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J. R. Evans, D. R. Edwards, S. R. Workman, R. M. Williams

Abstract. *Pesticides used in urban environments can be transported in runoff to downstream waters and cause adverse environmental consequences. This experiment assessed the effects of post-application irrigation depth (0, 6.4, and 12.7 mm) and formulation (liquid and granular) on concentration and transport of diazinon (a pesticide commonly used for lawn insect control) in runoff from "tall" fescue (*Festuca arundinacea *Schreb.) plots. The post-application irrigation was applied using rainfall simulators immediately following diazinon application. The rainfall simulators were again used approximately 2 h after diazinon application to apply the equivalent of a heavy rainfall (64 mm/h for approximately 1.5 h) to generate runoff. Runoff was sampled and analyzed for diazinon using the enzyme-linked immuno-sorbent assay method. Post-application irrigation depth had no effect on diazinon concentration but increased diazinon mass transported off the plot by increasing plot runoff. Flow-weighted mean runoff diazinon concentration for the liquid formulation of diazinon was roughly double that of the granular formulation (0.59 vs 0.29 mg/L), attributed to the higher solubility of the liquid formulation relative to the granular formulation. The results indicate that post-application irrigation can increase runoff losses of diazinon for heavy rainfall occurring soon after application, but that these losses can be reduced by use of the granular formulation.* ***Keywords.*** *Runoff, Pesticide, Diazinon.*

The use of pesticides in urban turf applications is increasing nationally (Harrison et al., 1993). Most pesticide applications can be categorized as "medium input", consisting of lawns, parks, and golf course fairways (Harrison et al., 1993) with areas of relatively intense management (e.g., golf greens) constituting "high input" applications. In Lexington, Kentucky (a city of approximately 250,000), for example, there are presently over 30 lawn care service companies that routinely apply herbicides and insecticides. There are undoubtedly many homeowners and other applicators who apply lawn chemicals without benefit of the experience and equipment of lawn care companies.

Accompanying the increase in urban pesticide application has been an increase in awareness of and concern for the potential environmental effects. Offsite pesticide losses can occur due to leaching and runoff. In the case of runoff, in particular, any adverse impacts on downstream aquatic fauna can occur relatively quickly. The short time between runoff occurrence and downstream effects can be compounded by the potencies of pesticides. In the case of diazinon, which is commonly used for lawn insect control, 5% of the amount normally applied to lawns in the equivalent of 10 mm runoff would result in the LC_{50} for the water fleas (*Ceriodaphnia dubia*) used in regulatory biomonitoring (Quin, 1995).

As Harrison et al. (1993) pointed out, most studies relating to pesticides in the environment have focused on conventional agricultural production systems, which account for approximately 80% of total U.S. pesticide use. Relatively few studies have been initiated to address the environmental implications of pesticide application in urban settings. Of the handful or so turf-related pesticide studies, the majority of those have been concerned with offsite pesticide losses due to leaching (e.g., Cohen et al., 1990; Gold et al., 1988; Starrett et al., 1996). Leaching losses have typically been reported as low fractions of amounts applied, even for pesticides with low (< 500) organic carbon adsorption coefficients (K_{oc}). Smith and Bridges (1996) found that less than 1% of applied dicamba and mecoprop leached from lysimeters. Starrett et al. (1996) found that leaching losses of metalaxyl (K_{oc} = 50) and isazofos (K_{oc} = 100) averaged 7.7 and 6.3% of applied for a variety of irrigation treatments, and suggested that the thatch/mat played a significant role in reducing leaching, similar to findings of Horst et al. (1996).

Wauchope (1978) performed an extensive review of studies that investigated runoff losses of pesticides applied to agricultural field. Excepting heavy rainfall falling one to two weeks following application, pesticide losses were found to generally be less than 0.5% of amounts applied. Losses in excess of 2% of the amount applied [termed "catastrophic" by Wauchope (1978)] were noted when pesticide application was followed shortly (one to two weeks) by a heavy rainfall event. Average losses were higher for organochlorine insecticides (due to their persistence) and wettable powders, amounting to approximately 1% and up to 5%, respectively. Although the majority of the land-uses in the studies cited by Wauchope

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(1978) involved row-crop production rather than grass/turf, information from subsequent studies indicates that pesticides applied to turf behave similarly, in some respects, to other land-applied materials. Harrison et al. (1993) and Smith and Bridges (1996) reported that the highest runoff losses of pesticide occurred soon following application. Smith and Bridges observed runoff 2,4-D and dicamba concentrations of 811 and 279 μg/L, respectively, 1 d following application. Harrison et al. (1996) noted comparable maximum dicamba concentrations but lower (210-312 μg/L) maximum 2,4-D concentrations. Smith and Bridges calculated runoff losses of 2,4-D, dicamba and mecoprop to range from 9 to 14% of applied over four simulated rainfall events with 75% occurring during the first post-application event.

Harrison et al. (1993) have characterized runoff and concentrations of pesticides as generally low. Nonetheless, there are confirmed reports of pesticides used primarily in turf applications causing sewage effluent problems. In August 1994, tests revealed peak diazinon concentrations of 0.5 mg/L in the 60 000 m^3/d effluent of Denton, Texas's municipal wastewater treatment plant (Quin, 1995). While mean annual concentrations can be assumed to be considerably less than peak concentrations, peak concentrations of this magnitude are commonly found exiting urban water treatment plants around the United States and are sufficiently high to cause the effluent to fail the water flea biomonitoring test (Quin, 1995).

Diazinon is classified as an organophosphate and is a commonly used pesticide for lawn insect control. It is used to control soil insects as well as fruit, vegetable and field crop pests. Diazinon is also highly toxic to birds, fish, and other wildlife (Chemicals and Pharmaceutical Press, Inc. 1995). Diazinon has a K_{oc} of 1750 and a water solubility of 40 mg/L at 20°C (CIBA-GEIGY, 1989). Nearly 2.6 million pounds of diazinon were used each year in the United States prior to 1983 (Vettorazzi, 1986).

Several municipalities are now investigating methods to reduce concentrations of diazinon and similar chemicals before the runoff enters streams and rivers. Most related studies, however, have assessed existing concentrations rather than methods to decrease those concentrations (by either preventive or remedial approaches). As a result, there are few methods of reducing concentrations that have been tested and proven effective. There are several possible solutions, however, to limiting the runoff of pesticides into surface water. One possibility is to irrigate lawns with a relatively small amount of water following pesticide application. The goal in using this practice is to transport as much pesticide as possible below the runoff zone of interaction at the soil surface. Diazinon application instructions state that the equivalent 6.4 mm (the label currently recommends "0.25 inches") of irrigation should be applied following pesticide application. Runoff of diazinon might also be reduced by appropriate selection of the formulation. Diazinon is available in both liquid and granular formulations. Since the two pesticide formulations might behave differently in terms of their runoff transport characteristics, one formulation might be preferable to the other in terms of minimizing runoff loss. As noted just previously, though, the performance of such measures is not documented in readily available media. The objective of this study was to determine whether post-application irrigation depth or formulation influence runoff concentrations of diazinon applied to simulated lawns.

PROCEDURE

The experiment was conducted at the University of Kentucky Agricultural Experiment Station's Maine Chance Farm using 6.1 × 2.4 m plots established in Kentucky 31 "tall" fescue (*Festuca arundinacea* Schreb.) 12 months prior to the experiment. The soil at the site is a Maury silt loam (fine, mixed, mesic *Typic Paleudalf*). The plots have a uniform 3% slope along the long axis and are level across the short axis. Metal borders were installed (4 cm below and 4 cm aboveground) along the upper and side edges of the plots to isolate runoff. Runoff flows from each plot into an aluminum gutter, which empties into a drain sump (fig. 1). The gutter exit is elevated relative to the sump bottom, enabling runoff samples to be collected before the runoff mixes with any water at the bottom of the sump. The plots are laid out in three rows of 10 plots, with a side-to-side separation distance of 0.8 m and a top-to-bottom separation distance of 3 m. Previous soil sampling for physical and chemical analysis indicated relatively homogenous properties with no significant trends or other anomalous characteristics in properties.

The specific null hypotheses to be tested were (1) post-application irrigation depth does not affect runoff quality, and (2) diazinon formulation does not affect runoff quality. The experimental variables were thus post-application irrigation depth, with levels of 0, 6.4, and 12.7 mm, and formulation, with levels of liquid and granular. Irrigation depths of less than 6.4 mm were not investigated because of the practical challenges of precisely applying such small depths on a plot scale. The experimental design was a balanced factorial with three replications of each treatment combination, resulting in a total of 18 plots (nine per diazinon formulation).

The granular diazinon (5% active ingredient) was manually applied uniformly over the plots. The liquid diazinon (25% active ingredient) was applied to the plots using a conventional hand-held pressurized applicator. Both formulations of diazinon were applied to the plots at the manufacturer's (label) recommended rate of 4.7 kg/ha active ingredient based on the labeled compositions (no analyses to verify composition were performed).

Rainfall simulators were used to apply the experimental irrigation depths 0.5 h after diazinon application. The rainfall simulators are based in many respects on a design reported by Miller (1987), differing most notably in the

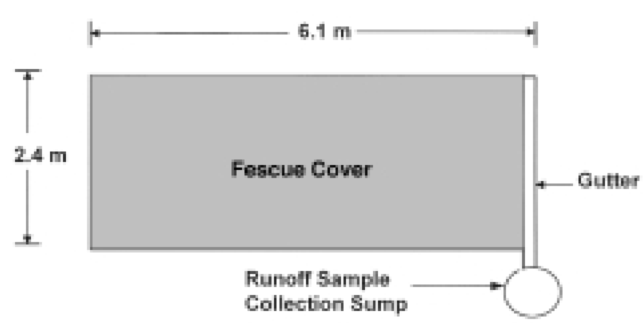

Figure 1–Plot schematic (not to scale).

frame and details of nozzle control. Approximately 2 h following diazinon application, the simulators were used to apply equivalent of a heavy rainfall (64 mm/h for 1.5 h) to the plots. The interval between the beginnings of simulated rainfall and runoff was recorded for each plot. Runoff was sampled at two minutes after the beginning of runoff and on a two-minute interval for the next three samples. The sampling interval for subsequent samples was eight minutes for the remainder of runoff. The goal in employing this sampling program was to characterize any rapid changes in runoff concentrations as accurately as possible by sampling more frequently at the beginning of runoff. Runoff samples were collected in 1-L unused, amber glass bottles and stored in the dark at 4°C until analyzed. Sample volumes and the times required to collect the samples were measured and recorded to enable calculation of runoff rate and volume for each plot. Runoff rates were calculated by dividing sample volumes by associated times required to collect the samples. Plot runoff volumes were calculated by numerically integrating the plot hydrographs with respect to time.

An enzyme-linked immuno-sorbent assay method (EnviroGard™ diazinon plate kit, Millipore Corporation, Bedford, Mass.) was used to determine runoff diazinon concentration for each sample. The analysis procedure followed that described by Millipore (1994). Calibration solutions of 30, 100, and 500 μg/L were prepared by mixing the stock solution of diazinon (supplied with kit) with appropriate amounts of distilled dilution water. These calibration solutions, a control (distilled water), and the runoff samples were then pipetted (100 μL) into two each kit wells, followed by the addition of 100 μL of diazinon-enzyme conjugate (supplied with kit) to each kit well. The wells were mixed, covered with tape, and allowed to incubate at ambient temperature for 1 h. After incubation, the wells were uncovered, and the contents emptied. The wells were then flooded with cool tap water and emptied five times. Next, 100 μL of substrate (supplied with kit) was added to each well, and the wells were covered and allowed to incubate at ambient temperature for 0.5 h. Following incubation, 100 μL of 1 N hydrochloric acid were added to each well followed by shaking to mix the contents. The optical densities of the well contents were measured with a plate reader at 450 nm wavelength. The calibration and control solution results were used to construct a calibration curve, against which the sample optical densities were compared to obtain diazinon concentrations. No calibrations involving high sediment loads were performed, since earlier runoff studies on these plots indicated very low (average of less than 10 mg/L) suspended solids concentrations.

The data on runoff rates and diazinon concentrations enabled calculation of flow-weighted mean runoff diazinon concentration and mass of diazinon transported off each plot during runoff. The flow-weighted mean concentrations, rather than concentrations measured throughout runoff, and mass transport values were analyzed using analysis of variance (ANOVA) to test for the significance of post-application irrigation depth and formulation effects.

Table 1. Mean* hydrologic variables

	Pesticide Formulation					
	Granular			Liquid		
	Irrigation Depth					
	0	6.4	12.7	0	6.4	12.7
R_R† (mm)	52.0a‡	23.0b	13.3c	55.8a	31.1b	31.6b
Q (mm)	3.16b	15.1a	17.35a	0.91b	7.31a	8.38a
Q/R (%)	4.42b	18.68a	20.65a	1.02a	8.66a	9.83a
CN	48.0b	64.5a	65.7a	42.1b	52.2a	55.7a

* Mean of three samples.

† R_R is rainfall prior to runoff, Q is runoff, Q/R is ratio of runoff to rainfall, and CN is curve number.

‡ For a given pesticide formulation, within-row means followed by the same letter are not significantly different (p > 0.05).

Results and Discussion

Hydrologic parameters calculated for the plots are given in table 1. Post-application irrigation significantly ($p < 0.05$) decreased mean rainfall depth prior to runoff, but there was no significant difference in rainfall prior to runoff between the 6.4 and 12.7 mm application depths. For the non-irrigated plots, a mean rainfall depth of 53.9 mm (standard deviation = 9.3 mm) was applied prior to runoff, while only 24.8 mm (standard deviation = 13.0 mm) of simulated rainfall was required to cause runoff on the irrigated plots. This result was expected, since the irrigation increased the soil moisture content at the time of the simulated rainfall. The irrigation significantly ($p < 0.05$) increased plot runoff from an average of 2.02 mm for the non-irrigated plots to 12.03 mm for the irrigated plots. The proportion of rainfall occurring as runoff ranged from approximately 1% for the non-irrigated plots to 21% for the irrigated plots. There were no significant differences in runoff depths between the 6.4 and 12.7 mm irrigation amounts. No adjustments to runoff depth calculations on the basis of suspended solids were made, because the suspended solids concentrations were negligible (as would be expected for runoff from well-established turf).

The effects of irrigation on runoff can further be characterized in terms of runoff curve number (Soil Conservation Service, 1972). The irrigated plots' mean curve number was 59, significantly ($p < 0.05$) greater than the mean curve number of 45 calculated for the non-irrigated plots. There were no differences in curve number attributable to pesticide formulation (i.e., CN values were consistent for all plots, indicating effective blocking for CN) and no difference in curve numbers between the 6.4 and 12.7 mm irrigation amounts. The curve number increase in response to the 6.4 mm irrigation was expected; the lack of a response to additional irrigation suggests that the water content of the soil surface had approached porosity upon addition of the lesser irrigation depth. In general, then, the effect of the post-application irrigation on the hydrologic parameters of the plots were as expected, but there was no effect of doubling the irrigation amount from 6.4 to 12.7 mm on the parameters.

Variability in the hydrologic parameters of table 1 was high, as indicated by the coefficients of variation. Similar studies involving plot (Edwards and Daniel, 1993), field (Edwards et al., 1996), and even watershed-scale (Edwards et al., 1997) have also reported high variability in storm runoff. High variability of runoff, then, seems to

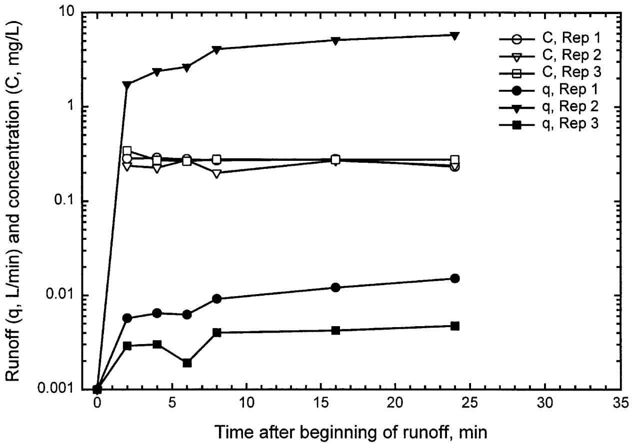

Figure 2–Relationships between runoff rate, diazinon concentration, and time for granular formulation with no irrigation.

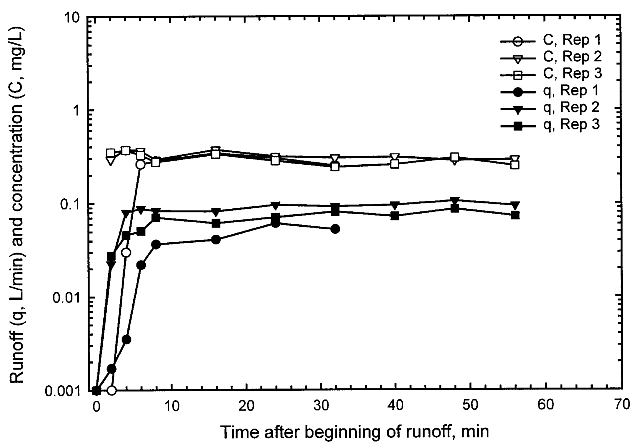

Figure 3–Relationships between runoff rate, diazinon concentration, and time for granular formulation with 6.4 mm irrigation.

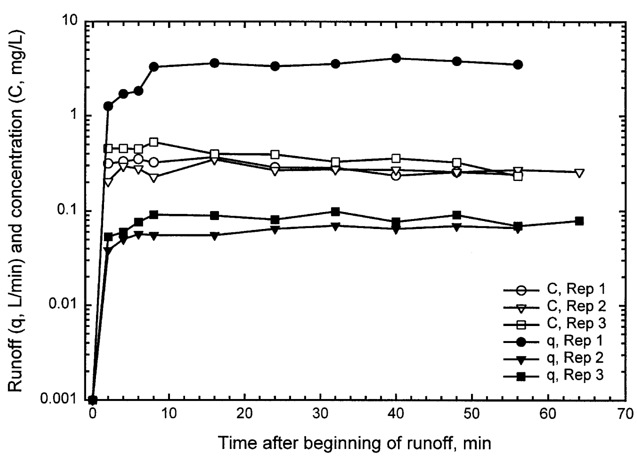

Figure 4–Relationships between runoff rate, diazinon concentration, and time for granular formulation with 12.7 mm irrigation.

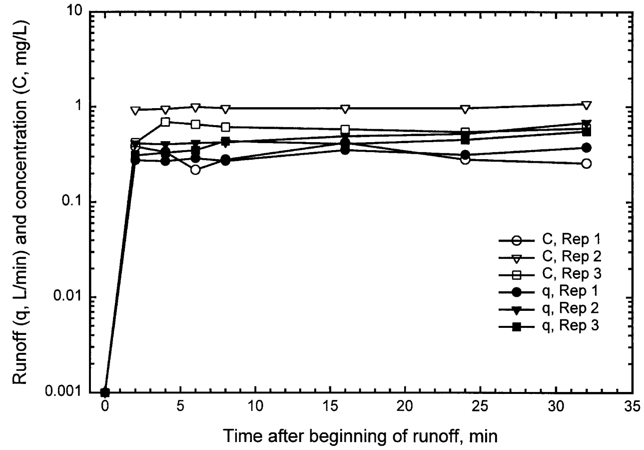

Figure 5–Relationships between runoff rate, diazinon concentration, and time for liquid formulation with no irrigation.

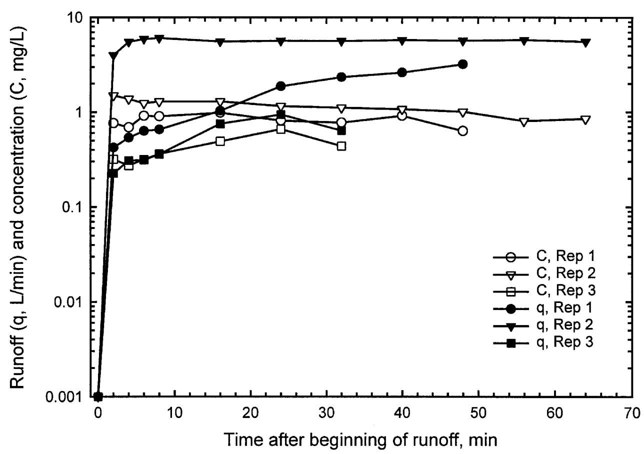

Figure 6–Relationships between runoff rate, diazinon concentration, and time for liquid formulation with 6.4 mm irrigation.

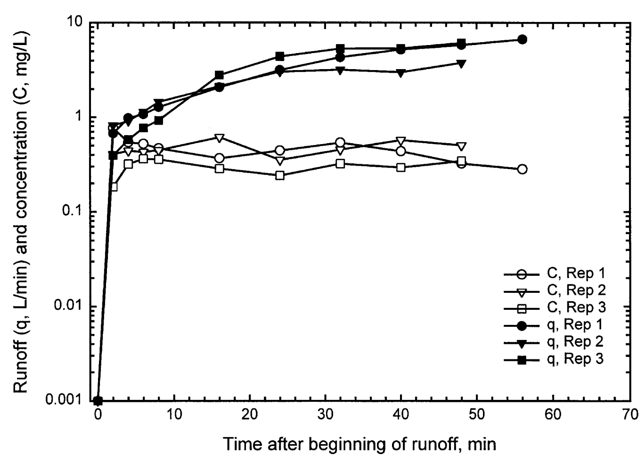

Figure 7–Relationships between runoff rate, diazinon concentration, and time for liquid formulation with 12.7 mm irrigation.

potentially be an inherent (if inconvenient) characteristic of plot and larger scale studies, especially as soil dryness increases (Edwards et al., 1993).

Figures 2-7 depict the relationships between time after the beginning of runoff, runoff rate, and diazinon concentration for all treatments and replications. In the absence of additional analysis, these figures would suggest that post-application irrigation had no significant influence on diazinon concentrations. This suggestion is supported by the ANOVA, which indicated that post-application irrigation had no significant effect on flow-weighted mean runoff diazinon concentration. One possible contributor to this finding is the relatively high tendency of diazinon to be absorbed in the organic carbon of the soil. As reported earlier, diazinon has a K_{oc} of approximately 1750 (CIBA-GEIGY, 1989) for silt loam soils, which is more than 10 times that of relatively mobile pesticides such as, for example, atrazine (CIBA-GEIGY, 1989) and indicates a relatively high degree of transport in the sediment-bound phase. The organic matter content of the soil (approximately 1.6%; Lim et al., 1997) and the presence of the fescue could have caused significant diazinon adsorption. Diazinon also has a relatively low water solubility (40 mg/L at 20°C; CIBA-GEIGY, 1989), which would further discourage transport in subsurface water. The combination of low solubility, high K_{oc}, and low sediment transport (as observed in this study) thus promote a relatively low degree of movement (whether in ground or surface water) in response to post-application irrigation. It is furthermore possible the irrigation depths applied were simply insufficient to force the pesticide into the soil. If the pesticide was moved down into the soil, it apparently was not at a sufficient depth to result in significant decrease in concentration of the pesticide in runoff. If post-application irrigation is to be effective in reducing runoff concentrations, it might have to be at a greater irrigation depths than that applied in this experiment, particularly in view of the solubility and K_{oc} of the pesticide. While the data for the liquid diazinon formulation with 12.7 mm irrigation depth suggest the beginning of a trend, additional experimentation with higher irrigation amounts would be necessary to establish any effects of higher irrigation amounts.

As suggested by a comparison of figures 2-4 to figures 5-7, pesticide formulation significantly ($p < 0.05$) affected runoff diazinon concentrations (table 2). Flow-weighted mean concentrations from the plots receiving liquid diazinon (0.59 mg/L) were just over double those from plots receiving granular diazinon (0.29 mg/L). Even though the runoff from the plots treated with the granular formation was higher than from the plots receiving the liquid formulation of diazinon (table 1), this finding appears not to be related to runoff amounts. As suggested in figures 2-7, runoff diazinon concentrations for a given formulation appeared to be relatively stable with regard to time in comparison to runoff rates. Figure 4, for example, shows that runoff rates varied by more than two orders of magnitude, but runoff diazinon concentrations were almost identical for all replications and sampling times. This phenomenon was investigated in more detail as shown in figures 8 and 9, which show diazinon concentration (lumped across post-irrigation treatments, since post-irrigation depth had no significant effects) plotted against runoff rate for the granular and liquid formulations, respectively. Regression of concentrations against runoff rates indicated no significant relationship between the two variables for either formulation. In similar fashion, analyzing the relationship between diazinon concentration and sampling time (figs. 10 and 11) showed that those two variables were unrelated for either formulation.

Figures 8 and 9 generally indicate more variation in concentrations at the lower runoff rates than at the higher runoff rates. The 11 data points in the upper-right region of figure 9 (which originated from a single plot) constitute an exception to this general result but have been included in the absence of any procedural reasons for questioning their validity. The data collected in this study do not permit a firm explanation of the relatively high variation at low runoff rates. It is possible, however, that this phenomenon was due to small-scale variations in diazinon application and runoff source areas. Although the diazinon was applied uniformly to the plots, some variation in application rates is inevitable, particularly as the area under consideration decreases. Likewise, runoff from a given area generally is

Table 2. Mean concentration, mass transport, and loss proportion of diazinon

	Pesticide Formulation					
	Granular			Liquid		
	Irrigation Depth					
	0	6.4	12.7	0	6.4	12.7
C* (mg/L)	0.26a†	0.30a	0.31a	0.62a	0.67a	0.41a
M_t (g/ha)	7.8b	45.2a	53.4a	6.0b	46.4a	32.6a
P (%)	0.17b	0.96a	1.14a	0.13b	0.99a	0.68a

* C is concentration, M_t is mass transport, and P is loss proportion.
† For a given pesticide formulation, within-row means followed by the same letter are not significantly different ($p > 0.05$).

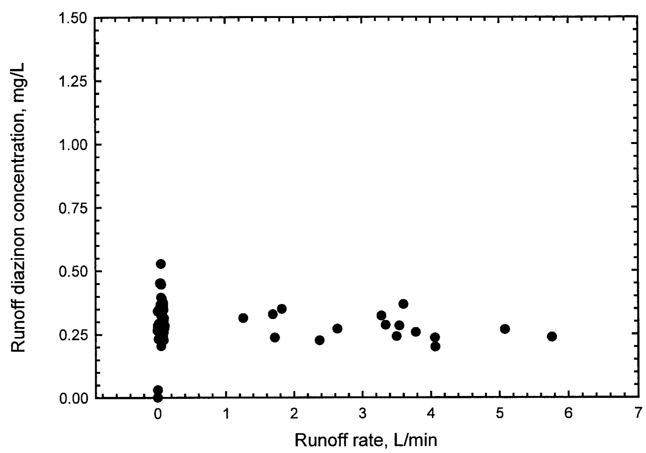

Figure 8–Relationship between runoff diazinon concentration and runoff rate for granular formulation.

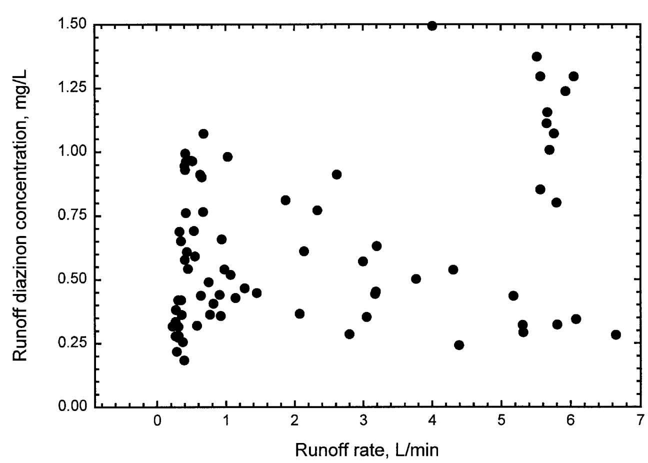

Figure 9–Relationship between runoff diazinon concentration and runoff rate for liquid formulation.

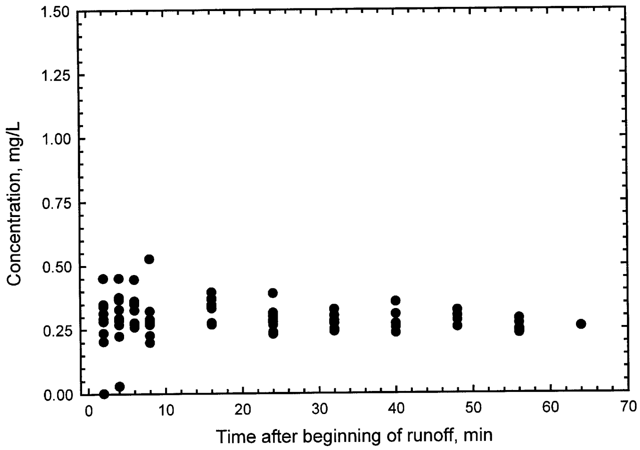

Figure 10–Relationship between runoff diazinon concentration and time for granular formulation.

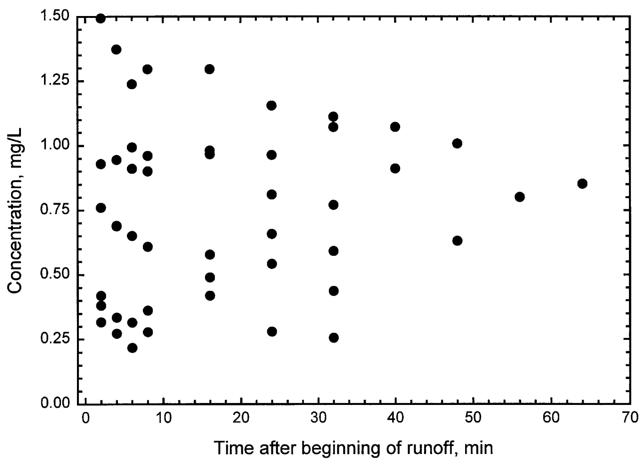

Figure 11–Relationship between runoff diazinon concentration and time for liquid formulation.

not uniform in terms of rate or origin, particularly at the beginning of runoff. The pattern of variation in figures 8 and 9 might reflect the occurrences of runoff from initially small proportions of the plots, some having relatively high diazinon concentrations and some having relatively low concentrations when evaluated at the same scale as the runoff-producing portions of the plots. The same mechanisms, coupled with the observation that the equilibrium diazinon concentrations were very similar among replications and treatments (figs. 2-4), might be responsible for the similar patterns of variation shown in figures 10 and 11.

Since diazinon concentrations were unrelated to either runoff or sampling time, the concentration differences between formulations appear not to have been affected by the runoff differences reflected in table 1. The concentration differences are instead attributed to differences in effective solubility between liquid and granular formulations. The active ingredient (diethyl O-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate) is the same for both the liquid and granular formulations of diazinon, so the concentration differences must be related to the pesticide's inert ingredients or the carrier. Diazinon concentrate (liquid formulation) is intended to be mixed with water and contains emulsifier to stabilize that mixture (Ortho, 1997). The granular formulation of diazinon, however, consists of diazinon coated in a carrier of a recycled newspaper (Jenkins, 1997). The chemical is intended to be dissolved out of the carrier, resulting in a slower release of the pesticide. This feature of the granular formulation is considered to be the reason for the significant concentration difference between the formulations even though the same amount of active ingredients was applied to each plot.

Although post-application irrigation had no effect on runoff diazinon concentration, the higher runoff associated with irrigation caused significant ($p < 0.05$) increases in mass transport (table 2). There were no significant differences in mass transport between the 6.4 mm and 12.7 mm irrigation depths, but the difference between no irrigation and irrigation was significant for both granular and liquid formulations (table 2). As measured in terms of mass transport, then, post-application irrigation was worse than no irrigation for this study and increased mass transport by more than sixfold over the non-irrigated plots.

Loss proportions were relatively low, with a maximum of only 1.14% of applied (table 2). In comparison to loss proportions summarized by Wauchope (1978), the loss proportions of this study are more than double the reported typical proportion but consistent with proportions associated with heavy rainfall occurring soon after pesticide application.

Summary and Conclusions

Liquid and granular formulations of diazinon were applied to fescue plots that subsequently received either 0, 6.4 or 12.7 mm irrigation. Heavy simulated rainfall (63.5 mm/h for 1.5 h) was applied to generate runoff samples that were analyzed by the Enzyme-Linked Immuno-Sorbent Assay Test (ELISA) method for diazinon. The data on runoff concentrations and mass transport were then subjected to ANOVA to determine the effects of post-application irrigation depth and pesticide formulation.

Post-application irrigation depth decreased the rainfall required to produce runoff while increasing runoff and SCS curve number but had no effect on the runoff diazinon concentration. Runoff concentrations were affected by pesticide formulation, however, with that of the liquid formulation (0.59 mg/L) being about double that of the granular formulation (0.29 mg/L), attributed to the relatively slow release of diazinon's active ingredient from the granular formulation. The mass transport of diazinon from irrigated plots was more than six times that of the non-irrigated plots due to higher runoff from the irrigated plots.

These findings suggest that under conditions of this study, post-application irrigation might have no beneficial effect on environmental impacts of diazinon application. The data from the plots treated with the liquid formulation and receiving 12.7 mm irrigation suggested that higher-than-recommended irrigation amounts might reduce runoff concentrations, but additional work would be required to explore this question. It must also be recognized that higher irrigation can generally be expected to promote more runoff and will thus tend to offset any benefits promoted by decreased concentrations, especially without a sufficient interval between irrigation and subsequent rainfall.

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