HERBICIDE CONCENTRATIONS IN SHALLOW GROUND WATER AND SURFACE RUNOFF FOR LAND CROPPED TO NO-TILL SOYBEANS

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Introduction

Tremendous progress has been made in the last decade in biological pest control methodology such as using pest-resistant crop varieties, promoting the enhancement of natural pest predators and parasites, using pheromone traps, releasing sterilized pest insects, and applying microbial insecticides and herbicides (Bacillus thuringiensis and Phytophthora palmivora are examples) (Schweizer 1988; Smith et al. 1983). However, since the late 1940's, synthetic organic chemicals have been and still are used as the primary means for pest control to sustain agricultural production. The amount of active ingredients applied to croplands increased 170% between 1964 and 1982 (Moody 1990). Currently over 300,000 tons of chemical pesticides are annually applied to 330 million acres of cropland in the U.S. (U.S. Department of Agriculture 1988; U.S. Bureau of Census 1989).

Ground water surveys conducted during the last few years have revealed the contamination of some of the Nation's aquifers with both inorganic and organic compounds, several of which are used in agriculture. As better and more sensitive pesticide analytical methods were developed, the number and frequency of occurrence of different pesticides detected increased. Cohen et al. (1984) reported the occurrence of 12 pesticides in ground water in 18 states; and just 2 years later, this had increased to at least 17 pesticides in 23 states (Cohen et al. 1986). A recent report indicates the presence of 46 different pesticides in ground water samples from 26 states as a result of "normal" agricultural practices (Williams et al. 1988).

Since ground water is the source of drinking water for about half the population of the U.S., these increasing detections of pesticides in our aquifers have raised questions regarding the environmental costs of farming practices such as chemigation and conservation tillage. The impact on ground water quality of USDA decisions that promote the use of conservation tillage to control soil erosion is of major national interest and concern because: a) conservation tillage practices initially require an increased use of pesticides, particularly herbicides to control weeds that conventional tillage had previously controlled, and b) the higher infiltration rates generally associated with conservation tillage increase the potential of these pesticides to leach below the root zone to ground water (U.S. Department of Agriculture 1989; Leonard 1988). The USDA Research Plan for Water Quality has as its general goal the protection and enhancment of quality of the Nation's surface and ground waters while sustaining agricultural activities. Emphasis is on effects of conservation tillage practices on surface and ground water quality, with the objective to develop economically and environmentally sound crop production systems. This information is lacking for most of Mississippi, particularly the uplands of northern Mississippi. This paper discusses the National Sedimentation Laboratory's initial and ongoing efforts in this very critical research area and presents the pesticide data obtained thus far (i.e., for the 1990 crop year). Nutrient results and details of field instrumentation are presented in companion papers (Schreiber et al. 1991; Cullum et al. 1991).

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.

MATERIALS AND METHODS

The study was conducted on the Nelson Research Farm located in the loess hills of northern Mississippi near the town of Como. These fragipan soils are of the Grenada, Loring, and Memphis series. In the fall of 1989, runoff and shallow ground water sampling sites were established on a 2.14-ha watershed (WSHD 1 in Figure 1, mean slope about 4%) which had been in minimum-till soybeans during 1988 and 1989. The runoff sampling site was instrumented for

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automatic data and discharge-weighted composite sample collection as described elsewhere (Grissinger and Murphree 1991; Cullum et al. 1991). The three shallow ground water sampling sites were located along one edge of the watershed so as to minimize disturbance to the watershed surface via foot traffic during sampling. Each ground water sampling site consisted of seven porous ceramic-cup samplers (Soilmoisture Equipment Corp. model 1920) and seven observation wells (sampling piezometers) each at soil depths of 0.15, 0.30, 0.46, 0.61, 0.91, 1.22, and 1.52 m (i.e., 0.5, 1, 1.5, 2, 3, 4, 5 ft) placed within the crop row and spaced 0.9 m apart. The sampling interval in each well was from the bottom upward about 7.5 cm.

Metribuzin (4-amino-6-tert-butyl-4,5-dihydro-3-

methylthio-1,2,4-triazin-5-one, trade name Lexone) at 0.42 kg/ha and metolachlor [2-chloro-6'-ethyl-*N*-

(2-methoxy-1-methylethyl)acet-o-toluidide, trade name Dual] at 2.24 kg/ha were applied broadcast by ground equipment in early May 1990 for preemerge weed control over the entire watershed. In late May, 0-20-20 fertilizer was applied broadcast at 224 kg/ha, followed 3 days later by no-till planting of soybeans [Glycine max (L.) Merr., Delta Pine 415] at 50-56 kg/ha. In mid-June, the watershed was treated with a broadcast application of acifluorfen-sodium [sodium $5-(2-chloro-\alpha, \alpha, \alpha-trifluoro-p-tolyloxy)-2-nitrobenzoate,$ trade name Blazer] at 0.28 kg/ha and bentazon [3-isopropyl-(1H)-benzo-2,1,3-thiadiazin-4-one 2,2-dioxide, trade name Basagran] at 0.56 kg/ha for postemerge weed control and with chlorpyrifos (O, O-diethyl O-3, 5, 6-trichloro-2-pyridyl phosphorothioate, trade name Lorsban) at 0.56 kg/ha for soil insect control. Ceramic-cup samplers and observation wells were covered during pesticide applications. Aliquots (about 300 mL) of all tank mixes were obtained for confirmation of application rates. None of these pesticides had previously been applied to this watershed.

Usually within 12 h of a rainfall event, the composite runoff sample, which was collected, was transported in its stainless steel container (40-L capacity) to the National Sedimentation Laboratory (NSL) and stored at 4°C (usually <72 h) for pesticide and other analyses. Each ceramic-cup sampler was pumped dry, the water being discarded; and 30 KPa tension was applied to the sampler. Each observation well was also pumped dry and the water, discarded. About 12-16 h later, the water (usually 0.1-0.3 L) in each ceramic-cup sampler was collected (by applying pressure to the sampler with a small hand pump) in a 1-L amber glass bottle with teflon-lined screw cap. At

about the same time, the depth to water in each observation well was measured and recorded; a 1-L sample was collected from each well (using a small, hand-operated vacuum pump with teflon intake line) in a 1-L bottle as just described. Excess well water was discarded. Shallow ground water samples were immediately transported to the NSL and also stored at 4°C (usually <72 h) for pesticide and other analyses.

Runoff and ground water samples were allowed to come to room temperature (about 25°C) and Millipore filtered at 0.45 µm. For metribuzin, metolachlor, and chlorpyrifos analyses, a 100-mL aliquot of the water phase was removed from each by volumetric pipette. To each aliquot was added 1 g reagent-grade KCI and 25 mL pesticide-grade EtOAc. Pesticide extraction was accomplished by sonification for 1 min, partitioning in a separatory funnel, and discarding the The EtOAc phase was dried over water phase. anhydrous Na_2SO_4 and brought to an appropriate volume for gas chromatographic analysis. The sediment (in runoff samples) from Millipore filtration was oven-dried (105°C, 16 h), weighed, and extracted with 100 mL distilled water, 1 g reagent-grade KCI, and 25 mL pesticide-grade hexane by sonification for 1 min. The mixture was partitioned in a separatory funnel and the water phase was discarded. The hexane phase was dried over anhydrous Na2SO4 and brought to an appropriate volume for gas chromatographic (gc) analysis.

Pesticide extracts were analyzed using a Tracor Model 540 gc equipped with Ni63 electron capture detector, a Hewlett-Packard model 3396A integrator, and a 15 m X 0.53 mm J & W Scientific DB 210 (1.0 µm film thickness) column. The carrier gas was ultra-high purity helium at 12.7 cc/min and the column makeup and detector purge gas was ultra-high purity nitrogen at 60 and 10 cc/min, respectively. Column oven, inlet, and detector temperatures were 180, 240, and 350°C, respectively. Under these conditions, retention times were 1.54, 2.02, and 3.17 min for metribuzin, chlorpyrifos, and metolachlor, respectively. Mean extraction efficiencies, based on fortified samples, were >90% for all three pesticides from both water and sediment. Pesticide residues were confirmed with a Tracor model 702 nitrogen-phosphorus detector.

Acifluorfen-sodium was extracted from acidified water and/or sediment with ethyl ether and determined as its methyl derivative according to the method of Adler et al. (1978). Mean recoveries, based on fortified samples, were 83-85%.

Bentazon was extracted from water and/or sediment with pesticide-grade EtOAc and determined as its

pentafluorobenzyl derivative according to the method of Gaynor and MacTavish (1981). Mean recoveries, based on fortified samples, were 85-88%.

RESULTS AND DISCUSSION

Pendimethalin[*N*-(1-ethylpropyl)-2,6-dinitro-3,4xylidine, trade name Prowl] and fluazifop-butyl {butyl (*RS*)-2-[4-(5-trifluoromethyl-2-pyridyloxy)phenoxy] propionate, trade name Fusilade} had been applied to WSHD 1 in late spring of 1989, prior to our study, but no residues of either of these herbicides or of any other pesticides could be detected in runoff and shallow ground water samples collected between the fall of 1989 and early May of 1990 when metribuzin and metolachlor were applied. For the 1990 crop year, shallow ground water samples for pesticide analyses were obtained from wells only.

There were only 4 runoff-producing rainfall events after metribuzin and metolachlor application in early May and prior to soybean harvest in early October (Table 1). The highest herbicide concentrations observed in discharge-weighted runoff samples were 111 and 535 µg/L (ppb) metribuzin and metolachlor, respectively, and occurred in the water phase of the first runoff only 6 d after application. These water-phase concentrations decreased rapidly for the first 30 d after herbicide application, and by 85 d (last runoff-producing rainfall event) were only 0.3 and 1.2 µg/L, respectively, each equivalent to <1% of the concentrations observed on day 6 (Figure 3). The next runoff occurred after harvest, but no herbicide residues could be detected (data not shown). The greatest runoff losses of metribuzin and metolachlor were about 11 and 56 g/ha, respectively, and occurred 13 d after application as a result of the largest runoff event (about 60 mm). These losses were solely in the water phase and represent 63% and 65%, respectively, of the total runoff losses of about 17 and 85 g/ha for the crop year. The total runoff losses of metribuzin and metolachlor, expressed as % of applied, were about the same, i.e. about 4%. Individual storm losses, expressed as % of applied, were also about the same for the two herbicides and result from a combination of factors. The water solubility of metribuzin (1200 mg/L) is 2.26 times that of metolachlor (530 mg/L) (Royal Society of Chemistry, 1987). However, metolachlor was applied at 5.33 times the application rate at which metribuzin was applied. For recommended application rates, the average field persistence of metolachlor (t1/2=15-25 d) is about one-half that of metribuzin (t1/2=30-60 d) (Weed Science Society of America 1983).

Another factor to consider is the organic carbon partition coefficient (K_{OC}) for each compound. The K_{OC} is an adsorption constant based on the fraction of organic carbon in the soil and is calculated from the adsorbed pesticide mass per unit mass of soil (C_S , usually in g/g) divided by the product of the pesticide concentration in solution in equilibrium with the soil mass (C_W , usually in g/cc) and the fraction of organic carbon in the soil (OC) (Leonard and Knisel 1988). The reported K_{OC} 's of 24 cc/g for metribuzin and 181 cc/g for metolachlor indicate a greater tendency for metribuzin to be partitioned toward the soil solution than metolachlor (Jury et al. 1987).

No metribuzin and metolachlor residues were found in the sediment phase of runoff, probably because of their relatively high water solubilities and relatively low Koc's compared to other pesticides which tend to partition more toward the soil/sediment mass. Also, sediment concentrations in runoff from this no-till watershed were relatively low (< 200 mg/L) for each of the 4 runoff events. No residues of acifluorfen-sodium, bentazon, or chlorpyrifos were detected in runoff from the single event which occurred 48 d after their application. In addition to having been applied at reduced rates, acifluorfen-sodium ($t_{1/2}$ =30-60 d) and bentazon (persistence< 6 w) had probably undergone extensive degradation by the time runoff occurred (Weed Science Society of America 1983). Chlorpyrifos, with its low water solubility (2 mg/L) and high $\rm K_{OC}$ (6070 cc/g), would not be detectable in runoff with very low sediment loads (Royal Society of Chemistry 1987; Jury et al. 1987).

Only three ground water-producing rainfall events occurred after metribuzin and metolachlor application (Table 2). No ground water resulted from the rainfall that produced the last runoff event in Table 1. On 5/14/90, only 9 of the 21 wells contained sufficient ground water for sampling. Metribuzin and metolachor concentrations were highest at site 1 at the 1.52-m depth, indicating significant movement of the herbicides into the fragipan, possibly in the polygonal seams. Herbicide concentrations at sites 2 and 3 were highest at the 0.61-m and 0.91-m depths, respectively, and may have resulted from water accumulating at the top of the fragipan after lateral movement downslope (Grossman and Carlisle, 1969). On 5/21/90, all 21 wells contained sufficient water for sampling but no pattern of herbicide distribution in the wells was apparent. At site 1, herbicide concentrations were higher at the 0.15-m, 0.30-m, 0.61-m, and 1.52-m depths, with relatively small amounts at the other 3 depths. At site 2, the higher

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herbicide concentrations were found at the 0.15-m, 0.46-m, 0.61-m, and 0.91-m depths; and at site 3, at the 0.15-m, 0.91-m, and 1.52-m depths. On 6/4/90, sufficient water for sampling was found in 15 wells, and the highest herbicide concentrations were at the 1.52-m depth at site 1, the 0.61-m depth at site 2, and the 1.52-m depth at site 3.

Metribuzin concentrations in shallow ground water for each sampling date, site, and well depth, were always lower than metolachlor concentrations. Therefore, relative application rate must be more important than relative water solubility and relative average field persistence, at least in this study. Nothing more should be said about distribution patterns of these two herbicides in the shallow ground water until several more years of data are collected for this no-till soybean watershed and for a companion conventional-till watershed nearby. Hopefully, more complete sets of samples for each sampling date will be obtainable.

Both metribuzin and metolachlor rapidly disappeared from the shallow ground water (Figure 4). The mean ground water concentrations for all sampled sites and depths on 5/14/90 (6 d after application) were 23 and 67 µg/L of metribuzin and metolachlor, respectively. On 6/4/90 (27 d after application), these mean concentrations had decreased to 1 and 3 µg/L, respectively. The most likely cause was extensive biodegradation. Other factors contributing to this rapid disappearance may have been: a) movement of the herbicides out of the watershed in lateral subsurface flow across the top of the fragipan and, b) movement of the herbicides deeper into or possibly through the fragipan. Herbicides moving across the top of the fragipan could manifest themselves in surface flow at some point downslope. Herbicides moving deeper into the soil profile have a higher potential for contaminating permanent ground water because of reduced microbial activity and biodegradation rates at greater depths (Federle, et al. 1986; Moorman and Harper 1989). In order to discern this, deeper ground water and extensive soil sampling, quantitation of subsurface water flow, and mapping of the fragipan surface by ground-pentetrating radar are planned for the 1991 and succeeding crop years.

No measureable ground water resulted from rainfall events which occurred after acifluorfen-sodium, bentazon, and chlorpyrifos application in mid-June.

Thus far in this research, none of the herbicide concentrations found in surface runoff and shallow ground water appear to present any water quality problems. The ten-day health advisory for drinking water is defined as "the concentration of a chemical in drinking water that is not expected to cause any adverse noncarcinogenic effects up to 14 consecutive days of exposure, within a margin of safety," and for metribuzin and metolachlor, respectively, is 5000 and 2000 μ g/L (U. S. Environmental Protection Agency, 1989). The analogous lifetime health advisories are 200 and 100 μ g/L, respectively, and are based on a 70-kg adult human drinking 2 L water per day over a lifetime, within a margin of safety (i.e., considering uncertainty and relative source contribution factors).

In summary, metribuzin and metolachlor concentrations in runoff water and shallow ground water were initially relatively high but decreased rapidly to almost undetectable levels. The importance of rainfall timing relative to pesticide application is re-emphasized. The inconclusiveness of the results of this 1-crop-year study reinforces the need for additional years of data for this and other tillage systems and the need for deeper ground water sampling, quantitation of shallow ground water movement, and comprehensive soil sampling. Information about the effects of conservation tillage practices on pesticide transport in surface runoff and percolation to shallow ground water is needed for development of improved agrichemical transport models and resulting agrichemical management systems.

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