PESTICIDE CONCENTRATIONS IN SHALLOW GROUND WATER AND SURFACE RUNOFF FOR LAND CROPPED TO CONVENTIONAL- AND NO-TILL SOYBEANS[1]

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INTRODUCTION

The Agricultural Research Service of the USDA has a ground and surface water quality protection program in which the general goal is to "assess what effect agriculture has on water quality and develop new agricultural management practices and systems that are cost effective and will protect and enhance water quality" (U. S. Department of Agriculture 1991). There is increased emphasis on increasing our knowledge/understanding of the fate and transport of agrichemicals in agricultural ecosystems. Another research emphasis area is the evaluation and optimization of no-till and other conservation tillage and residue management systems to increase soil organic matter, infiltration, and soil biological activity and to reduce runoff and erosion while controlling agrichemical buildup in ground water.

Increasing detections of agrichemicals in our Nation's aquifers have raised questions regarding the environmental costs of recommended farming practices such as conservation tillage. Conservation tillage practices initially require an increased use of herbicides to control weeds that are usually controlled with conventional tillage practices. Additionally, increased infiltration generally associated with conservation tillage is of concern because of the potential increased threat of contamination of these aquifers with agrichemicals. Information about the effects of conservation tillage practices on ground and surface water quality is lacking for most of Mississippi, particularly the loessial uplands in the northern part of the State. This paper discusses the USDA-National Sedimentation Laboratory's continuing efforts in this important research area and presents some of the findings to date regarding pesticide transport. Information about nutrient transport, water movement, and field instrumentation is presented in companion papers (Schreiber 1992; Cullum 1992).

MATERIALS AND METHODS

The study was conducted on the Nelson Research Farm located in the loessial uplands of northern Mississippi in Tate county near the town of Como. The fragipan soils are of the Grenada, Loring, and Memphis series. Runoff and shallow ground water sampling sites were established on a 2.14-ha watershed (WSHD 1) in the fall of 1989 and on an adjacent 2.10-ha watershed (WSHD 2) in the fall of 1990 (Figure 1). Each watershed had a mean slope of about 4% and had been in minimum-till soybeans during 1988 and 1989. Each runoff sampling site was instrumented for automatic data and discharge-weighted composite sample collection as described in detail by Grissinger and Murphree (1991) and Cullum et al. (1991). Three shallow ground water sampling sites were located along one edge of each watershed to minimize disturbance to the watershed via foot traffic during sampling (Figure 1). Detailed descriptions of the ground water sampling sites and of the runoff and ground water sampling and handling procedures were reported previously (Smith et al. 1991).

Pesticide analyses of soil, sediment, and water were also conducted as previously reported (Smith et al. 1991), with the following exceptions. The gas chromatographs were equipped with Dynatech Precision GC-411V autosamplers to facilitate unattended injection of samples. A PE Nelson 2700 chromatography data system, consisting of three model 970 interfaces, Turbochrom 3 software, and a microcomputer with color printer, was used for automated quantification and reporting of pesticide peak data including gas chromatograms. A multi-level calibration procedure was used with standards and samples injected in triplicate. Calibration curves were updated every tenth sample. Limits of detection were 0.05-0.5 ppb depending upon the pesticide.

In May 1990 and 1991, metribuzin (4-amino-6-*tert*-butyl-4,5-dihydro-3-methylthio-1,2,4-triazin-5-one, Lexone™) at 0.42 kg/ha and metolachlor [2-chloro-6'-ethyl-*N*-(2-methoxy-1-methylethyl)acet-*o*-toluidide, Dual™] at 2.24 kg/ha were applied broadcast by ground equipment to each watershed for preemerge weed control. In late May fertilizer (0-20-20) was also applied broadcast at 224 kg/ha in 1990 and at 280 kg/ha in 1991. Also in late May, WSHD 1 was no-till planted both years in soybeans [*Glycine max* (L.) Merr., Delta Pine 415] at 50-56 kg/ha. WSHD 2 was conventionally tilled both years just prior to soybean planting (same rate as WSHD 1). In mid-June of both years, each watershed was treated with a broadcast application of acifluorfen-sodium [sodium 5-(2-chloro-α,α,α-trifluoro-*p*-tolyloxy)-2-nitrobenzoate, Blazer™] at 0.28 kg/ha and bentazon [3-isopropyl-(1*H*)-benzo-2,1,3-thiadiazin-4-one 2,2-dioxide, Basagran™] at 0.56 kg/ha for postemerge weed control and with chlorpyrifos (*O,O*-diethyl *O*-3,5,6-trichloro-2-pyridyl phosphorothioate, Lorsban™) at 0.56 kg/ha for soil insect control. Sampling instrumentation was covered during pesticide and fertilizer applications. Aliquots of all spray tank mixes were obtained for confirmation of pesticide application rates.

Results and Discussion

Runoff

As reported previously (Smith et al. 1991), only 4 runoff-producing rainfall events occurred during the 1990 crop year, after the preemerge herbicides metribuzin and metolachlor were applied to WSHD 1 (no-till) and prior to soybean harvest in early October. Metribuzin and metolachlor concentrations in the water phase of runoff were 111 and 535 ppb (µg/L), respectively, 6 d after application (Table 1). By 27 d after application, these values had decreased to <3 ppb; by day 85, the herbicides were almost undetectable. A strikingly similar downward trend in concentrations was observed during crop year 1991 (Table 2). Metribuzin and metolachlor concentrations were 223 and 525 ppb, respectively, 5 d after application (first runoff-producing rainfall) and by day 103, neither herbicide could be detected in runoff water. However, total losses of metribuzin and metolachlor in runoff water during crop year 1991 were about 20 and 9%, respectively, of the amounts applied, or about 5 and 2.5 times the respective losses (about 4% for each herbicide) during crop year 1990. This can be explained by examining the runoff pattern each year. In both years, the first runoff event occurred within 1 w after herbicide application; however, the first runoff in 1991 was about 7 times the first runoff in 1990. By the time the second runoff event occurred each year (day 13 in 1990 and day 23 in 1991), less herbicide was available at the soil surface for runoff because of other loss factors such as biodegradation, leaching, and possibly volatilization and photodegradation. Although almost 60 mm runoff occurred in the second event in 1990, the loss was only about 2.5% of that applied for each herbicide.

In crop year 1991, herbicide concentrations and losses in the water phase of runoff from the no-till (WSHD 1) and conventional-till (WSHD 2) watersheds were almost the same (Tables 2 & 3). Metribuzin and metolachlor concentrations were highest in the first runoff event (4-5 d after application) and reached levels noted above for WSHD 1 and 241 and 590 ppb for WSHD 2. Total seasonal losses of the herbicides from the watersheds (20 and 9% metribuzin and metolachlor from WSHD 1 and 23 and 11% from WSHD 2, respectively) were similar also, but higher for WSHD 2 by a factor of about 1.2 for each herbicide. Total runoff from WSHD 2 (76 mm) during the growing season was greater than that from WSHD 1 (64 mm), also by a factor of about 1.2, accounting for the differences in solution-phase losses of the herbicides from the watersheds.

No metribuzin and metolachlor residues were detected in the sediment phase of runoff from WSHD 1 in either 1990 or 1991 because of the low sediment concentrations in runoff (about 35-550 mg/L, Tables 1 & 2). The relatively low organic carbon partition coefficients (Koc's) and relatively high water solubilities (S_{H_2O}'s) of metribuzin and metolachlor (Figure 2) resulted in these herbicides being transported in runoff almost entirely in the water (solution) phase. Metribuzin and metolachlor residues were detected in the sediment phase of runoff from WSHD 2 in 1991, because of the much higher sediment concentrations in runoff (about 7000-55,000 mg/L, Table 4) resulting from tillage operations (cultivations). Highest herbicide concentrations in sediment were about 90 and 312 ppb (µg/kg) for metribuzin and metolachlor, respectively, and occurred in the first runoff (4 d after application). Total seasonal herbicide losses in sediment, were only 0.1-0.2% of applied and again reflected the strong partitioning of the herbicides toward the solution phase of runoff. The increased sediment concentrations in runoff 22 and 63 d after herbicide application were the result of cultivations in June and July.

No residues of acifluorfen-sodium, bentazon, or chlorpyrifos were detected in runoff from events that occurred after their application in mid-June each year because the compounds were applied at reduced rates and had probably undergone extensive degradation by the time the first runoff event occurred (Smith et al. 1991).

Shallow Ground Water

Not all runoff-producing rainfall events produced shallow ground water for sampling as evidenced by the observation well data in Tables 5 & 6 for WSHD 1 in crop years 1990 and 1991, respectively, and in Table 7 for WSHD 2 in crop year 1991. Herbicide concentrations in the wells of WSHD 1 (both years) showed that both metribuzin and metolachlor rapidly move downward to the fragipan (about 0.6 m below soil surface) with the first rainfall event after herbicide application. Furthermore, the herbicides penetrated at least 0.9 m into the fragipan, particularly at site 1 (most upslope site) with concentrations reaching 46 and 151 ppb for metribuzin and 72 and 254 ppb for metolachlor in 1990 and 1991, respectively. Fragipan penetration by water (and solutes) may result from movement into "fingers" (polygonal seams) of more permeable material that naturally occur in the fragipan. Herbicide concentrations in ground water at sites 2 & 3 suggest substantial lateral movement of the herbicides downslope. The data further suggest some herbicide accumulation in the upper part of the fragipan as well as penetration into the fragipan. The other ground water-producing rainfall events in 1990 occurred 13 and 27 d after herbicide application resulting in water in 21 and 15 wells, respectively (Table 5). The rainfall on day 13 (112 mm) occurred only 1 w after the first rainfall, whereas the rainfall on day 27 (26 mm) occurred 2 w after the second rainfall, allowing the soil profile more time to dry between rainfall events. Herbicide concentrations were quite variable and randomly distributed both times from 0.15 m down to 1.5 m. In 1991, the other ground water-producing rainfall event in WSHD 1 occurred 23 d after herbicide application resulting in water in 6 of the 21 wells (Table 6). This second rainfall (59 mm) occurred >2 w after the first rainfall (71 mm), thus allowing the soil profile that time interval to dry. Again, herbicide concentrations were variable, with no distribution pattern evident other than general movement to and into the fragipan.

In 1991, the first ground water-producing rainfall event occurred only 4 d after herbicide application on WSHD 2. The herbicides penetrated the fragipan at the two uppermost sites (1 & 2) but remained above the fragipan at site 3 (Table 7). However, maximum herbicide concentrations found were <9 ppb regardless of depth. The second rainfall event, which produced runoff on both watersheds and ground water in WSHD 1, failed to produce ground water in any of the wells in WSHD 2.

Herbicide concentrations in shallow ground water decreased rapidly during the growing season. The next ground water-producing rainfall events did not occur until after soybean harvest in October of each year and no herbicides could be detected. Probable contributing factors were rapid herbicide biodegradation (short half-lives, $t_{1/2}$'s in Figure 2), movement of the herbicides out of the watersheds in lateral subsurface flow, and movement of the herbicides deeper into or possibly through the fragipan.

Conclusions

With regard to herbicides in runoff, losses were primarily dependent on the amount of runoff in the first runoff event after application and were independent of established tillage practice such as no-till, which reduced sediment loss by about two orders of magnitude compared to conventional tillage. Substantial herbicide losses (as much as 10-20%) resulted when 35 mm or more of runoff occurred within 1 w of broadcast (surface) applications of relatively water soluble herbicides such as metribuzin and metolachlor. With regard to herbicides in shallow ground water, the no-till practice provided a greater potential for herbicide leaching into the soil profile.

Current/Future Efforts

In the fall of 1991, deeper (3.0 m) observation wells were installed at all shallow ground water sampling sites. These wells penetrated an additional 1.5 m into the fragipan. In the spring of 1992 prior to soybean planting and herbicide applications, efforts will be made to install 6-m deep observations wells at all shallow ground water sampling sites. These wells will entirely penetrate the fragipan to the coastal plain sand (parent material) below. If any of the agrichemicals move through the fragipan, the potential for contamination of deeper, more permanent ground water increases dramatically. Laboratory studies are ongoing to determine the relative biodegradation rates of metribuzin and metolachlor in soil material taken from above, within, and below the fragipan. Future efforts include using FTIR (Fourier Transform Infrared Spectrometry) to characterize soil organic matter, as affected by tillage practice, and relate organic functional group analyses to herbicide leaching/retention.

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Agricultural and Forestry Experiment Station for their cooperation.

[1] *Mention of a pesticide in this paper does not constitute a recommendation for use by the U. S. Department of Agriculture nor does it imply registration under FIFRA as amended. Names of commercial products are included for the benefit of the reader and do not imply endorsement or preferential treatment by the U.S. Department of Agriculture.*

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Table 1

Herbicide concentrations and losses in water phase of runoff from WSHD 1 (no-till) during the 1990 crop year

Sampling Date	Time after applic. (days)	Sed. conc. (mg/L)	Runoff (mm)	Metribuzin Conc. (ppb)	Metribuzin Loss (g/ha)	Metribuzin Loss (% of applied)	Metolachlor Conc. (ppb)	Metolachlor Loss (g/ha)	Metolachlor Loss (% of applied)
5/14/90	6	37	5.41	110.7	5.95	1.41	534.6	28.74	1.28
5/21/90	13	54	59.94	17.7	10.54	2.51	93.9	55.94	2.49
6/04/90	27	134	4.22	2.4	0.10	0.02	16.5	0.69	0.03
8/01/90	85	204	2.46	0.3	0.01	0.00	1.2	0.03	0.00
						3.94			3.80

Application date = 5/08/90

Table 3

Herbicide concentrations and losses in water phase of runoff from WSHD 2 (conventional-till) during the 1991 crop year

Sampling Date	Time after applic. (days)	Sed. conc. (mg/L)	Runoff (mm)	Metribuzin Conc. (ppb)	Metribuzin Loss (g/ha)	Metribuzin Loss (% of applied)	Metolachlor Conc. (ppb)	Metolachlor Loss (g/ha)	Metolachlor Loss (% of applied)
5/27/91	4	20124	38.56	241.1	92.88	22.08	590.2	227.41	10.14
6/14/91	22	55055	26.24	10.2	2.69	0.64	70.4	18.45	0.82
7/26/91	63	42361	4.45	0.5	0.02	0.01	5.2	0.23	0.01
9/03/91	102	6957	5.69	0.2	0.01	0.00	0.9	0.05	0.00
						22.73			10.97

Application date = 5/23/91

Table 2

Herbicide concentrations and losses in water phase of runoff from WSHD 1 (no-till) during the 1991 crop year

Sampling Date	Time after applic. (days)	Sed. conc. (mg/L)	Runoff (mm)	Metribuzin Conc. (ppb)	Metribuzin Loss (g/ha)	Metribuzin Loss (% of applied)	Metolachlor Conc. (ppb)	Metolachlor Loss (g/ha)	Metolachlor Loss (% of applied)
5/27/91	5	204	35.94	223.2	79.78	18.96	524.8	187.56	8.36
6/14/91	23	551	21.74	11.0	2.38	0.54	24.9	5.38	0.24
7/26/91	64	143	3.71	1.2	0.04	0.01	2.4	0.09	0.00
9/03/91	103	154	2.18	0.0	0.00	0.00	0.0	0.00	0.00
						19.51			8.60

Application date = 5/22/91

Table 4

Herbicide concentrations and losses in sediment phase of runoff from WSHD 2 (conventional-till) during the 1991 crop year

Sampling Date	Time after applic. (days)	Sed. conc. (mg/L)	Runoff (mm)	Metribuzin Conc. (ppb)	Metribuzin Loss (g/ha)	Metribuzin Loss (% of applied)	Metolachlor Conc. (ppb)	Metolachlor Loss (g/ha)	Metolachlor Loss (% of applied)
5/27/91	4	20124	38.56	90.1	0.70	0.17	312.4	2.42	0.11
6/14/91	22	55055	26.24	4.5	0.07	0.02	11.3	0.16	0.01
7/26/91	63	42361	4.45	1.2	0.00	0.00	11.2	0.02	0.00
9/03/91	102	6957	5.69	2.4	0.00	0.00	9.3	0.00	0.00
						0.19			0.12

Application date = 5/23/91

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Table 5
Herbicide concentrations in shallow ground water
in WSHD 1 (no-till) for crop year 1990

	Depth	0.15m	0.3m	0.46m	0.6m	0.9m	1.2m	1.5m
		ppb						
5/14/90	Site							
Metribuzin	1	nw	nw	nw	nw	nw	7.0	46.3
	2	nw	nw	nw	99.2	1.2	0.0	0.0
	3	nw	nw	nw	nw	40.2	0.1	9.8
Metolachlor	1	nw	nw	nw	nw	nw	11.8	72.0
	2	nw	nw	nw	219.8	2.0	0.0	0.0
	3	nw	nw	nw	nw	270.0	1.1	28.4
5/21/90								
Metribuzin	1	13.7	10.4	0.4	12.0	0.2	1.1	15.2
	2	13.8	0.5	9.2	21.4	8.3	0.0	0.1
	3	5.4	0.4	0.2	0.2	9.4	1.2	2.0
Metolachlor	1	45.7	28.6	1.0	28.0	0.0	2.3	30.4
	2	57.8	1.0	18.8	64.6	22.7	0.0	0.0
	3	34.8	2.3	1.0	1.1	50.8	5.3	10.6
6/4/90								
Metribuzin	1	nw	nw	0.0	nw	0.1	0.6	3.6
	2	nw	0.0	1.4	4.8	1.1	2.7	0.0
	3	nw	nw	0.0	0.0	0.4	0.3	0.5
Metolachlor	1	nw	nw	7.7	nw	0.5	1.6	8.5
	2	nw	0.3	4.6	7.8	2.2	3.2	0.2
	3	nw	nw	0.3	0.2	3.7	2.7	4.7

Application date = 5/08/90
nw = no water in well

Table 6
Herbicide concentrations in shallow ground water
in WSHD 1 (no-till) for crop year 1991

	Depth	0.15m	0.3m	0.46m	0.6m	0.9m	1.2m	1.5m
		ppb						
5/27/91	Site							
Metribuzin	1	nw	nw	nw	nw	2.0	49.5	151.4
	2	nw	nw	nw	25.1	0.3	nw	2.1
	3	nw	nw	nw	30.4	43.0	28.1	6.8
Metolachlor	1	nw	nw	nw	nw	1.4	82.2	254.0
	2	nw	nw	nw	27.3	0.7	nw	3.1
	3	nw	nw	nw	72.3	68.2	38.5	10.7
6/14/91								
Metribuzin	1	nw	nw	11.5	nw	0.8	10.6	nw
	2	nw	nw	nw	nw	nw	nw	nw
	3	nw	nw	nw	nw	4.4	4.4	0.7
Metolachlor	1	nw	nw	22.3	nw	1.3	26.5	nw
	2	nw	nw	nw	nw	nw	nw	nw
	3	nw	nw	nw	nw	13.1	7.0	1.5

Application date = 5/22/91
nw = no water in well

Table 7
Herbicide concentrations in shallow ground water
in WSHD 2 (conventional-till) for crop year 1991

	Depth	0.15m	0.3m	0.46m	0.6m	0.9m	1.2m	1.5m
		ppb						
5/27/91	Site							
Metribuzin	1	nw	nw	nw	nw	5.8	0.3	2.2
	2	nw	nw	nw	nw	4.1	0.0	7.5
	3	nw	2.2	0.9	0.5	nw	nw	nw
Metolachlor	1	nw	nw	nw	nw	5.2	0.6	3.0
	2	nw	nw	nw	nw	3.9	0.4	8.2
	3	nw	1.9	0.6	7.9	nw	nw	nw
6/14/91								
Metribuzin	1	nw	nw	nw	nw	nw	nw	nw
	2	nw	nw	nw	nw	nw	nw	nw
	3	nw	nw	nw	nw	nw	nw	nw
Metolachlor	1	nw	nw	nw	nw	nw	nw	nw
	2	nw	nw	nw	nw	nw	nw	nw
	3	nw	nw	nw	nw	nw	nw	nw

Application date = 5/23/91
nw = no water in well

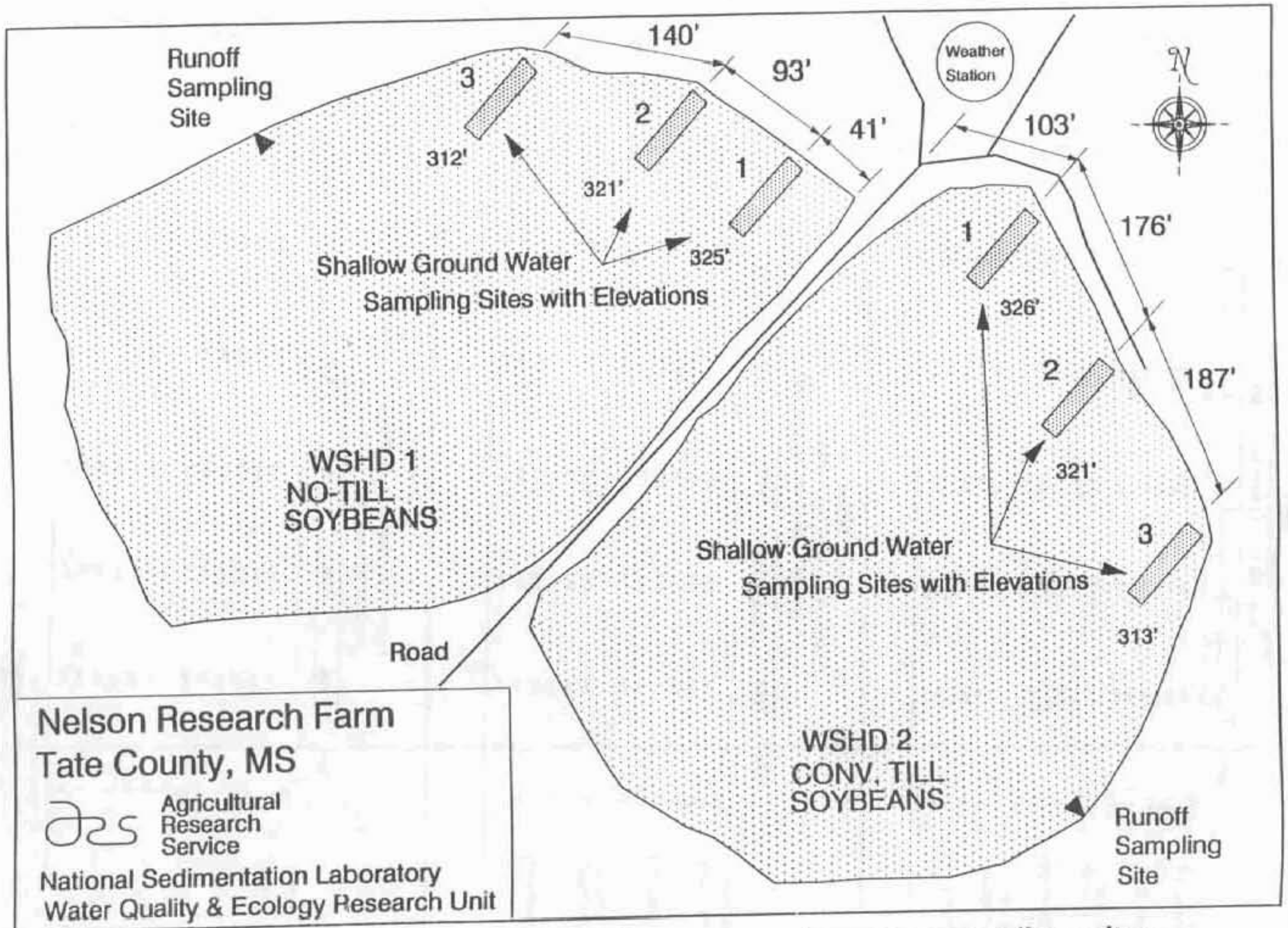
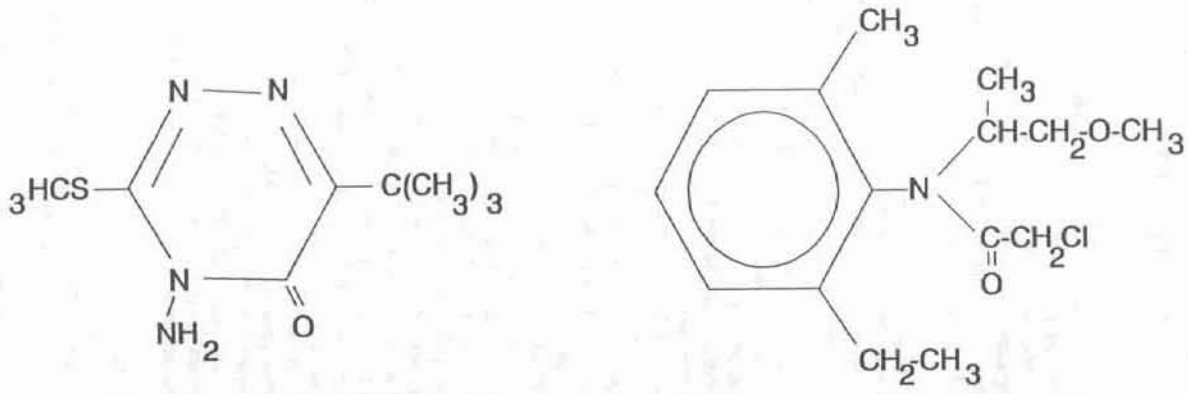


Figure 1. Watershed runoff and shallow ground water sampling sites.



METRIBUZIN	METOLACHLOR
S_{H_2O}=1200 ppm	S_{H_2O}=530 ppm
K_{oc}=24 cc/g	K_{oc}=181 cc/g
$t_{1/2}$= 30-60 d	$t_{1/2}$= 15-25 d

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Figure 2. Basic structures and selected properties of herbicides found.