Alfalfa Herbicide Pollution Pathways and Mitigation Practices

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Introduction

Investigations on the pathway for movement of pesticide residues to ground water are needed to determine if mitigation measures can be developed that allow continued use, but that are also protective of underground aquifers. For example, on coarse-textured sandy soils, guidelines for irrigation management have been suggested to minimize movement of residues lost to deep percolation, whereas in hardpan soils with low infiltration rates, improved incorporation of pre-emergence herbicides is recommended to reduce concentrations in runoff water that eventually recharges ground water.

These two scenarios are not representative of all geographical settings where residues have been detected in California's ground water, so further investigations required on movement of pesticides to ground. This report describes an investigation on the pathway for movement of hexazinone and diuron residues to ground water in an area dominated by cracking clay soils. Residues of these pre-emergence herbicides were detected in wells sampled near the town of Tracy, California where the predominant cropping pattern was a rotation of alfalfa with corn and beans. Tracy is centrally located on the western side of the Central Valley of California. The residues were related to agricultural applications, especially since hexazinone could only have been used on alfalfa.

Movement through cracks in clay soils is a potential pathway for pesticide residue movement to ground water. Another potential pathway noted in this area was through the percolation of water collected in ponds at the edge of the fields. The ponds collected runoff water that was generated from rainfall or irrigation events. Pond water could have been lost to evaporation, percolation, or in same cases it was reused through an irrigation return system. Given that the ground water in this area was shallow at around 15 feet and that the ponds were generally 6 to 9 feet deep, they appeared to be potential candidates for recharging the shallow ground water with water containing pesticide residues.

Field Study

A field study was initiated in the winter of 1999 to determine the predominant pathway for movement of residues to ground water. The objectives were to:

1. Evaluate the fate of diuron and hexazinone applied to an alfalfa crop,
2. Determine potential for downward movement of water from the ponds,
3. Evaluate the effect of a surfactant on the offsite movement of hexazinone and diuron.
4. Investigate the effectiveness of trifluralin and paraquat as potential replacements.

Site and Study Description

This study was conducted within an alfalfa field located near Tracy, California. The field was approximately 34 acres in size entering the third season of alfalfa cultivation. The predominant soil-mapping unit was a Capay clay (fine, smectitic, thermic Typic Haploxerert). The ground water was shallow and located at around 15 feet.

Diuron and hexazinone are applied as pre-emergence herbicides to alfalfa during the dormant season in December and January to control existing winter weeds and to prevent subsequent weed germination. The timing of application coincides with the rainy season to incorporate the herbicide residues into soil. The method of irrigation is border check using siphons to deliver water from an open ditch. Each irrigated check was 27 ft wide by 1100 ft in length, which was equivalent to 0.68 acres. The rate of water flow onto the check was constant for each irrigation, and it was measured at 202 gallons per minute for the first irrigation of the season and just slightly greater at 212 gallons per minute for the second irrigation. Runoff water was diverted from the tail end of the field to a small pond situated on the Northwest corner of the field.

A randomized complete block design with 4 replicate blocks was utilized to compare environmental fate and efficacy among the following three main treatment effects:

1. Grower standard pre-emergence herbicide treatment of hexazinone and diuron applied at 0.5 and 1.5 lbs/acre, respectively.
2. Effect of a surfactant added to Treatment 1 at a rate of 2 gal/acre.
3. Efficacy and fate of alternative herbicides using trifluralin and paraquat applied at 0.5 and 1.5 lbs/acre, respectively

Each treatment was applied to one check resulting in a total of 12 checks used for the study. In order to measure potential spatial differences due to water movement due to rainfall or irrigation, each check was equally subdivided into thirds, with each third approximately 15 feet wide by 366 feet in length. Samples were taken from each third to represent the head, middle, and tail portions of the check.

Treatment Applications

Pre-emergence treatments of diuron and hexazinone with and without surfactant were applied as a tank mix on December 23, 1999. Paraquat was also applied on December 23 followed by a sequential application of trifluralin in a granular application on January 19, 2000. Deposition was measured during application by placing 11.5 x 11.5 inch squares of Kimbie sheets on the soil surface. Three sheets were collected after being placed in each replicate check, one in each of the upper, middle, and lower sub-sampling areas.

Pond Water Sampling

It is important to note that the water entering the pond was the result of runoff from a larger area than the experimental area. Therefore, a pond sample did not directly represent the herbicide concentrations or mass as a result of runoff from the treatment areas. However, they were important as an indication of the potential fate of residues entering the pond.

A technique was developed to determine pond volume from water depth measurements. First, the volume of the pond was estimated using a 3-dimensional survey technique. Then a relationship was established between pond depth and estimated volume. This relationship was calibrated by relating measured inflow volume of runoff water to the concomitant increase in pond depth. Inflow was measured using a 200 mm throat broad crested RCB flume equipped with a stilling well and pressure transducer to measure head. An additional transducer was placed at the bottom of the pond to measure pond depth. There was good agreement between volume deduced from pond depth and direct measurement. Pond depth was then used to determine the volume of infiltrated water, the rate of infiltration as calculated through temporal changes in wetted area.

Chemical Analysis and Quality Control

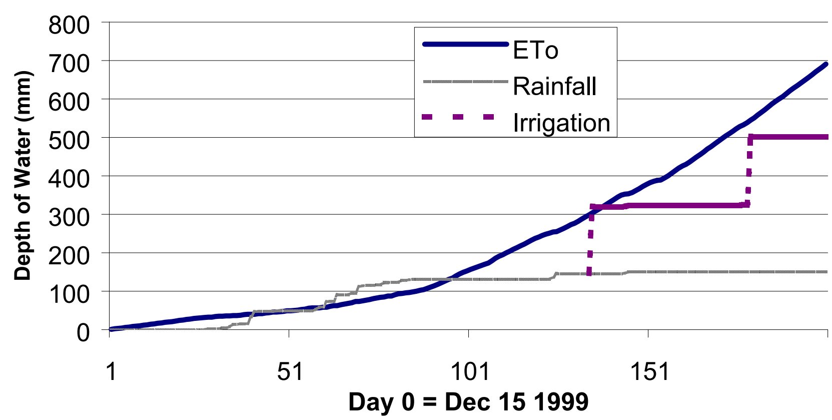
The selected laboratories developed and validated a method for analyzing Kimbie sheet, soil, sediment, vegetation, and water samples for hexazinone and diuron. The analytical method was approved by DPR. This study was done in accordance with EHAP SOP QAQC001.001.

Results and Discussion

Water Distribution and Movement

A comparison of the cumulative amount of rainfall and irrigation to cumulative ETo provides reference for the potential runoff and percolated water produced during the study (Figure 1). Prior to the initial date of this study, which will be indicated as 15 Dec. 1999, very little rainfall was recorded in the fall.

Figure 1. ETo rainfall and rainfall plus irrigation water volumes, Tracy, CA 1999-2000



The cumulative amount of rainfall eventually was greater than cumulative ETo and thus would have potentially produced some percolation or runoff water. During this period, however, runoff water was not observed from the treated sites, so the frequency and amount of rainfall was not sufficient to generate runoff water samples. Soil water content at the second soil coring date was consistently greater than background samples, indicating that rainfall did produce percolation that was measured down to the lowest depth sampled.

Rainfall after day 85 was minimal. The contributions of water from the two irrigations are visible as the two sharp upward spikes in the curve for accumulated rainfall plus irrigation. The irrigations supplied enough water to cover the cumulative deficit in ETo.

Both irrigation events were similar in terms of total run time and onflow volumes, averaging 6.88 in depth (Table 1). Runoff depth varied between irrigations from 0.17 to 0.49 acre inch/acre. Differences between irrigations were caused by small differences in on flow volumes, run times and antecedent soil moisture content. The proportion of tail water caused by runoff was 2.5% of the first and 7.1% of the second irrigation applied volumes. Runoff from the second irrigation was considered more reflective of typical conditions.

The moisture profiles of the soil cores were reflective of a potential distribution caused by the dynamics of border check irrigation. Moisture at the head end of the check was greater than at the tail end, which is caused by greater opportunity time of water that contacts the head end of the check. Increases in water content at the lowest depth indicated that the irrigation treatments caused drainage past this depth and provided a potential leaching environment.

Soil and Vegetation Sampling

Background sampling: Diuron residues were detected in all surface samples at the 0-3 inch depth and only sporadically in the next lower depth at 6 inches (Figure 2). Upon summation of residues from all depths, the detections indicated an average recovery of 0.12 kg/ha, which corresponded to approximately 8% carry-over from the previous years application.

Hexazinone residues were essentially undetected, which was likely due to its lower application rate (Figure 3). Paraquat and trifluralin had not been previously applied and they were not detected in background samples.

Prior to First Irrigation: The amount of rainwater received by the plots between pesticide application and commencement of soil sampling on April 3 was 5.1 inches. A test for the effect of surfactant indicated greater concentration of diuron in treatments with added surfactant whether or not the deposition data were used as a covariate in the ANOVA. Although location effects were not significant in the split-plot ANOVA, regression within treatments indicated residues increased from the head to tail end of the standard treatment. The distribution pattern for hexazinone appeared similar to diuron, in that there were no significant effects in the statistical analysis, a result that may have been due to the lower application rate (Figure3).

The distribution of residues throughout the soil profile was different between diuron and hexazinone. Very little diuron was detected beneath the first 0-3 inch depth, whereas, concentrations of hexazinone in the deeper segment were equal to those measured in the first segment (Figures 2 and 3). Little to no residues were measured for either herbicide in the third segment, which represented the 12-inch depth. Based on a comparison of their physical-chemical properties, greater movement through soil would be expected for hexazinone, caused primarily by its lower soil adsorption value (Koc).

The mass of residues recovered from the total soil core length averaged 0.58 kg/ha for diuron and 0.09 kg/ha for hexazinone. These values represented a decrease from the application day values of 66% for diuron and 79% for hexazinone. Diuron was only sporadically detected in vegetation samples. But residues were consistently detected at the surface and next lower depth in soil sampled from the drain and pond. Samples were sporadically measured at the depth 3.

After Second Irrigation: The alfalfa field received two surface irrigations prior to this soil coring. The average depth of water received by the plots between pesticide application and commencement of soil sampling on June 26 was 19.7 inches. The magnitude of the residues for both pesticides was reduced to levels that were similar to those measured in the background samples. Statistical tests for effects of treatment and location were not significant. However, the observed patterns were similar to the previous soil coring date (Figures 2 and 3).

Figure 2. Distribution of diuron in soil at three sampling dates and compared between minus and plus surfactant treatments.

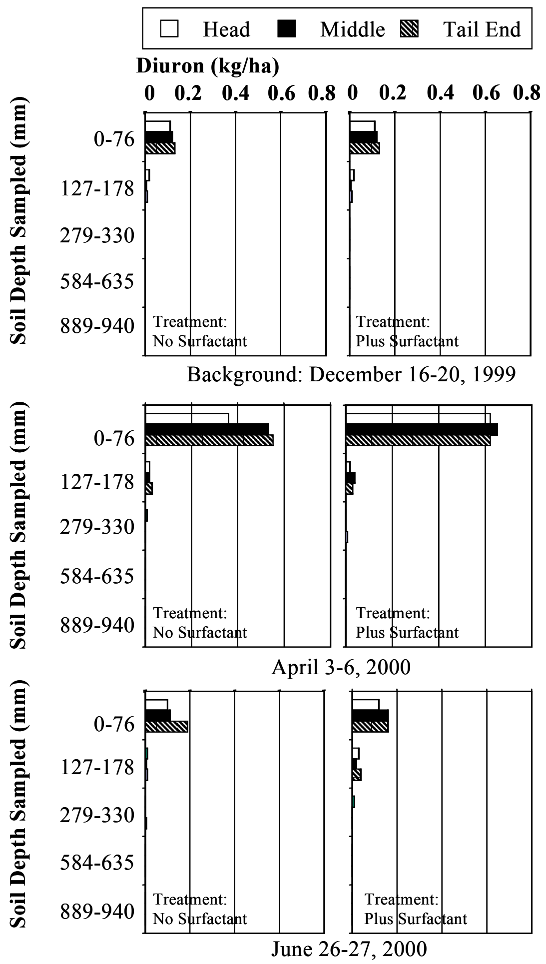
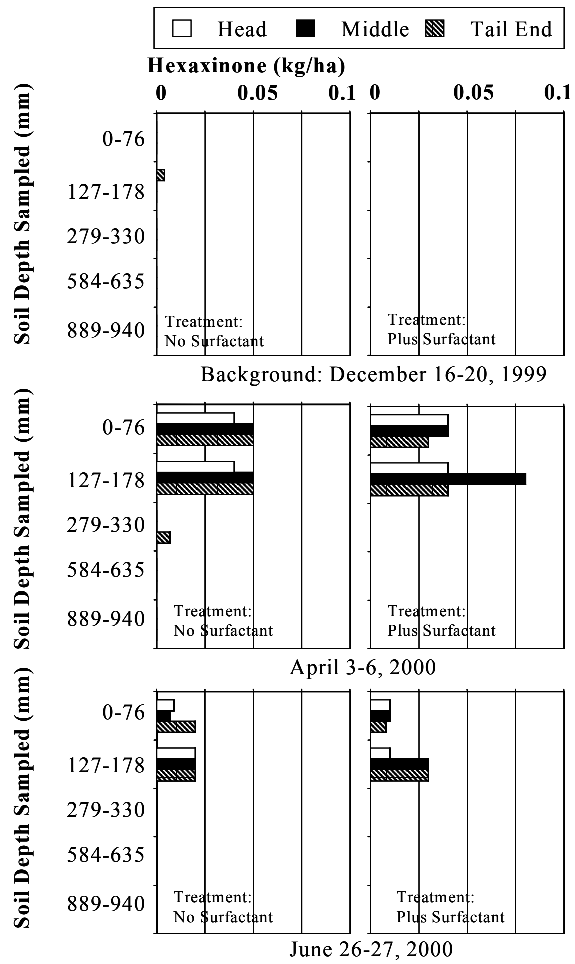


Figure 3. Distribution of hexazinone in soil at three sampling dates and compared between minus and plus surfactant treatments.



Runoff Water Measurement and Sampling

Herbicide Concentration and Mass in Runoff Water: Significant differences in diuron concentration were measured between irrigations with the concentrations for the first irrigation runoff approximately twice the concentration of the second (Table 1). Hexazinone concentrations also appeared greater at the first irrigation; however, the level of probability indicated only a trend (P= 0.0726). The addition of the surfactant did not significantly affect the concentration of herbicides in runoff water. The mass of both diuron and hexazinone in the runoff waters was calculated as the product of the concentration and volume of runoff water (Table 1). No significant differences in mass of herbicide leaving the field were found between treatments or irrigations. Although the concentration of diuron herbicide was reduced in half from the first irrigation, the runoff volume had tripled in the second irrigation resulting in no significant differences in the mass leaving the field. The results for hexazinone were similar. No triflurilan or paraquat was detected in runoff waters.

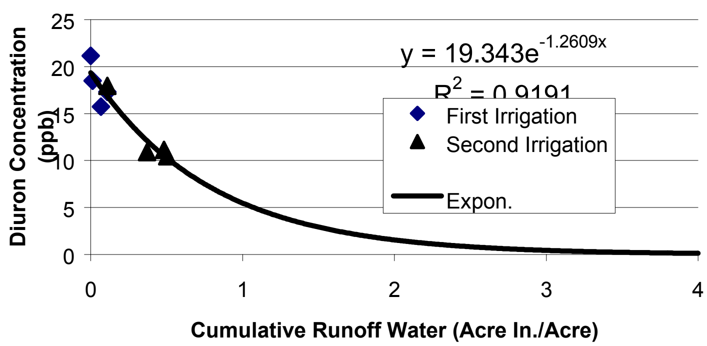
Table 1. Average concentration and mass of residuals with treatments across irrigations and irrigations across treatments

Treatment	Diuron (ppb)	Hexazinone (ppb)	Diuron (g/Acre)	Hexazinone (g/Acre)
1	13.27	0.423	0.4285	0.0134
2	17.37	0.7	0.3691	0.0115
P =	0.2024	0.2773	0.6082	0.627
Irrigation				
1	20.53 A	0.945	0.3135	0.0123
2	10.08 B	0.258	0.4841	0.0127
P =	0.0174	0.0726	0.1857	0.9039

Decline in concentration as a function of runoff volumes: The concentration of herbicide in the runoff water declines as cumulative runoff water volume increased both in a single and multiple irrigations. The initial 5-gallon sample collected at each irrigation had a higher concentration than samples collected later in each irrigation. The concentration of diuron in the initial sample collected in the second irrigation was more similar to those of the pervious irrigation however all subsequent samples were lower. Hexazinone followed a similar pattern.

Using data collected from both irrigations, a relationship between concentration in the runoff water and cumulative runoff was constructed (Figure 4). Using an exponential fit, a significant relationship was found in both herbicides. The model predicts less than 0.5 ppb Diuron in the runoff water at a cumulative runoff of 3.0 inches per acre. The model constructed for Hexazinone predicts less than 0.02 ppb at a cumulative runoff of 1.5 inches per acre.

Figure 4. Diuron Concentration in Runoff Water vs. Runoff Volume, T1 R1 Tracy 2000



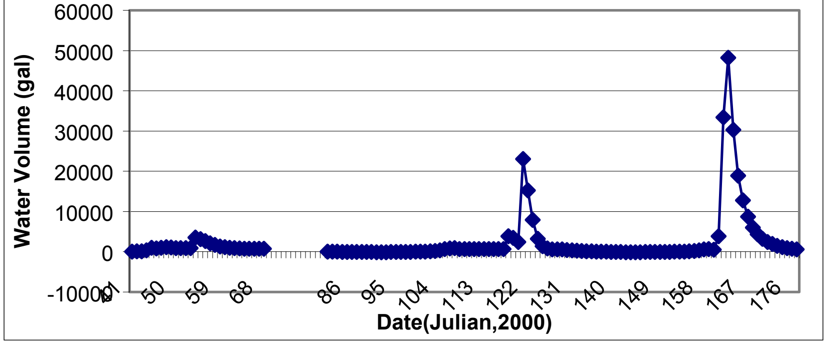
Holding Pond
The holding pond captured the unmeasured runoff from the entire field. Although runoff from the experimental area did not occur from rainfall, some water was collected in the holding pond from the drain check/field road area at the tail end of the field (pond volume vs. time). During the irrigations, runoff was collected from the experimental area and the rest of the field. The non-experimental area was treated with both diuron and hexazinone as in Treatment 1. Seven individual irrigation sets totaling 50 checks contributed variable runoff volumes. An attempt was made by the irrigator to minimize runoff from the field as a whole so as not to exceed the capacity of the pond. There was no pond water-recycling pump. Therefore, the concentration of the pond water was not strictly reflective of the concentration of herbicides in the runoff of a specific treatment; however, they were similar.

Pond Volume
At full capacity, the pond holds 105,000 gallons. Full capacity occurs water no longer drains from the field. The pond was empty prior to each irrigation event. The pond capacity provides for near 3000 gallons per acre irrigated. The first irrigation resulted in less runoff than the second. The maximum pond capacity was reached the second irrigation. Runoff volume from the experimental area averaged over both irrigations 4.8 percent on the inflow, or 0.33-acre inch/acre. If the entire 34-acre field were irrigated in a fashion like the experimental area, 11.2 acre-inches of runoff would result. Only 4.5-acre inch of runoff was captured on average between the two irrigations indicating current operations resulted in considerably less runoff volume.

Pond Infiltrated Water
Due to infiltration occurring during the 4 days of runoff, collection the infiltrated volumes were greater than the difference between maximum depths and empty. Pressure transducers were used to make continuous measurements of pond depth and depth of water inflow through a flume. The volume of water infiltrating via the pond was calculated using a relationship developed between the infiltrated water and pond depth.

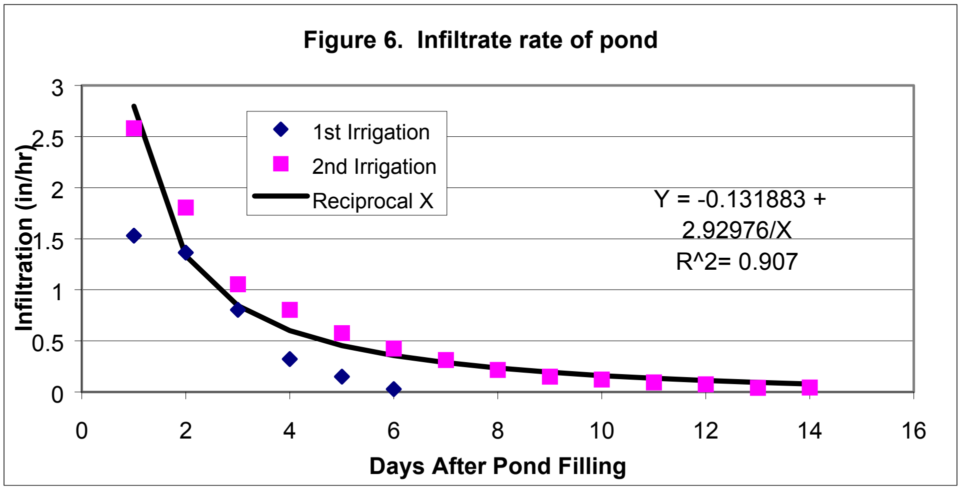
By applying this relationship to the known pond depth over the season, it was possible to estimate the infiltration both during and after pond filling (Figure 5). The first irrigation resulted in near 65,000 gallons while the second infiltrated 179,000 gallons. The majority of the water was infiltrated in just a few days. The total volume of runoff water infiltrated by the pond as a result of both irrigations was 244,000 gallons.

Figure 5. Infiltrated Pond Water Volume



Pond Infiltration Rate

The rate of water infiltration is dependent upon the area wetted by the pond at any given time. The relationship between pond depth and wetted area is shown in Figure 6. Using this relationship, infiltrated water was calculated during the infiltration period each irrigation. Infiltration rate (inches/hour) was highest at 2.5 in/hr when the pond was deepest declining to less than 0.03 in/hr in 6 to 14 days (depending on the irrigation). The infiltration rate drops rapidly indicating the lower reaches of the pond are less permeable. This is probably due to cracking in the upper area of the pond and a residual organic muck in the bottom.



Holding Pond Concentration

The initial pond sampling of water (filtered) found a level of 2.16 ppb of diuron and 0.583 ppb hexazinone. At sampling the pond volume was low. The source of the water was thought to be field runoff. At this time rainfall, did not exceed ETo minimizing the dilution effect of rainfall. Samples were again collected after the inflow to the pond has cased from the first irrigation. Diuron was found at 12.35 ppb and hexazinone at 1.02 ppb. After the second irrigation, pond concentrations were 11.76 and 0.894 ppb for diuron and hexazinone, respectively. The pond concentrations of both diuron and hexazinone were similar to those found in the Treatment 1 runoff waters. The holding pond concentrations are not the same as the concentrations in the treatment runoff due primarily to the irrigation system operation causing less runoff. Runoff volume from the entire field was 2.5 times less than the average runoff of the treatments. The concentration of diuron in the pond in the first irrigation was about twice that of the average treatment runoff. Hexazinone concentrations however were similar.

Using the seasonal irrigation requirement of 48 inches per acre and the average runoff measured in the two irrigations results in a 2.3-inches/acre volume for each acre. Under such a scenario, combined with the relationship between developed the diuron concentration and cumulative water runoff shows that little herbicide would be exiting the field with runoff waters by the end of the season. After the last irrigation in late September pond samples were collected October 4th, finding concentrations of 2.33ppb diuron and 0.36 ppb hexazinone.

Holding Pond Residue Mass

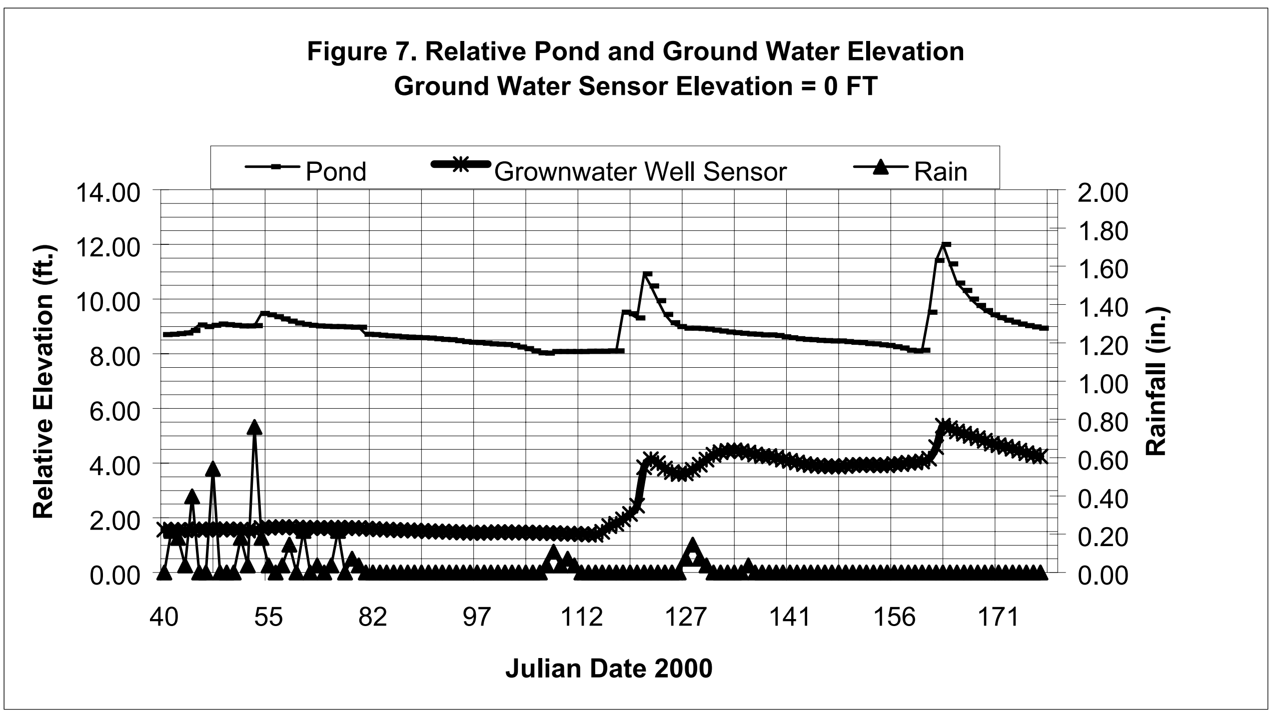
The mass of both diuron and hexazinone in the infiltrated pond water was calculated as the product of the average concentration of the pond waters and the calculated infiltrated volume as a result of both irrigation runoff events.

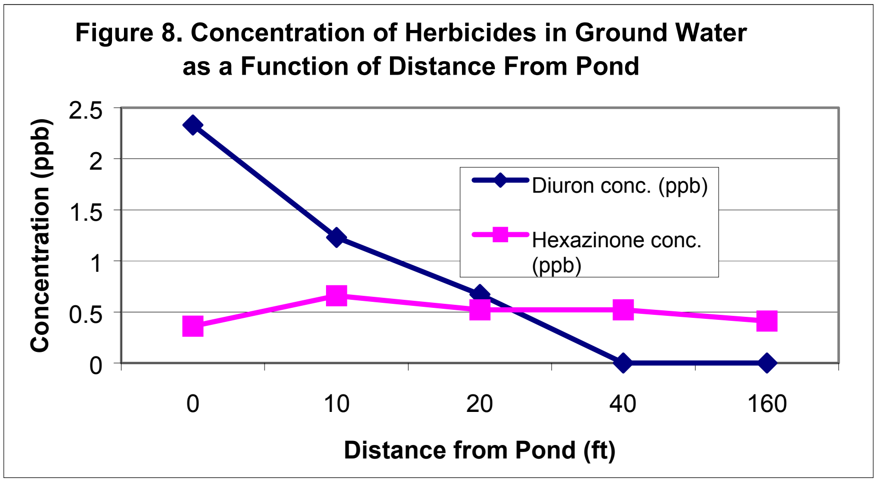
Table 2.

Irrigation	Volume (gal)	Conc. Diuron (ppb)	Mass Diuron (g)	Conc. Hex (ppb)	Mass Hex (g)
1	65000	12.35	3.04	1.019	0.25
2	175000	11.76	7.79	0.894	0.59
	240000		10.83		0.84

Holding Pond Relation to Ground Water

Simultaneous measurements were made of pond water depth and ground water depth through the measurement period. The shallow ground water appears to be strongly influenced by the infiltrating water volume (Figure 7.)





October 24th sampling of borehole water at distances 10, 20, 40 and 160 ft indicate a little hydraulic gradient. The last irrigation had been over 40 days prior to this measurement; therefore the pond would have been empty for near 25 days. The concentration of diuron in the water declined with distance from the pond water at near 2.5 ppb and non-detectable at 40 feet and further (Figure 8.) The hexazinone concentrations were similar in the pond and all sampling distances at about 0.5 ppb.

Yield and Efficacy

The three harvest sub-samples were needed due to variable alfalfa size and stunted growth occurring from a high stem nematode population. Vole feeding also contributed to variable growth. These factors resulted in a high coefficient of variability. There were no significant yield differences between treatments.

Herbicide Efficacy

The hexazinone plus diuron treatments provided improved season long control of most winter weeds compared to paraquat and trifluralin treatments with an improvement of 50%. Paraquat was initially effective in burn down of emerged weeds. However, paraquat binds rapidly to soil so soil residual herbicide in available in soil solution to suppress new weed germination and subsequent growth. The later application of trifluralin was ineffective in preventing germination of the winter annual broadleaf weeds. Later germinating summer broadleaves were controlled effectively with the hexazinone and diuron. The trifluralin treatment provided the best control only on the grass species of Yellow Foxtail.

Initially the addition of soil adjuvant accelerated vegetative burn down caused by hexazinone and diuron. However, by the April evaluation, both hexazinone-diuron treatments had measurably equal results.

Conclusion

Background sampling found about 8% of the application rate of diuron as a residual from the previous year's application. Movement of diuron and hexazinone in this cracking clay soil was confined to the upper reaches of the soil profile even though water percolated past the deepest depths sampled (three feet). The mass of residues recovered from the total soil core length prior to the first irrigation represented a decrease from the application day values of 66% for diuron and 79% for hexazinone, however no measurable runoff occurred. The distribution of residues throughout the soil profile was different between diuron and hexazinone. Very little diuron was detected beneath the first 0-3 inch depth, whereas, concentrations of hexazinone in the deeper segment were equal to those measured in the first segment. Little to no residues were measured for either herbicide in the third segment, which represented the 12-inch depth. Based on a comparison of their physical-chemical properties, greater movement through soil would be expected for hexazinone, caused primarily by its lower soil adsorption value (Koc). After the second irrigation (June), the magnitude of the residues for both pesticides was reduced to levels that were similar to those measured in the background samples. Statistical tests for effects of treatment and location were not significant. Trifluralin or paraquat was detected in soil samples.

Significant differences in diuron concentration were measured between irrigations with the concentrations for the first irrigation runoff approximately twice the concentration of the second (Table 1). Hexazinone concentrations also appeared greater at the first irrigation; however, the level of probability indicated only a trend (P= 0.0726). The addition of the surfactant did not significantly affect the concentration of herbicides in runoff water. No significant differences in the mass of herbicide leaving the field as runoff were found between treatments or irrigations. Although the concentration of diuron herbicide was reduced in half from the first irrigation, the runoff volume had tripled in the second irrigation resulting in no significant differences in the mass leaving the field. The results for hexazinone were similar. The mass of diuron and as mean of treatments was 0.7976 g/acre for the two irrigation events. Hexazinone was lower at 0.249g/acre. The mass was carried in 0.66-acre inch/acre of runoff water.

Concentrations of both diuron and hexazinone decline with increasing runoff volumes. No trifluralin or paraquat was detected in runoff waters. A model constructed from collected data predicts less than 0.5 ppb diuron in the runoff water at a cumulative runoff of 3.0 inches per acre. The model constructed for hexazinone predicts less than 0.02 ppb at a cumulative runoff of 1.5 inches per acre. It is suspected under the constraint of management, the runoff of the entire field was similar to the first irrigation since the pond was never full for the rest of the season's irrigations. Based on this conjecture, a total of 1.6-acre inch/acre would have been available as runoff. The model predicts a concentration near 2.88 ppb for diuron by season's end. After the irrigation season (October24), pond concentration was similar at 2.4 ppb. However agreement is not as good with hexazinone at a predicted 0.16 ppb and sampled of near 0.5 ppb.

The holding pond captured the unmeasured runoff from the entire field. The non-experimental area was treated with both diuron and hexazinone as in Treatment 1; however, runoff volume per acre was managed to be smaller than the experimental area. Given these differences, the runoff concentrations from the experimental area were similar to those measured in the pond. The mass of residues infiltrated for diuron was 10.83 grams while hexazinone was 0.84 grams as a result of the two irrigations. These values could have been larger or smaller depending on the runoff management. However even with a controlled runoff the model predicts the concentration to be relatively low by season's end. The rate of infiltration is rapid at near 2.5 inches per hour at maximum capacity dropping to a low of 0.1 inches per hour near empty. It is suspected cracking of the pond wall during the drying cycle enhances the infiltration rate. The pond-infiltrated water has a direct effect of raising localized groundwater levels measured twenty feet south into the field. Each irrigation event increased the groundwater level as a direct response to pond filling and infiltrating stages. Concentration of diuron measured in the groundwater at season's end declined with distance from the pond starting at 2.5 ppb with a linear decline with distance to non-detectable at 40 feet. Hexazinone, by virtue of its lower soil adsorption value (Koc), was constant from the pond water to the farthest distance measured (160 ft).

Mitigation

The surfactant treatment was similar to the non-surfactant in terms of field distribution and runoff concentrations and volume.

Alternative herbicide materials that do not move as easily in soil and in runoff waters are an option, however they (in the case paraquat and trifluralin) did not provide the weed control of diuron and hexazinone combination. Since alfalfa hay price is established on high quality and weed free forage, significant impact can be expected with out adequate weed control.

The species of broadleaf and grass weeds in alfalfa vary as the season progresses from winter to summer. This trial demonstrates the importance of having soil residual herbicides that are applied in winter and effective on the winter spectrum of weeds. It is also apparent that no single herbicide treatment used in this experiment can effectively control the wide range of species that germinate throughout the year. Managing weeds in alfalfa will have to rely on different chemistry's of herbicides with post emergence activity and soil residual properties that are efficient in controlling the numerous mix of weeds.

Management of the residue containing runoff water seems the most likely mitigation practice in this and similar cases. Pumping the runoff from the pond to reuse in the same or adjacent field as soon as sufficient volumes are available will reduce the volume available for infiltration, reduce the high infiltration fuller pond conditions and the time for infiltration to take place.

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