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EFFECT OF LAND APPLICATION OF POULTRY WASTE ON PESTICIDE LOSS

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ABSTRACT

EFFECT OF LAND APPLICATION OF POULTRY WASTE ON PESTICIDE LOSS

The poultry industry in Arkansas is a large, concentrated, growing industry that produces a high volume of fecal waste. Most of this waste is surface applied as pasture fertilizer. Pesticides are commonly used in the poultry industry for fly and litter beetle control and are often a component of the surface-applied poultry waste. No information exists in the scientific literature regarding the transport of this pesticide component to nearby water supplies. Our research focused on cyromazine, a feed-through larvicide used to control flies in caged-layer hen houses. Tetrachlorvinphos and carbaryl are also used in poultry waste, but these pesticides have a relatively low solubility in water and rapid decomposition rate. Cyromazine, however, is highly soluble and stable in water. Since it may be readily washed from the pasture by heavy rainfall and may persist in surface and soil water, cyromazine appears to be potentially a much greater long-term threat to water quality than either carbaryl or tetrachlorvinphos. Therefore, the objective of this investigation was to examine the extent of cyromazine loss as a result of land application of caged layer manure. To quantify cyromazine loss from pasture plots treated with caged layer manure, research was conducted at the University of Arkansas Agricultural Experiment Station at Fayetteville. Plots of uniform slope were bordered to isolate surface

runoff, fitted with runoff collectors, and established in fescue pasture. Suction lysimeters were placed at the 60 cm depth to sample soil water in the unsaturated zone. Caged layer manure was analyzed for cyromazine concentration and applied to the plots at three different rates. Rainfall was applied by simulator at two intensities. Surface runoff and lysimeter samples were measured and analyzed for cyromazine concentration. A solid phase extraction procedure was used to separate the cyromazine from the water samples and analysis was done by high performance liquid chromatography (HPLC). Results showed that a heavier manure application increased both the runoff and cyromazine concentration. Higher rainfall intensity also increased total cyromazine loss in the runoff, but provided enough runoff volume to decrease the cyromazine concentration. Soil water from the unsaturated zone was monitored for a year following the manure application, but neither cyromazine nor its metabolite, melamine, were detected.

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Keywords -- Agriculture / Pesticides / Water Quality / Poultry Waste / Surface Runoff / Solute Transport / Leaching

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INTRODUCTION

The poultry industry has recently become the focus of environmental concern because its operations tend to be heavily localized in certain areas of the country and produce a high volume of concentrated fecal waste. In 1990, United States poultry farms produced a total farm value of nearly 15 billion dollars worth of poultry and eggs (NASS, 1991) but also produced approximately 13 million metric tons (dry weight) of poultry fecal waste. Most of this production was concentrated in the southern part of the country. The states of Arkansas, Georgia, North Carolina, and Alabama together produced over 41% of the total. Arkansas led the nation in 1990 by producing over 950 million broilers, 3.6 billion eggs, 22 million turkeys, and approximately 1.7 million metric tons (dry weight) of poultry fecal waste (USDA, 1991).

The poultry fecal waste is most commonly surface-applied to pastures at a rate sufficient to meet the fertilizer needs of the forage being produced. This rate is usually about 2-5 tons/acre (dry weight). Such practices may cause water quality problems, especially if a heavy manure application is closely followed by an intense rainfall. Although the pasture runoff is most likely to affect surface water, the ground water may also be vulnerable, particularly in regions such as northwestern Arkansas where the soil tends to be shallow and the underlying limestone bedrock may be fractured (karstic).

Land-applied poultry manure contains several substances and organisms that may cause water quality problems, including carbon, nitrogen,

phosphorus, pathogens, and sometimes pesticides. All these have been investigated, at least to a limited extent, except pesticides.

Several pesticides are commonly used in the poultry industry to control insect populations that develop due to dense animal confinement. Cyromazine (N-cyclopropyl-1,3,5-triazine-2,4,6-triamine), a feed-through larvicide marketed under the trade name Larvadex, is commonly used in caged layer operations to control manure-breeding flies. This compound, when added to the hen feed at a rate of 5 ppm and excreted in the manure, prevents maturation of fly larvae (Miller and Corley, 1978). Carbaryl (Sevin) (1-Naphthyl-N-methylcarbamate) and tetrachlorvinphos (Rabon) (2-chloro-1(2,4,5-trichlorophenyl)-vinyl dimethyl phosphate) are used to control litter beetles that develop during broiler production.

Due to limited finances and work force, we selected one pesticide as the primary focus of our research. Cyromazine was chosen for the following reason: it shows much greater water solubility and environmental persistence than either of the other pesticides considered in this study. Water solubility is 13,600 ppm for cyromazine (CIBA-GEIGY Corporation, 1990) compared to 40 ppm for carbaryl and 11 ppm for tetrachlorvinphos (Leistra, et al. 1984). The half-life in aerobic soil is approximately 140 days for cyromazine (CIBA-GEIGY Corporation, 1990), but only 11 days for tetrachlorvinphos, while carbaryl decomposed completely in 53 days (Odeyemi, 1982). Under anaerobic conditions cyromazine is stable (CIBA-GEIGY Corporation, 1990), but carbaryl disappears completely in 42 days (Odeyemi, 1982). These characteristics potentially make cyromazine a much greater

long-term threat to water quality than either carbaryl or tetrachlorvinphos.

A. Purpose and Objectives.

The general objective of this research was to examine the extent of cyromazine loss as a result of land application of caged-layer manure. To accomplish the general objective, we had the following subobjectives.

1. Characterize and describe cyromazine loss under controlled field conditions using simulated rainfall.

2. Monitor a field scale watershed for loss of cyromazine in runoff under natural rainfall conditions.

B. Related Research and Activities.

Field and controlled research data are completely lacking regarding pesticide loss as a function of land application of poultry waste. Because of this, pertinent literature regarding the environmental chemistry and fate of these compounds in the environment will be reviewed.

Cyromazine (Larvadex) is very soluble in water (13.6 g/L) and exhibits relatively low adsorption capacity [K_{ds} (1-5)] for soils low in organic matter (CIBA-GEIGY Corporation, 1990). Cyromazine can persist for relatively long periods of time compared to other pesticides. Brake et al. (1991) found that cyromazine continued to be active in caged layer manure 20 weeks after it was removed from the food supply. Persistence in the environment depends upon environmental conditions. Under aerobic conditions the half-life ($t_{1/2}$) in soils has been shown to be approximately 142 days; however, under anaerobic

conditions the compound is considered stable. Lim et al. (1990) reported that when cyromazine does break down, the primary metabolite produced is melamine (1,3,5-Triazine-2,4,6-triamine). Unfortunately, little is known concerning the fate of this compound in the aqueous environment.

Solubility of carbaryl in water is approximately 40 ppm. The compound is relatively unstable in the environment and is degraded predominantly by abiotic alkaline hydrolysis (Thomson and Strachan, 1981, Stanley and Trial, 1980). Odeyemi (1982) found in an incubation study that carbaryl disappeared in sewage water, agricultural soil, and fresh water after 42, 53, and 60 days, respectively. Carbaryl is also removed from aqueous solution by adsorption onto sediment and bottom mud (Mount and Oehme, 1980).

Information on tetrachlorvinphos is limited. Solubility in water is reported to be 11 ppm with decomposition following first order rate kinetics (Leistra, et al., 1984). Half-life in soil is estimated to be less than 11 days.

Methods and Procedures

Plots of uniform slope (5%) were established at the University of Arkansas Agricultural Experiment Station in Fayetteville on a Captina silt loam (fine-silty, mixed, mesic Typic Fragiudult). Each plot was 1.5 m wide (across the slope), 6 m long (down the slope), and was established in tall fescue grass (Festuca arundinacea) to simulate pasture. Each plot was also surrounded by a metal border to isolate the plot runoff water and was fitted

with a runoff collector as described by Edwards and Daniel (1993).

Manure samples were taken several times during the year at the caged layer operation that supplied the manure for the research plots. Cyromazine was fed to the layers only during the late spring and summer when flies become a serious problem. All caged layer manure samples were analyzed for cyromazine and melamine to characterize the concentrations of these compounds in the manure pit. The caged layer manure was also sampled and analyzed before being applied to the plots. It was found to be 88% water by weight. The manure was applied manually to the surface of the plots as uniformly as possible at rates of 0, 4.43, and 17.71 Mg ha⁻¹ (dry weight) or 0, 36.9, and 147.6 m³ ha⁻¹ (wet volume).

To reduce variability in the soil water content, all plots were saturated with water using low intensity irrigation and allowed to drain for 96 h before manure application. The manure was applied and allowed to dry for 24 hours prior to the rainfall event. Rain was applied at rates of 50 mm h⁻¹ for 30 minutes of runoff (low intensity) and 100 mm h⁻¹ for 30 minutes of runoff (high intensity) using a simulator described by Edwards et al. (1992).

The experiment had two levels of rainfall intensity and three levels of manure application, with three replications of each treatment, for a total of 18 plots. Treatments were assigned to plots in a randomized block design, and the plots with the zero manure application rate served as the controls.

Discrete runoff samples were collected in clean polyethylene containers at five-minute intervals during runoff. The sample volumes and the times required to take the samples were recorded. This information was used to

develop hydrographs, calculate runoff amounts, and construct flow-weighted composite samples from the discrete samples. All composite samples were stored in amber glass bottles in the dark at 4°C until extracted and analyzed.

Water samples were taken from the unsaturated zone in the soil profile by using porous pan microlysimeters installed at a depth of 60 cm beneath the surface of the plots. Soil water was sampled only from beneath the plots with 0 and 17.71 Mg ha⁻¹ manure applications and receiving the high rainfall intensity. The discrete soil water samples from each of these plots were composited (flow weighted) and analyzed at two-week intervals.

All composite water samples were analyzed for the presence of cyromazine and melamine using an adaptation of the procedure described by CIBA-GEIGY Corporation (1989). Samples were first centrifuged to remove all solid particles. Cyromazine and melamine were separated from the liquid by solid phase extraction. Concentrated acetic acid (0.82 mL) was first added to the 40 mL aliquot of water sample to make a 2% acetic acid solution. A disposable extraction column (Bakerbond spe, sulfonic acid, 3 mL) was fitted on a vacuum manifold (Baker spe-10), and a large reservoir column (75 mL) was attached. The column was conditioned with 3 mL of 2% (v/v) acetic acid/deionized water, pulled through with low vacuum pressure at 1-2 drops s⁻¹. The wash was discarded. Then, the sample was loaded into the reservoir column and pulled through at a rate of 2-3 mL min⁻¹. The eluate was discarded. The column packing was washed with 20 mL of 90% (v/v) methanol/water. This wash was pulled through at a rate of 2-4 drops s⁻¹ and

discarded. A second wash consisting of 10 mL of pure methanol was pulled through at a rate of 2-4 drops s^{-1} and discarded. The cyromazine and melamine were then eluted from the column with 10 mL of 5% (v/v) ammonium hydroxide/methanol. The eluate was pulled through at a rate of about 2 drops s^{-1} , collected in a volumetric flask (10 mL), transferred to a test tube, and evaporated to dryness in a 40°C analytical evaporator (N-Evap). The residue was then dissolved in 1.5 mL of 95% (v/v) acetonitrile/water and transferred to a 2 mL sample vial. Analysis was done by high performance liquid chromatography (HPLC), using a Zorbex NH_2 column. The mobile phase was 95% acetonitrile and 5% water. The injection volume was 50 μL , wavelength was 214 nm, the absorbance units for full scale (AUFS) were 0.1, and flow rate was 2 mL min^{-1} . The retention times were approximately 3.44 and 5.24 min for cyromazine and melamine, respectively.

Monitoring of a field scale watershed was done by placing an autosampler in a channel of the surface runoff from a field treated with caged layer manure. Samples were collected during runoff events caused by natural rainfall and analyzed for the presence of cyromazine and melamine.

Principal Findings and Significance

For this research project, a better method for extracting cyromazine and melamine from water samples was needed. A solid phase extraction procedure was developed, obtaining faster and more complete recoveries.

Samples of the caged layer manure taken in March 1991, approximately six months after the cyromazine was removed from the feed ration, indicated that concentrations of cyromazine and melamine had fallen below the detection limit. By late May 1991, when cyromazine had been added continuously to the feed ration for approximately six weeks, the cyromazine concentration detected in the manure was 4 mg L^{-1} . The manure applied to the research plots in August 1991 contained cyromazine at a concentration of $633 \text{ } \mu\text{g L}^{-1}$, but no melamine.

Results showed the mean runoff for the control plots was 3.5 and 19.9 mm for the low (50 mm h^{-1}) and high (100 mm h^{-1}) rainfall intensity, respectively (Fig. 1). Based on the least significant difference test, plots receiving the high intensity rainfall had significantly ($\alpha=0.1$) more runoff than plots receiving the low intensity rainfall at all rates of manure application. At the high rainfall intensity, plots with manure applied had significantly

($\alpha=0.1$) more runoff than plots that received no manure. At the low rainfall intensity, only plots receiving 17.71 Mg ha⁻¹ manure applications had significantly ($\alpha=0.1$) more runoff than the plots receiving no manure.

The mean cyromazine concentration in runoff from plots receiving the high intensity rainfall was significantly ($\alpha=0.1$) lower than from plots with the same manure application, but receiving the low intensity rainfall (Fig. 2). This held at both levels of manure application. The cyromazine concentration was significantly ($\alpha=0.1$) higher in runoff from plots receiving the heavier manure application despite the rainfall intensity. No cyromazine was found in the runoff from any of the control plots, and melamine was not detected in any of the runoff samples. The mean total cyromazine loss in runoff during the simulated rainfall event was significantly ($\alpha=0.1$) greater for plots receiving the heavier manure application despite the rainfall intensity (Fig. 3). At a given manure application rate, the total cyromazine loss in runoff was generally greater for plots receiving the high intensity rainfall, but the difference was significant ($\alpha=0.1$) only at the 17.71 Mg ha⁻¹ manure rate.

The cyromazine lost in runoff also was compared (as a percentage) to the total amount of cyromazine applied to the plot in the manure. For example, the average cyromazine loss from plots receiving the 4.43 Mg ha⁻¹ manure rate was 10.5 and 23.0% for the low and high rainfall intensities, respectively (Fig. 4). At a given manure application rate, the percent cyromazine loss in runoff was significantly ($\alpha=0.1$) higher for plots receiving the high

intensity rainfall than for plots receiving low intensity rainfall. For a given rainfall intensity, the different manure application rates showed no significant difference ($\alpha=0.1$) in the percent cyromazine loss in runoff.

Soil water from the unsaturated zone beneath the plots was monitored for a year following the manure application and simulated rainfall event. Neither melamine nor cyromazine was found in any soil water sample. The detection limit was $5 \mu\text{g L}^{-1}$.

Results of the field scale watershed study are inconclusive at this time. The owner of the field fertilized his pasture with caged layer manure in March. Since flies are not a problem during the cold season, the hens that produced this manure had not received any cyromazine for the previous six months. Analysis of the manure and field runoff samples gave no detection of cyromazine or its metabolite, melamine. If the field owner had used manure produced during the cyromazine feeding season, the results might have been quite different. However, since the maximum annual rate of fertilizer had already been applied to the field, we were unable to reapply manure during the cyromazine season to look at these results.

Conclusions

The concentration of cyromazine in the caged layer manure fluctuated widely during the year, depending on when and for how long it was added to the feed ration. When cyromazine was present in manure spread on a pasture surface and a runoff event occurred soon after the manure application, some cyromazine was dissolved and transported in the runoff.

Wauchope (1978) reviewed published reports of pesticide runoff losses from agricultural land in the United States. He classified as catastrophic any runoff event in which more than 2% of the applied active ingredient was lost in the runoff. This indicates that the cyromazine losses detected in this experiment (up to 23.7%) are rather large losses when compared to other pesticides.

Heavier manure applications increased runoff, cyromazine concentration in the runoff, and consequently total cyromazine loss in the runoff. Since the manure was 88% water, it provided considerable soil moisture prior to the rainfall event. This may explain the increased runoff that resulted. A heavier manure application apparently provided enough additional cyromazine to produce higher concentrations even for this larger volume of runoff.

Higher rainfall intensity increased runoff, total cyromazine loss, and the percent cyromazine loss from the pasture. The higher rainfall intensity provided a greater volume of available surface water to dissolve the cyromazine and transport it from the pasture. This allowed greater dilution of the cyromazine and thus decreased its concentration in the surface runoff.

However, the increase in the volume of runoff was so large that the net effect was a substantial increase in the cyromazine loss in the surface water.

Since neither cyromazine nor melamine was detected in any of the soil water samples, this study gave no indication that these compounds would be any threat to ground water quality beneath pastures treated with caged layer manure. However, this does not imply that these compounds would never pose a threat to ground water under any soil series or conditions.

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