Seasonal Occurrence and Export of Five Herbicides from a North Carolina Coastal Plain Watershed

J. M. Novak, D. W. Watts, K. C. Stone, M. H. Johnson

Abstract. *Herbicide detection in surface water sources has caused concern about contamination of these sources and adverse effects on human and aquatic health. Understanding surface water herbicide transport from agriculturally intensive watersheds is useful for development of herbicide best management practices to reduce off–site movement. The seasonal occurrence and load of five herbicides exported by a stream were determined for a North Carolina Coastal Plain watershed. Grab samples were collected across the watershed, and composite samples were collected at the watershed outlet using a flow–proportional sampler. Samples were extracted for the herbicides alachlor [2–chloro–N–(2,6–diethylphenyl)–N–(methoxymethyl) acetamide], ametryn [N–ethyl–N'–(1–methylethyl)–6–methylthio–1,3,5–triazine–2,4–diamine], atrazine [6–chloro–N–ethyl–N'–(1–methylethyl)–1,3,5–triazine–2,4–diamine], cyanazine [2–([4–chloro–6–(ethylamino)–1,3,5–triazin–2–yl]amino)–2–methyl propanenitrile], and metolachlor [2–chloro–N–(2–ethyl–6–methylphenyl)–N–(2–methoxy–1–methylethyl) acetamide]. Herbicides were detected in 15% (n = 415) of the grab samples with atrazine, cyanazine, and metolachlor detected in 3% to 6%, while alachlor and ametryn were detected in 1% of the samples. The mean stream water herbicide concentrations in grab samples were < 0.9 μ g L^{-1}. Herbicides were detected during all four seasons, with most detections occurring during the summer. The low number of herbicide detects and low total mass of these five herbicides exported from the watershed (<0.01% of herbicide applied) suggests that the five investigated herbicides have had a minimal influence on the quality of water exiting this watershed.*

Keywords. *Herbicides, Export, Stream, Coastal Plain watershed.*

Herbicide usage is an important management tool for agricultural production in the eastern Coastal Plain region (Pait et al., 1992). Herbicides provide beneficial weed control and typically have minimal off–site movement if used properly. However, herbicides have been frequently detected in groundwater (Koterba et al., 1993; Bruggeman et al., 1995; Maas et al., 1995) and surface water sources (Ferrari et al., 1997; Holman et al., 2000; Watts et al., 2000) in the Coastal Plain region of several eastern states. In a surface water survey conducted by the USGS across several Mid–Atlantic states, commonly used herbicides such as atrazine and metolachlor were detected in almost 72% and 75% (n = 2545), respectively, of their samples (Ferrari et al., 1997). Another study in North Carolina (Holman et al., 2000) also reported frequent detections for atrazine (45%) and metolachlor (58%) in its water sources. In that study, metolachlor concentrations in samples were <2.23 μg L^{-1}, and 92 out of 94 samples with atrazine detections had concentrations of <3 μg L^{-1}. In both studies (Ferrari et al., 1997; Holman et al., 2000), herbicide detection patterns were highly seasonal, with high concentrations measured early in the planting season. Following spring herbicide application, the first runoff–inducing rain or irrigation event after application can move potentially significant quantities of herbicides into surface waters (Larson et al., 1997). Trace herbicide amounts can also be detected in surface water sources as late as the fall season (Larson et al., 1997).

Herbicide contamination in surface water sources may also pose a human health concern since some coastal communities are supplementing drinking water demands by using surface water sources. Identification of herbicides present in surface water sources, seasonal concentration variations, and quantification of herbicide fluxes are therefore important parameters to consider when water conveyors assess the proper water–treatment processes. Water treatment methods usually vary because of differences in herbicide chemistry and concentrations present in the water source. Selection of effective methods to remove these chemicals avoids the problem of incomplete purification or detoxification of these compounds (Miltner et al., 1989). Although prior surface water quality studies (Ferrari et al., 1997; Holman et al., 2000) have identified herbicide types and seasonal concentration fluctuations in the Coastal Plain region of several Mid–Atlantic states, very few Coastal Plain watershed–scale herbicide flux studies exist in the literature. The limited number of studies is usually attributed to the difficulty of accurately assessing both herbicide inputs and exports on a watershed scale. The reported high frequency of herbicide detections in surface water sources across several

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Mid–Atlantic states emphasizes the importance of continued investigations to determine potential off–site movement of herbicides and to quantify fluxes from sites of application.

Concern about herbicide usage degrading surface water quality in the Coastal Plain region has prompted us to evaluate herbicides in a black water stream draining an eastern North Carolina watershed. This watershed is under intensive agricultural production, and herbicides are frequently used (Novak et al., 1998). Our objectives were to determine the seasonal occurrence and total export of five commonly used herbicides from a Coastal Plain watershed.

Materials and Methods

Study Area

The Herrings Marsh Run (HMR) watershed is located in the Cape Fear River basin of Duplin County, North Carolina, and is part of the Middle Coastal Plain physiographic region (Daniels et al., 1999). The landscape features, soil types, aquifers, and meteorological characteristics have been previously described (Novak et al., 1998). Briefly, the watershed contains well–drained sandy soils (Paleudults) in upland flat to rolling positions and contains poorly drained wetland soils (Fluvaquents) in riparian areas along streams. A shallow water table occurs between 1 to 2 m deep, and two principal aquifers are described (Surficial and Cretaceous) within the watershed. A typical, low–gradient, organic carbon–enriched black water stream system drains the watershed and contributes flow to larger tributaries of the Cape Fear River. The watershed is under intensive agricultural production, with 57% of the watershed area involved in agricultural activity. Although agriculture within the watershed has a heavy reliance on many different agricultural chemicals (Novak et al., 1998), we limited our investigation to five commonly used herbicides that had a well–established history of application (table 1). The 2312–ha HMR watershed was subdivided into four subwatersheds (SW1 to SW4) by observing drainage patterns in response to local relief (fig. 1).

Stream Grab Sampling

Stream grab sampling sites were located at the exit of the four subwatersheds as well as the watershed outlet (Red Hill in fig. 1). These samples were collected in midstream using amber–colored bottles. The bottles were initially washed with soap, rinsed with Milli–Q water, and then rinsed with methanol. Prior to sampling, the bottle and cap were rinsed three times with stream water. Samples were then packed in ice and transported back to the laboratory. In 1994 and 1995,

Table 1. Estimated quantities (kg a.i.) of select herbicides applied in the HMR watershed (estimates provided by the North Carolina Cooperative Extension Service).

Herbicide	1992	1993[a]	1994	1995
Alachlor	940	—	579	579
Ametryn	487	—	372	372
Atrazine	630	—	394	394
Cyanazine	33	—	70	70
Metolachlor	835	—	669	669

[a] No data available.

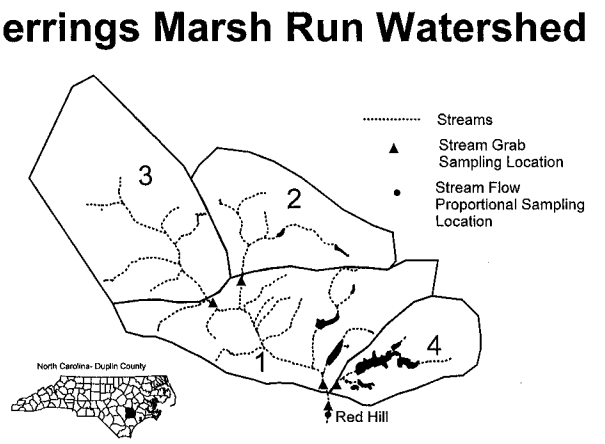

Figure 1. Stream system and location of grab and flow proportional sampling areas in the Herrings Marsh Run watershed of Duplin County, North Carolina (numerals are used to indicate subwatershed boundaries).

stream grab samples were collected weekly from March to October and then twice per month from November to February. This resulted in a total of 205 and 210 grab samples collected during 1994 and 1995, respectively. Seasonal pesticide detection trends were evaluated by segregating pesticide detects in grab samples during spring (March, April, and May), summer (June, July, and August), fall (September, October, and November), and winter (December, January, and February).

Flow Proportional Sampling

At the watershed outlet, a Sigma 800SL automated, refrigerated (7°C) flow–proportional sampler equipped with an integral flowmeter was established in July 1994 and samples were collected through December 1995. The sampler was programmed with a sequence to composite 14 subsamples per bottle after each 1288 m^3 of flow or every 204 minutes, depending upon which sequence occurred first. Flow readings were automatically determined every 15 minutes. The sampling sequence resulted in the collection of 346 flow–proportional samples from July 1994 until December 1995. The quantity of herbicides exported from the watershed was determined by multiplying the representative flow for each bottle by the concentration of each herbicide.

Analytical Procedures

Stream samples were extracted for the five compounds using methods outlined previously (Novak and Watts, 1996). Briefly, 50 mL of water was extracted using a Waters C_{18} solid phase extraction cartridge. The compounds were quantified with a Varian 3600 CX gas chromatograph (Walnut Creek, Cal.) equipped with a nitrogen and phosphorus detector. Our minimum detection limit for each compound was reported previously (Novak and Watts, 1996). Compounds detected in six samples were confirmed using gas chromatographic/mass spectrometric procedures described previously (Novak et al., 1998). The variation in predicted herbicide concentrations by these two instruments was usually <10%.

Results and Discussion

Watershed and Subwatershed Pesticide Detection Patterns

On a total watershed basis, we detected herbicides in approximately 15% of the grab samples over two years (n = 415, table 2). The percentages of grab samples containing one of the five herbicides (total sample basis) were: 6% for metolachlor, 4% for atrazine, 3% for cyanazine, 1% for ametryn, and 1% for alachlor. This suggests that metolachlor, atrazine, and cyanazine appear to be relatively more susceptible to off–site movement than ametryn or alachlor. Frequent detections of metolachlor, atrazine, and cyanazine were also reported in surface water sources across several Mid–Atlantic states (Ferrari et al., 1997; Holman et al., 2000).

Some physical and chemical properties of these five herbicides, which may explain their frequency of detection, are presented in table 3. Although metolachlor has a short half–life, its frequent detection may be due to its high rate of application (table 1), its high water solubility, and its low soil sorption coefficient (table 3). Atrazine detection may also be explained by its heavy use (table 1), low soil sorption coefficient, and long half–life. Although atrazine has lower water solubility, it is susceptible to off–site movement via runoff and leaching due to its long persistence and low soil sorption. In spite of low amounts of cyanazine application (70 kg a.i. yr^{-1}, table 1) and lower persistence, its medium water solubility and low soil absorption coefficient may contribute to its mobility and transport to surface water via runoff and leaching.

Table 2. Yearly number of herbicide detections in stream grab samples by subwatershed (SW) and at the HMR watershed outlet (Red Hill).

Location	Year	Total samples with herbicide detections[a]	Number of samples containing: 1 herbicide	2 to 6 herbicides
Red Hill	1994	7	7	0
	1995	5	4	1
SW1	1994	3	3	0
	1995	3	2	1
SW2	1994	9	9	0
	1995	21	10	11
SW3	1994	6	6	0
	1995	3	3	0
SW4	1994	3	2	1
	1995	1	1	0
Total	1994	28	27	1
	1995	33	20	13

[a] Total number of yearly grab samples collected at Red Hill and at each subwatershed outlet was 41 and 42 in 1994 and 1995, respectively.

Table 3. Average soil half–life, water solubility, and average soil sorption coefficient for the five herbicides (*Herbicide Handbook*, 1994).

Herbicide	Half–life[a] (days)	Water solubility (mg L^{-1})	Sorption coefficient K_{oc} (L kg^{-1})
Alachlor	21	200	124
Ametryn	60	200	300
Atrazine	60	33	100
Cyanazine	14	160	190
Metolachlor	15 – 25	488	200

[a] Determined in aerobic soil.

On the other hand, very few samples contained ametryn or alachlor, regardless of the high usage within the watershed (table 1). Only one surface water sample per thousand samples collected across several Mid–Atlantic states was reported to contain ametryn (Ferrari et al., 1997). Although ametryn has a comparatively long half–life, low ametryn detection in surface water samples may be explained by its high sorption coefficient (table 3). Alachlor behavior in the Coastal Plain region varies considerably since there is a large difference in the reported detection frequency in surface water samples collected across several Mid–Atlantic states. Alachlor was detected in 38% (n = 1692) of the surface water samples collected across several Mid–Atlantic states (Ferrari et al., 1997). In contrast, alachlor was not detected in a few hundred surface water samples collected across North Carolina (Holman et al., 2000). Our result of a low alachlor detection percentage is in agreement with a North Carolina study (Holman et al., 2000) and may be due to alachlor's rapid degradation in soil (Potter and Carpenter, 1995).

Collection of samples on a subwatershed basis revealed that pesticide detection variations did occur (table 2). Occasionally, herbicides were detected in stream grab samples at the outlets of SW1, SW3, SW4, and Red Hill throughout the time course. Primarily, the majority of these grab samples contained only one herbicide (table 2). In contrast, grab samples from the outlet of SW2, particularly in 1995, frequently contained a mixture of herbicides (50% in 1995, table 2). For instance, among the 42 samples collected at the SW2 outlet in 1995, atrazine and metolachlor were detected in 6 and 20 samples, respectively (table 4). Although atrazine and metolachlor were frequently detected at the outlet of SW2, sufficient assimilation by in–stream processes and/or stream water dilution had occurred because very low concentrations of these compounds were measured at the watershed outlet (Red Hill, table 4). The frequent atrazine and metolachlor detections are probably a subwatershed issue and may require some local modifications of pesticide management within the watershed.

We noted that one–half of the 1995 SW2 samples with herbicide detections contained a mixture of herbicides (table 2). This could be due to the high amounts of precipitation that fell soon after spring 1995 herbicide application. Approximately 60.8 cm of precipitation fell on the watershed from May 1 to July 31, 1995. Correspondingly, during this same time period, 7 of the 10 samples collected at the SW2 outlet contained a mixture of herbicides. The three samples containing a mixture of herbicides collected at the outlets of Red Hill, SW1, and SW3 were also collected within this same time period (table 2). The high amount of rainfall (48% of the yearly total) shortly after typical herbicide application probably produced sufficient runoff/leaching to transport several herbicides into the stream system.

Although herbicides were detected in stream water samples at each subwatershed outlet and at Red Hill, the mean concentrations of alachlor, ametryn, atrazine, cyanazine, and metolachlor were, in general, <0.9 μg L^{-1} (table 4). The mean atrazine, cyanazine, and metolachlor concentrations measured in this study are much less than the

Table 4. Number of stream grab samples containing a herbicide and mean, standard deviation, and maximum concentration measured in samples at the HMR watershed outlet (Red Hill) and at outlets of each subwatershed.

Location	Year	Pesticide	No. of grab samples with detections[a]	Concentrations (μg L^{-1}) Mean	Std. Dev.	Maximum
Red Hill	1994	Atrazine	4	0.17	0.01	0.18
		Cyanazine	1	—	—	0.10
		Metolachlor	2	0.55	0.06	0.59
	1995	Atrazine	1	—	—	0.15
		Alachlor	2	2.29	1.73	3.51
		Cyanazine	2	0.47	0.09	0.53
SW1	1994	Atrazine	2	0.23	0.04	0.26
		Cyanazine	1	—	—	0.13
	1995	Atrazine	1	—	—	0.20
		Cyanazine	2	0.45	0.27	0.64
SW2	1994	Cyanazine	4	0.39	0.29	0.81
		Metolachlor	5	0.39	0.08	0.53
	1995	Alachlor	1	—	—	0.61
		Ametryn	1	—	—	0.26
		Atrazine	6	0.59	0.31	1.15
		Cyanazine	4	0.30	0.22	0.63
		Metolachlor	20	0.86	0.79	3.92
SW3	1994	Ametryn	1	—	—	0.41
		Atrazine	5	0.42	0.16	0.59
	1995	Alachlor	1	—	—	1.02
		Ametryn	1	—	—	1.97
		Cyanazine	1	—	—	0.11
SW4	1994	Alachlor	1	—	—	0.45
		Atrazine	3	0.31	0.05	0.36
		Metolachlor	1	—	—	0.56
	1995	Metolachlor	1	—	—	1.01

[a] Total number of yearly grab samples collected at Red Hill and at each subwatershed outlet was 41 and 42 in 1994 and 1995, respectively.

3, 1, and 70 μg L^{-1}, respectively, adult lifetime advisory levels for these compounds (EPA, 1996). Only in one Red Hill sample out of 415 collected (0.2%) did we measure an alachlor concentration that exceeded the alachlor 2 μg L^{-1} maximum contaminant level (EPA, 1996). The low percentage of grab samples with detects, low mean herbicide concentrations, and a very small percentage of samples exceeding water quality standards imply minimal influence of these herbicides on stream water quality exiting the HMR watershed.

Seasonal Detection Patterns

Seasonal herbicide detection patterns occurred in grab samples on a watershed basis, but they did not occur in all subwatersheds (fig. 2). Pooling stream grab data across the entire watershed, we found that most herbicide detections in 1994 and 1995 (34% and 42%, respectively, total sample basis) occurred during the summer season. On a watershed basis, herbicides were also detected, but less frequently, during the spring, fall, and winter seasons.

On a subwatershed basis, only herbicide detections at the outlet of SW2 showed a strong seasonal trend (fig. 2). While herbicides were detected during all four seasons at the SW2 outlet (fig. 2), the highest percentage of herbicide detections (10% to 22%, total basis) in 1994 and 1995 occurred during the summer season. Our seasonal stream water herbicide detection pattern is similar to previous reports (Ferrari et al., 1997; Larson et al., 1997; Holman et al., 2000).

Herbicide Export from the Watershed

The flow–proportional sampler at the HMR watershed outlet was utilized to provide a better understanding of a continuous trend of herbicide exports (table 5). Although intensive amounts of some herbicides were applied in the watershed over the time course (table 1), few flow proportional samples were found to contain the five herbicides (7%, or 24 out of 346). Only two of the 24 flow–proportional samples contained a mixture of herbicides. The low percentage of flow–proportional samples containing the herbicides is fairly similar to the low percentage of herbicides detected in stream grab samples at the watershed outlet during 1994 and 1995 (Red Hill, 12% to 17%, table 2).

From July 1994 to December 1995, a very low mass of the five herbicides was exported from the HMR watershed (60.28 g). Metolachlor showed the greatest mass export (51.29 g), accounting for 85% of the total herbicide mass exported. Calculating the percentage of yearly applied herbicide lost from the HMR watershed showed that <0.01% of the applied herbicides were exported.

Conclusions

Herbicides were infrequently detected in surface water samples collected over a two–year period within an agriculturally intensive North Carolina Coastal Plain watershed. Among the stream grab samples that contained

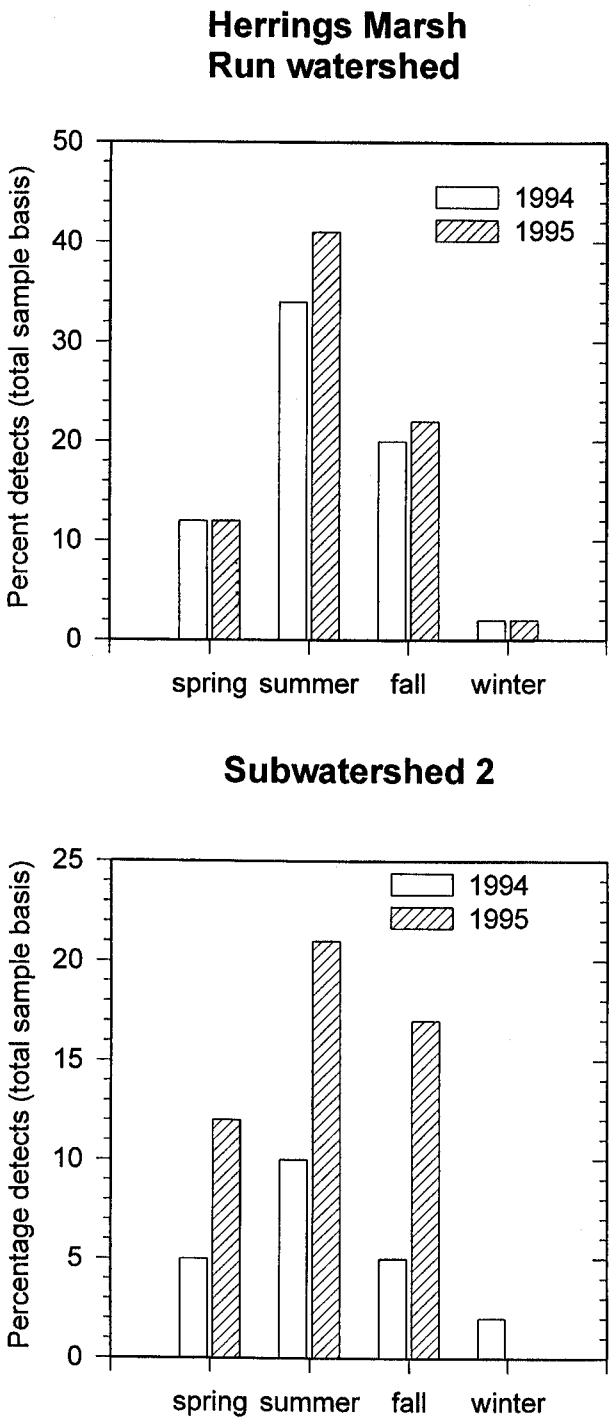

Figure 2. Seasonal herbicide detection pattern across the Herrings Marsh Run watershed and at the outlet of subwatershed 2 during 1994 and 1995.

herbicides, atrazine, cyanazine, and metolachlor were the most frequently detected. While herbicides were detected during the entire year, most detection occurred during the summer season. A very low mass of herbicide applied within the watershed was exported over the time course. Although toxicological tests or herbicide metabolite assay were not performed on stream samples, the low number of herbicide detects and the low concentrations in this continuously flowing stream system suggest that these five herbicides have had a minimal effect on the quality of water exiting this watershed. These results complement the reported conclusion of the groundwater study conducted in this watershed (Novak et al., 1998) in that the herbicides investigated pose a minimal threat to water quality in the Coastal Plain region of North Carolina.

Table 5. Herbicide detections, range of concentrations, and measured total grams of herbicides exported from the HMR watershed from July 1994 to December 1995.

Compound	No. of detections[a]	Concentration range ($\mu g\ L^{-1}$)	Total export (grams)
Alachlor	1	0.71	0.44
Ametryn	2	0.24	4.05
Atrazine	2	0.17	2.91
Cyanazine	10	0.10 – 0.57	1.59
Metolachlor	9	0.3 – 1.83	51.29
Total	24	—	60.28

[a] Total samples collected was n = 346.

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