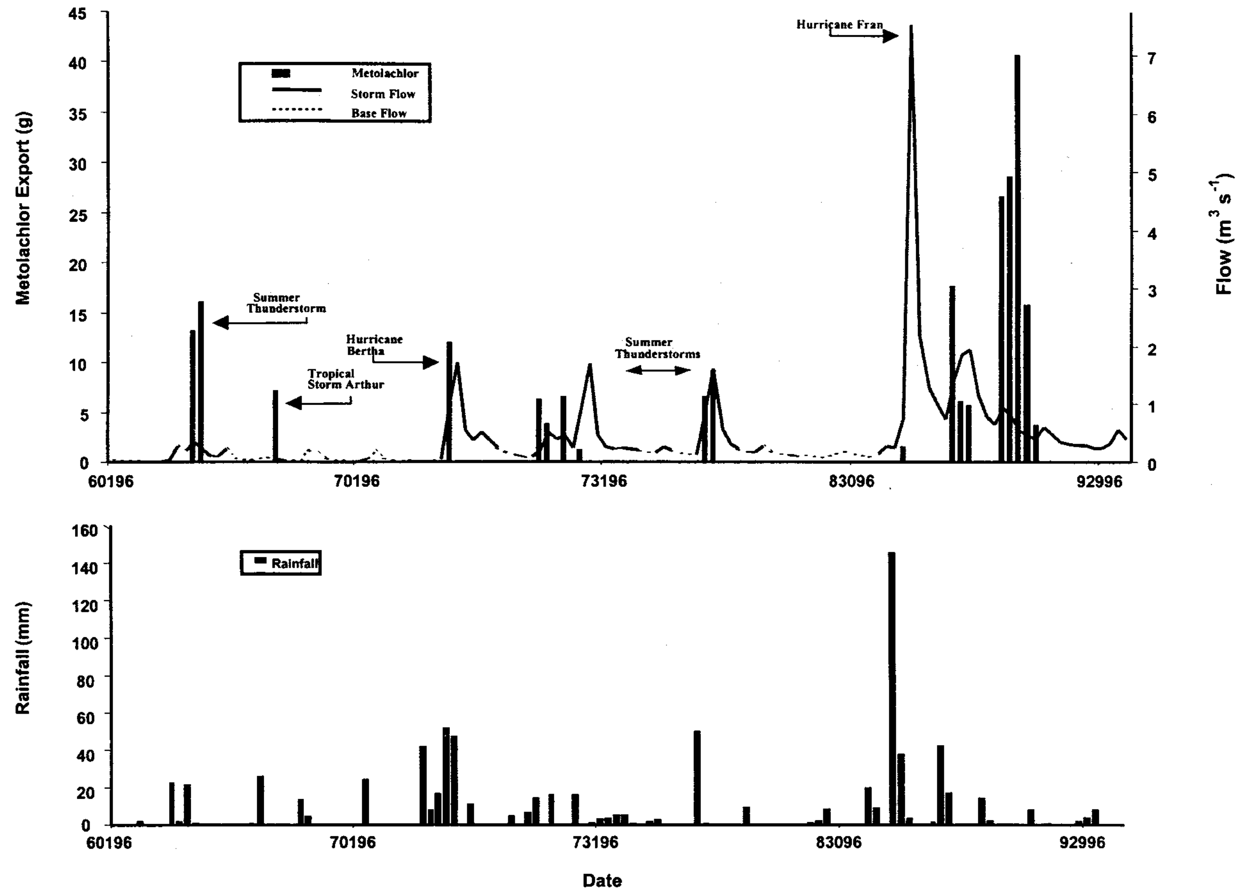

FIGURE 1
(Upper) Daily average flow (both base and storm flow conditions) and daily metolachlor exports at the Herrings Marsh Run watershed outlet.

(Lower) Daily rainfall.

decreasing the rate of water flow and lowering water elevation during flood conditions (Castelle et al., 1994).

At the end of July, several small summer storms over a seven-day period produced the next storm flow event (Table 1). Even though the storms themselves produced only a small total amount of rainfall (52.8 mm), the discharge was much larger than would have been normally expected. This increased discharge may have been due to the comprised riparian areas that had lost a portion of their ability to impede surface flow to the stream channel. A brief one day storm occurred during the second week of August and produced 50 mm of rainfall (Table 1). Again a large increase in the average daily flow was measured at the watershed outlet, and storm flow conditions existed for four days. During both of these summer storm periods, metolachlor was measured at the beginning of the storm flow event; however, no metolachlor was detected after the peak stream discharge (Fig. 1). This pattern was noted by Jaynes et al. (1999), who reported a tendency of increasing metolachlor concentrations at the onset of a flow event. After the summer storm in early August, the flow at the outlet returned to base conditions for the remainder of the month.

During the first week of September, Hurricane Edouard passed within 800 km of the North Carolina coast. The outer storm bands of this hurricane just reached the North Carolina coast producing 30 mm of rainfall on September 2nd and 3rd. The rainfall from this storm elevated the watershed outlet just above storm flow conditions on September 3rd and 4th. Hurricane Fran followed directly behind Hurricane Edouard depositing 183 mm of rainfall on the watershed within two days (Sept. 5th and 6th) (Table 1). Stream discharge had increased dramatically by September 6th producing a daily average flow at the watershed outlet 38 times (7.5 m^3 s^{-1}) minimum storm flow conditions. This flow level was the highest daily average recorded at the watershed outlet during the seven years that flow was measured.

A small amount of metolachlor was detected in samples collected on September 5th, approximately 20 hours after storm flow conditions first reached the watershed outlet. Unfortunatly, due to the severity of Hurricane Fran, the autosampler was non-operational from September 6th through September 10th. Once sampling resumed, metolachlor was detected in samples collected on eight of the next 11 days. Metolachlor exports were detected until September 21st. In the two weeks following the onset of storm conditions caused by Hurricane Fran, a total of 146 g of metolachlor was exported from the watershed. The highest concentration (5.1 $\mu g\ L^{-1}$) and highest total amount (26.0 g) measured in a single sample during the entire time this outlet had been monitored (July 1994 through Sept. 1996) occurred during a two-hour sampling period on September 19th, 1996. The maximum concentration that was measured in this study never approached the EPA's adult Health Advisory Level (HAL) of 70 $\mu g\ L^{-1}$.

Frequency of Metolachlor Detection

Prior to storm flow sampling, the Herrings Marsh Run watershed outlet had been continuously monitored and sampled during both base and storm flow from July 1994 through May 1996. Over that time period (700 days), metolachlor was detected in only 11 separate samples, nine of which were collected during storm flow conditions (unpublished data). During the summer of 1996, metolachlor was detected in samples collected on 19 separate days (Fig. 1). Considering that storm flow was recorded on 60 days during this four-month period, then metolachlor was leaving the watershed in measurable amounts on 32% of the sampled days. Almost half of the detections (9 of 19) came after September 5th and the occurrence of Hurricane Fran. Detection numbers and exported amounts may have been slightly higher than reported due to the sampler being disabled for five days.

Although overall detections of metolachlor were substantially higher in the summer of 1996 compared to the previous two-and-a-half years, total exports of metolachlor were relatively small. A total of only 228 g of metolachlor was calculated to be exported from the watershed from June 1st through September 30th. The rate of metolachlor applied throughout the watershed in 1996 was not available. However, Novak et al. (1998) reported that 669 kg (active ingredient) of metolachlor was applied in both 1994 and 1995. If it is assumed that 1996 metolachlor applications were similar to previous years, then the total amount exported was equal to only 0.04% of applied. On a watershed basis, metolachlor losses were equal to approximately 0.1 g ha^{-1}. Even though the Herrings Marsh Run watershed outlet was sampled only during storm flow conditions in 1996, and in light of the past record of only two detections in 700 days occurring during base flow, one could assume that any metolachlor leaving the watershed during base flow conditions in the summer of 1996 would have been insignificant.

CONCLUSION

Aided by the active tropical cyclone season of 1996, six distinct storm flow events were measured from June though September. The increased rainfall during this time period promoted an increase in the amount of discharge recorded at the watershed outlet. These storm events contributed to increased metolachlor detections during this time period compared to the previous 700 days of active monitoring. The maximum concentration measured during this study was considerably lower than EPA limits. Total amount of metolachlor exported during this period increased compared to previous measurements, but was still very small (0.04%) in terms of total amounts applied within the watershed. One storm in particular (Hurricane Fran) caused a substantial increase in metolachlor detections and exports recorded. This illustrates the effects that noncontrollable, naturally occurring weather events can have on the quality of water leaving an agricultural watershed.

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