Movement of Diuron and Hexazinone in Clay Soil and Infiltrated Pond Water

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ABSTRACT

Pre-emergence herbicide residues were detected in domestic wells sampled near Tracy, CA. This study sought to determine the source of contamination by comparing soil distribution of diuron [N'-(3,4-dichlorophenyl)-N,N-dimethylurea] and hexazinone [3-cyclohexyl-6-(dimethylamino)-1-methyl-1,3,5-triazine-2,4(1H,3H)-dione] in an agricultural field where the soil was a cracking clay to infiltration of residues in water captured by an adjacent holding pond. Diuron and hexazinone were applied in December to a 3-yr-old alfalfa (*Medicago sativa* L.) crop. Water content of soil taken after major rainfall but before irrigation at 106 d after application was elevated at the lowest depth sampled centered at 953 mm, indicating water was available for percolation. Herbicide residues (reporting limit 8 µg kg^{-1}) were confined above the 152 mm soil depth, even after subsequent application of two border-check surface irrigations. The pattern of distribution and concentration of residues in the soil were similar to results obtained from the LEACHM model, suggesting that macropore flow was limited to a shallow depth of soil. Herbicide residues were measured in runoff water at the first irrigation at 20 µg L^{-1} for diuron and 1 µg L^{-1} for hexazinone. Runoff water captured in the pond rapidly infiltrated into the subsurface soil, causing a concomitant rise in ground water elevation near the pond. Herbicide residues were also detected in the sampled ground water. We concluded that the pond was the predominant source for movement to ground water. Since addition of a surfactant to the spray mixture did not reduce concentrations in runoff water, mitigation methods will focus on minimizing infiltration of water from the pond.

M OVEMENT OF PESTICIDE RESIDUES from agricultural applications to ground water has been well documented (Hallberg, 1989). In California, the approach to regulation of pesticides detected in ground water is to allow continued use if management practices can be identified that mitigate the threat of contamination. This course of action balances economic considerations with environmental protection. The effectiveness of this approach relies on elucidating the pathways for movement of residues to ground water with concomitant development of farm management practices that are 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 (Troiano et al., 2001). In contrast, low infiltration rates in areas with hardpan soils

result in runoff of residues so improved incorporation of pre-emergence herbicides into the soil is recommended to reduce concentrations in runoff water.

These two scenarios are not inclusive of all geographical settings where residues have been detected in California's ground water (Troiano et al., 2000). Pre-emergence herbicide residues were detected in seven wells sampled within a 1554-ha area located near the town of Tracy, CA: atrazine was detected in five wells at 0.16 to 2.8 µg L^{-1}, diuron in one well at 0.06 µg L^{-1}, hexazinone in three wells at 0.051 to 0.11 µg L^{-1}, and simazine (6-chloro-N,N'-diethyl-1,3,5-triazine-2,4-diamine) in one well at 0.098 µg L^{-1}. Tracy is centrally located on the western side of the Central Valley of California (Fig. 1). The predominant cropping pattern was a rotation of alfalfa with corn (*Zea mays* L.) and bean (*Phaseolus vulgaris* L.). The residues were related to agricultural applications, especially since the only reported pesticidal use of hexazinone was on alfalfa. The affected area was surveyed for any obvious potential pathways to ground water. The predominant soil was a clay soil that developed surface cracks on drying. Rapid movement through soil, termed *macropore flow*, has been identified as a potential pathway for contamination (Bouma et al., 1981: Harris et al., 1994; Lin et al., 1998). Movement of atrazine in cracking-clay soils in another area of California had been investigated (Graham et al., 1992). That study indicated potential movement of herbicides into cracks with some residues detected below the plow layer, but movement to shallow ground water was not confirmed.

Another potential pathway observed during the survey was water-holding ponds located within or near the cropped fields. The ponds collected runoff water generated from rainfall or irrigation events. Through interviews, the ground water in this area was determined to be shallow at around 4500 mm. Since the ponds were between 2400 and 3000 mm deep, excavation of the ponds decreased the length of travel to ground water so recharge from the pond was another potential source for contamination. Infiltration of water from tail-water recovery pits in Nebraska was determined to be a source of ground water contamination for nitrate and atrazine (Spalding et al., 1979).

In response to the detections near Tracy, an investigation was conducted in an alfalfa field to determine fate of diuron and hexazinone herbicide residues by measuring their mass distribution in soil cores, runoff water, and vegetation. Water characteristics of an accompanying water-holding pond were measured by monitoring the changes in pond-water depth over time to determine

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Abbreviations: ANOVA, analysis of variance; CIMIS, California Irrigation Management Information System; ET, evapotranspiration; LEACHM, Leaching Estimation and Chemistry Model; RL, reporting limit.
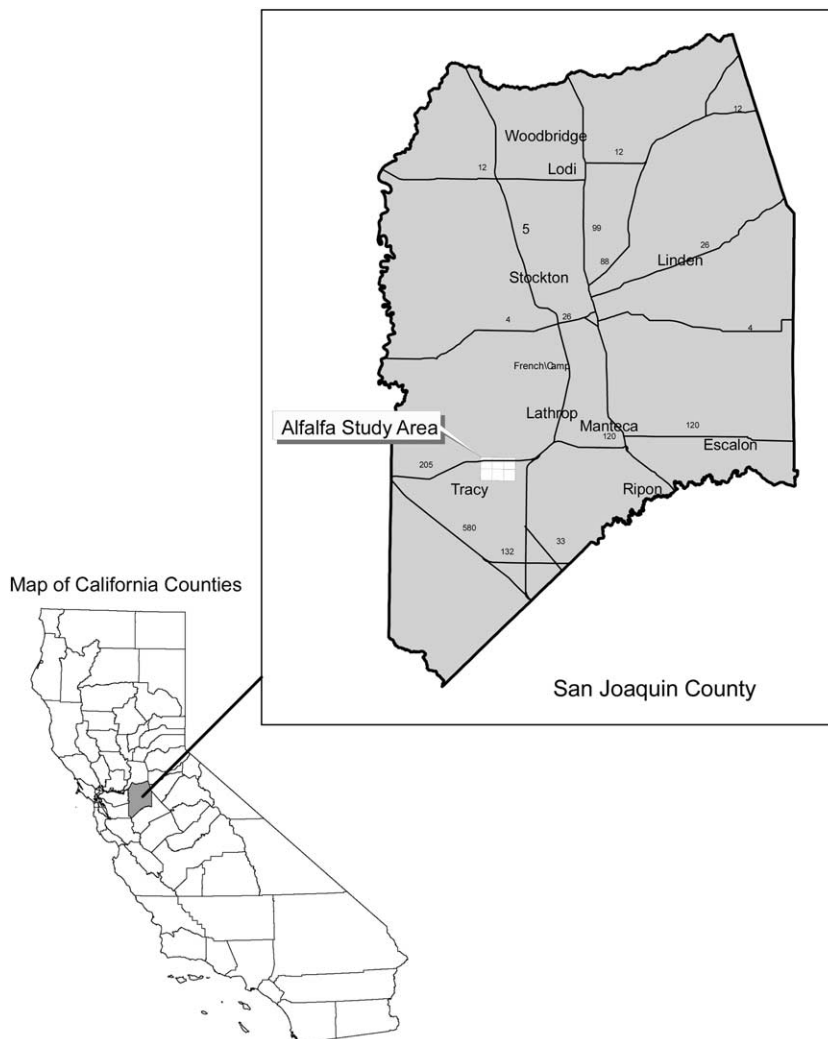
Fig. 1. Location of the alfalfa study site near Tracy, CA.

infiltration characteristics. Water infiltration from the pond was related to changes in elevation of closely associated ground water. An additional objective was to determine potential mitigation of the addition of a surfactant to the spray mixture. Theoretically, the surfactant would have facilitated greater interaction between the pesticide residue and soil matrix reducing potential runoff of residues (Huggenberger et al., 1973).

MATERIALS AND METHODS

Site and Study Description

The study was conducted within an alfalfa field located near Tracy, CA, and near a domestic well where hexazinone residues had been detected. The field was approximately 17 ha in size, entering the third season of alfalfa cultivation. The soil mapping unit was a Capay clay, which is a fine, smectitic, thermic Typic Haploxererts and determined to be a cracking-clay in the Xerert dominant suborder. Capay clay is typically described has having two horizons (Soil Conservation Service, 1992). The first horizon spans down to the 510-mm depth containing grayish brown and dark grayish brown clay with strong coarse prismatic structure. The lower horizon spans down to the 1520-mm depth containing grayish brown, dark

grayish brown, dark brown, and pale brown clay. The lower layer is calcareous and the structure changes from moderate coarse prismatic to massive, which is a change from structured to structureless soil. Analysis of chemical and physical properties of soil collected from the site was conducted by the DANR Analytical Lab, University of California-Davis (Table 1).

Alfalfa hay price is established on high quality and weed-free forage and significantly drops in value when weeds are present. Diuron and hexazinone are applied as pre-emergence herbicides to alfalfa during the dormant season usually in December or January to control existing winter weeds and to prevent subsequent weed germination. The climate is Mediterranean so the timing of application coincides with the rainy season and the winter rains are used to incorporate the herbicide residues into soil. Average monthly rainfall drops precipitously throughout the subsequent spring and summer months with no rainfall recorded in the month of July for the past 18 yr. In response to this pattern of rainfall, irrigations commence in the spring to make up for the water deficit and in this study year, irrigation was initiated in late April 2000. The method of irrigation was border-check, where water was applied to the elevated end of the field and advanced down the length of the check. Each irrigated check was 8.2 m wide by 335.4 m long, which was equivalent to 0.28 ha. The head-to-tail end of checks was aligned from south to north, respectively. Water

Table 1. Measured physical and chemical properties for Capay clay soil collected from the test site.

Soil depth	Sand	Silt	Clay	Bulk density	pH	EC	Moisture retention −33 kPa	−1500 kPa
mm	—————— % ——————			g cm^{-3}		S m^{-1}	——— L L^{-1} ———	
0–300	25	34	41	1.44	6.8	0.1	0.34	0.19
300–600	25	35	40	1.6	7.2	0.1	0.33	0.20
600–600	25	37	38	1.63	7.5	0.2	0.33	0.17
900–1200	27	39	34	1.56	7.6	0.5	0.31	0.16

was siphoned into the head of the border checks from a supply ditch that ran along the south end of the field, providing an average flow rate of 795 L min^{-1} for the first irrigation of the season and just slightly greater at 833 L min^{-1} for the second irrigation. Amount of irrigation water supplied to the check was measured by determining the hydraulic head, siphon size, and number of siphons per check. Runoff water generated from either rainfall or irrigation was diverted from the tail end of the field to a pond.

Distribution of diuron and hexazinone residues was compared between two treatments. One treatment represented grower standard pre-emergence herbicide treatment of hexazinone and diuron applied at 0.56 and 1.68 kg ha^{-1}, respectively. The second treatment was an addition of surfactant to the herbicide mixture. The soil surfactant treatment was added to enhance infiltration into the soil, thereby reducing surface herbicide concentrations that would readily move off site during a storm or irrigation event. The surfactant was a proprietary blend of nonionic and anionic surfactants designed to enhance water and herbicide infiltration into the soil profile (Garrco Products, Converse, IN). A randomized complete block design was used with four replicate blocks (Fig. 2). A third treatment was included comparing efficacy of paraquat

and trifluralin application to the grower standard, but these data are not reported. Each replicate treatment was applied to one check. The border-check irrigation method can affect distribution of residues because water can redistribute residues as it advances down the length of the check. To measure potential spatial differences due to irrigation, each check was subdivided into thirds, with each third approximately 111.6 m in length. Soil and vegetation samples were taken from each third, representing the head, middle, and tail portions of the check.

Herbicide Application

Pre-emergence treatments of diuron and hexazinone were applied as a tank mix to a semi-dormant alfalfa field on 23 Dec. 1999. Applications were made using a 9.2-m wide sprayer applying a volume of 309 L ha^{-1} under pressure at 0.151 MPa. For treatments with surfactant, the surfactant was added at a rate of 18.71 L ha^{-1}. Deposition was measured during application by placing 0.305 by 0.305 m squares of foil-lined, cotton sheets on the soil surface and collecting them immediately after application. Each sheet was mounted on a piece of cardboard to prevent direct contact with the soil surface. Three
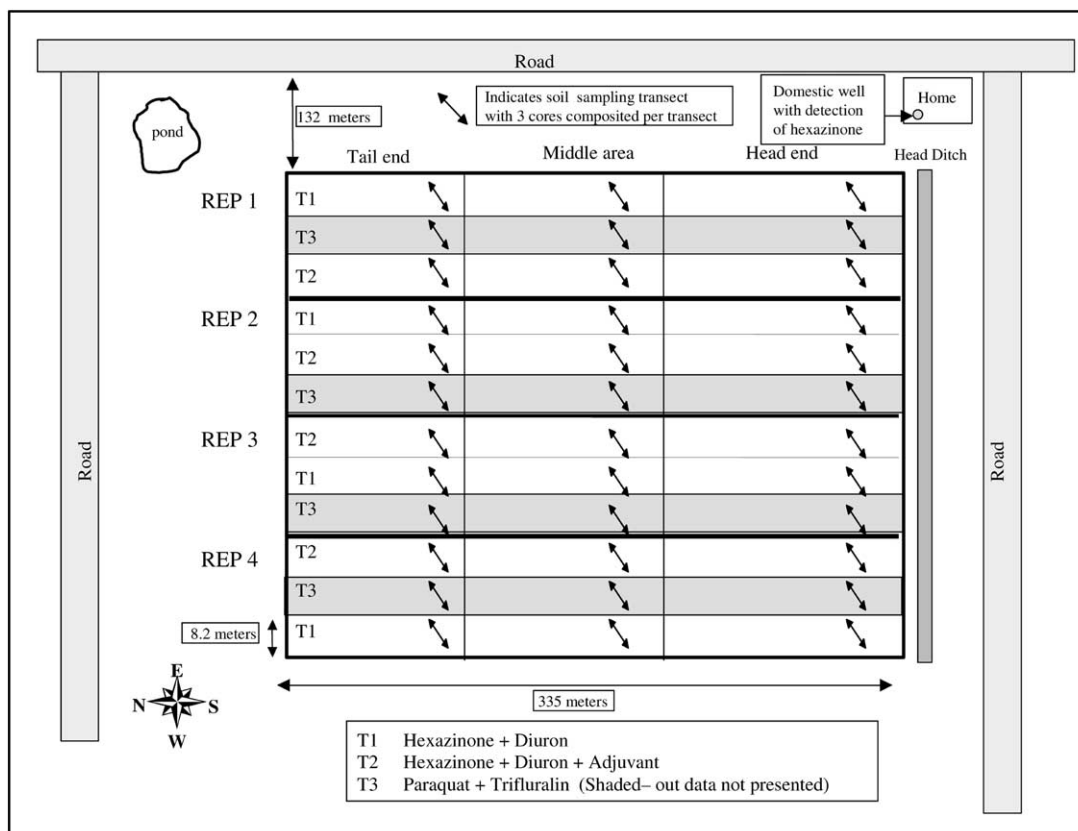

Fig. 2. Plot study design encompassing 3.4 ha of a 17-ha alfalfa field and located in the eastern end of the field.

sheets were placed in each replicate check, one in each of the upper, middle, and lower subsampling areas. The average deposition rate for diuron was 1.69 ± 0.41 kg ha^{-1} and for hexazinone was 0.42 ± 0.07 kg ha^{-1}. The rate for diuron was close to its target value of 1.68 kg ha^{-1} but the hexazinone value was lower than the target value of 0.56 kg ha^{-1} ($P < 0.05$). There appeared to be a bias in deposition between treatments for diuron, where the average rate for the plus surfactant treatments was greater than for the treatment without surfactant (Table 2). Tests for effects of spatial location within treatments were not significant, indicating even application along the length of the checks.

Soil and Vegetation Sampling

Background soil samples were collected between 16 Dec. and 20 Dec. 1999, before herbicide application on 23 December. After herbicide application, samples were collected between 3 Apr. and 6 Apr. 2000, which was before the first irrigation on 27–28 April. Soil was again sampled between 26 and 27 June 2000, which was after the second irrigation on 10 June 2000. Soil samples were collected from depths of 0 to 76, 76 to 152, 305 to 381, 610 to 686, and 914 to 990 mm. Data are reported as the center of the sample at 38, 114, 343, 645, and 953 mm, respectively. Each soil sample was a composite of three boreholes that were simultaneously sampled from a 3 m long transect located at a 45° angle within each split plot. The three subsamples were placed into a glass jar, mixed, and sealed. Soil samples were similarly collected in the pond at the December and April sampling dates, after which the pond was too muddy for sampling.

Soil was sampled using a bit that was 33.4 mm in diameter and 102 mm in depth. Samples were obtained from the first depth by inserting the sampler down to the 76-mm depth and collecting all soil from the tube. For deeper depths, the samples

were obtained from a central portion of the length of the bit that was calibrated at 60 cm^3. This area was isolated from the rest of the core by inserting knives into slots located on either end of the centrally calibrated area. Soil was removed from the ends and the isolated sample collected into a glass mason jar. Before inserting the sampling bit into the borehole, a larger diameter auger that was 64 mm in diameter was used to clear the borehole of soil down to the next appropriate depth for sampling. The smaller soil sampling bit was cleaned between each sample with soapy water, rinsed twice in sequence with deionized water and then methanol, and air-dried before reuse. Excess soil from the sampling was collected in a bucket and removed from the field. The sample borehole was refilled with noncontaminated soil and the sample borehole plugged at the surface with a mixture of soil and bentonite. Samples were placed on dry ice and kept frozen until chemical analysis. At the time of analysis, a portion of each soil sample was used to determine percentage moisture. Bulk density was calculated based on the dry weight of the sample and the volume of the soil sample.

Vegetation samples were taken at the background and at the April soil coring. Alfalfa plants were collected from the areas that encompassed each of the soil cores. The vegetation was placed directly into a 1.1-L glass jar and the jar lid sealed. The samples were transported on wet ice and then stored at 3.3°C until analysis.

Runoff Water Sampling

Runoff water was monitored from two of the four replicates from each treatment. A soil berm was formed at the tail end of those checks to facilitate runoff collection. Water was collected in a basin comprised of a 19-L plastic bucket that was installed at the lowest point inside the bermed check. A battery-powered pump and float switch placed in the collection

Table 2. Mass of diuron and hexazinone recovered in entire length of soil cores and deposition sheets, expressed as kilograms recovered per hectare. Statistical test indicated for overall linear effect of location in checks and conducted on values transposed to base 10 logarithms.

Sampling interval and location	N	Diuron		Hexazinone	
		Minus surfactant	Plus surfactant	Minus surfactant	Plus surfactant
		Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
			kg ha^{-1}		
Deposition sheets, 23 Dec. 1999					
Total	12	1.52 ± 0.32	1.85 ± 0.44	0.40 ± 0.07	0.44 ± 0.06
Head	4	1.53 ± 0.11	2.02 ± 0.58	0.40 ± 0.04	0.46 ± 0.07
Middle	4	1.51 ± 0.05	1.84 ± 0.45	0.41 ± 0.10	0.44 ± 0.06
Tail end	4	1.52 ± 0.35	1.68 ± 0.26	0.38 ± 0.08	0.41 ± 0.06
Linear effect		NS†		NS	
Background soil, 16–20 Dec. 1999					
Total	12	0.14 ± 0.04	0.11 ± 0.04	0.00 ± 0.01	0.00 ± 0.00
Head	4	0.14 ± 0.05	0.10 ± 0.03	0.01 ± 0.01	0.00 ± 0.00
Middle	4	0.13 ± 0.03	0.12 ± 0.05	0.00 ± 0.01	0.00 ± 0.00
Tail end	4	0.14 ± 0.05	0.10 ± 0.04	0.00 ± 0.00	0.00 ± 0.00
Linear effect		NS		NS	
Soil before first irrigation, 3–6 Apr. 2000					
Total	12	0.51 ± 0.15	0.67 ± 0.15	0.11 ± 0.05	0.11 ± 0.05
Head	4	0.40 ± 0.09	0.64 ± 0.25	0.09 ± 0.04	0.09 ± 0.02
Middle	4	0.56 ± 0.15	0.70 ± 0.11	0.11 ± 0.03	0.15 ± 0.05
Tail end	4	0.59 ± 0.16	0.67 ± 0.10	0.13 ± 0.07	0.08 ± 0.05
Linear effect		$P = 0.02$		NS	
Soil after second irrigation, 26–27 June 2000					
Total	12	0.15 ± 0.08	0.20 ± 0.04	0.04 ± 0.01	0.04 ± 0.02
Head	4	0.12 ± 0.05	0.18 ± 0.05	0.03 ± 0.00	0.03 ± 0.01
Middle	4	0.11 ± 0.02	0.19 ± 0.05	0.03 ± 0.01	0.05 ± 0.01
Tail end	4	0.22 ± 0.11	0.24 ± 0.04	0.04 ± 0.02	0.04 ± 0.04
Linear effect		$P = 0.04$		$P = 0.04$	

† NS, no significant effect; otherwise the probability level is given.

basin moved runoff water into a 3.8-L sample collection jar. A larger capacity gas-operated pump was utilized to assist the lower flow battery-operated sampling pump during times of higher runoff. Pumps operated until runoff was complete. Both pumps were metered and withdrew water simultaneously from the same collection bucket. Once the initial sample jar was full, the remaining water was pumped through a water meter and then through a proportional sampling device, which collected 2% of the outflow volume in a series of 19-L buckets. A 1-L subsample was collected from each 19-L bucket and it was stored in an amber glass bottle that was sealed with a Teflon-lined cap. This subsample represented the average concentration of herbicide residue moving offsite for the volume indicated by the water meter. The water samples were placed on wet ice until arrival at a storage facility and remained at 3.3°C until analysis.

Holding Pond Soil and Water Sampling and Ground Water Depth Measurement

At the beginning of the study, the holding pond was dry so soil samples were collected from two locations at the bottom of the pond. Soil sampling and handling procedures were the same as described for sampling in the field. Water samples were collected in a 1-L amber glass bottle sealed with a Teflon-lined cap. Samples were placed on wet ice and refrigerated at 3.3°C until chemical analysis. It is important to note that the water entering the pond was the result of runoff from a larger area than the experimental area, for example, the 12 experimental checks were a portion of the total planted area. Although pond-water samples were not a direct measure of loss of herbicide mass from runoff that originated solely in the treatment areas, pond-water concentration was an important indicator of the potential fate of herbicides applied to the field. Water samples were collected after each irrigation when pond inflow had stopped.

A technique was developed to determine pond volume from water depth measurements. First, the volume of the pond was estimated by surveying the three-dimensional measurements of the pond. A relationship was then 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 (Plasti-Fab, Tualatin, OR) equipped with a stilling well and pressure transducer to measure head (Clemmens et al., 1984). An additional transducer was placed at the bottom of the pond to measure pond depth. Temporal changes in pond depth were used to estimate pond water volume and, subsequently, infiltrated water according to Eq. [1]:

$$y = 0.0002x^2 + 0.12026x \qquad [1]$$

where y = pond water volume (m^3) and x = pond water depth (mm) ($r^2 = 0.998$).

Changes in depth to ground water in an area adjacent to the pond were measured with a pressure transducer. The transducer was placed into an open-ended, close-fitting PVC pipe and then affixed in the borehole.

Chemical Analysis

Chemical analysis for diuron and hexazinone were contracted to the Center for Analytical Chemistry (California Department of Food and Agriculture, Sacramento, CA). Soil samples were extracted with a hexane and acetone mixture, vegetation and sediment samples were extracted with acetonitrile, and water samples were processed through a C18 SPE column (Phenomenex, Torrance, CA) that was eluted with methanol. Reconstituted extracts were analyzed with liquid chromatography (model 2690, Waters Corp., Milford, MA) and mass spectrometry methodology (Finnigan LCQ Decca, Thermo Electron Corp., Madison, WI). Specific methods of analysis are available on request. A standard operating procedure had been developed to assure verification of laboratory results (Segawa, 1995). During method development, the laboratory established acceptable warning and control limits, and sample reporting limits (RL). For continuing quality control, a solvent blank and two matrix spikes were analyzed with each extraction set. Extraction sets were analyzed again if the spikes did not fall within the established warning and control limits. Each sample was tracked from initial sampling to final analytical result with an accompanying chain of custody form. Reporting limits for diuron and hexazinone were 8 μg kg^{-1} for soil, 0.25 μg L^{-1} for water, 10 μg kg^{-1} for sediment, and 100 μg kg^{-1} for vegetation samples.

Data Analysis

Study objectives were to determine fate of herbicides applied to the soil and to compare addition of surfactant on herbicide distribution within the field. With respect to fate of herbicides, the relative potential for downward leaching of residues within the field was compared with movement of residues in runoff water that eventually infiltrated from a holding pond at the edge of the field. Extent of downward movement within the field was measured in soils cores and compared with soil water movement produced from rainfall and irrigation. In addition, expected soil distributions of water content and herbicide residues were predicted using the LEACHM model version 4 (Hutson, 2003). Since LEACHM uses convection–dispersion methodology to model water flow, deviations between observed soil concentrations and predicted values could indicate the extent to which movement was dominated by preferential pathways. This method to deduce preferential flow by comparison of observed to model predictions of soil distribution has been previously reported by Gish et al. (2004) and Tindall and Vencill (1995). Data for physical and chemical properties of diuron and hexazinone used in the model were obtained from the Oregon State University Extension website, which is a compilation of data from two USDA publications (Table 3) (Vogue et al., 1994; Augustijn-Beckers et al., 1994; Wauchope et al., 1992). Values for soil texture and bulk density were taken from measured data (Table 1). Rainfall data was obtained from the Tracy Pestcast weather station, which was located <3 km from the experimental site (Univ. of California, 2002). Estimates for reference evapotranspiration (ET$_o$) were obtained from a CIMIS (California Irrigation Management Information System; California Dep. of Water Resources, 2001) weather station located in Manteca, CA, which was located approximately 22 km east of the experimental site. Surface flux density for water intake was set at 390 mm d^{-1}, which was calculated from the irrigation events. Crop growth was included to provide for loss of water through plant transpiration and the roots were distributed with 60% apportioned in the first 305-mm soil depth. This estimate was determined from a stylized depiction of the root distribution of a mature plant, which indicates that a large portion of active roots are located in the first 305 mm of soil (Weaver, 1926).

The contribution of residue movement to ground water from the pond was determined from the calculated water balance, the measured concentration of herbicides in pond water, and the response measured in nearby shallow ground water with respect to changes in elevation from the surface and herbicide concentration.

Table 3. Estimates for pesticide active ingredient physical and chemical properties. Data obtained from Oregon State University Extension website (Vogue et al., 1994).

Active ingredient	Soil half-life	Water solubility	K_{oc}
	d	mg L^{-1}	L kg^{-1}
Diuron	90	42	480
Hexazinone	90	33 000	54

For surfactant treatment, effects on recovered mass were measured using a split-plot analysis of variance (ANOVA) for a randomized complete block design with surfactant treatment as the main effect and location in the field as the split-plot factor (i.e., head, middle, and tail end location) (SAS Institute, 1988). The effect of field location was measured using orthogonal regression contrasts measuring linear and quadratic spatial effects. Since data from the deposition sheets indicated potential differences in application between surfactant treatments, the deposition data were used as a covariate in ANOVA. In addition, potential for heterogeneity of variance was indicated using Levene's Test for homogeneity of variance so values were transposed to base 10 logarithms before statistical analysis (SAS Institute, 1988).

Recovered pesticide mass was determined as the product of concentration and mass of soil or water. The first two soil cores were contiguous so the concentration for the first 76-mm soil depth was used to directly estimate mass recovered from the first soil segment. To account for discontinuity in sampling between the remaining soil depths, estimates were integrated as the product of the average concentration and bulk density between depths. Herbicide residues were expressed on a kg ha^{-1} basis to facilitate comparison to application rates.

RESULTS

Water Distribution and Movement

A comparison of cumulative ET$_o$ to the cumulative amount of rainfall and irrigation provided a reference for potential amount of runoff and percolated water
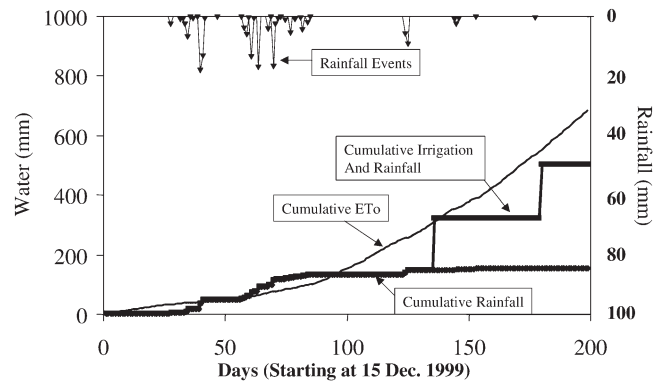

Fig. 3. Comparison of cumulative reference evapotranspiration (ET$_o$) to cumulative rainfall and to cumulative rainfall plus irrigation water volumes as indicated by the bottom and left axes. Specific rainfall events and water depth are indicated on the top and right axes.

produced during the study (Fig. 3). In the 75 d before the initiation of this study on 15 Dec. 1999, only 9 mm of rainfall was recorded. In addition, rainfall was not measured for the first 30 d of the experimental period. Except near the soil surface, water content of background soil cores was much lower than that measured for the next two sampling intervals (Fig. 4, Graph A vs. Graphs B and C). Average estimated mass of water in the entire soil core was 190 ± 13 g.

The cumulative rainfall amount eventually became greater than cumulative ET$_o$ at around Day 60 (Fig. 3). Rainfall runoff water was not observed during this period, so the frequency and amount of rainfall was not sufficient to generate significant runoff water samples from the experimental checks. Soil water content at the second soil coring date, which was before the first irrigation event, was consistently greater than background samples, indicating that water from rainfall per-
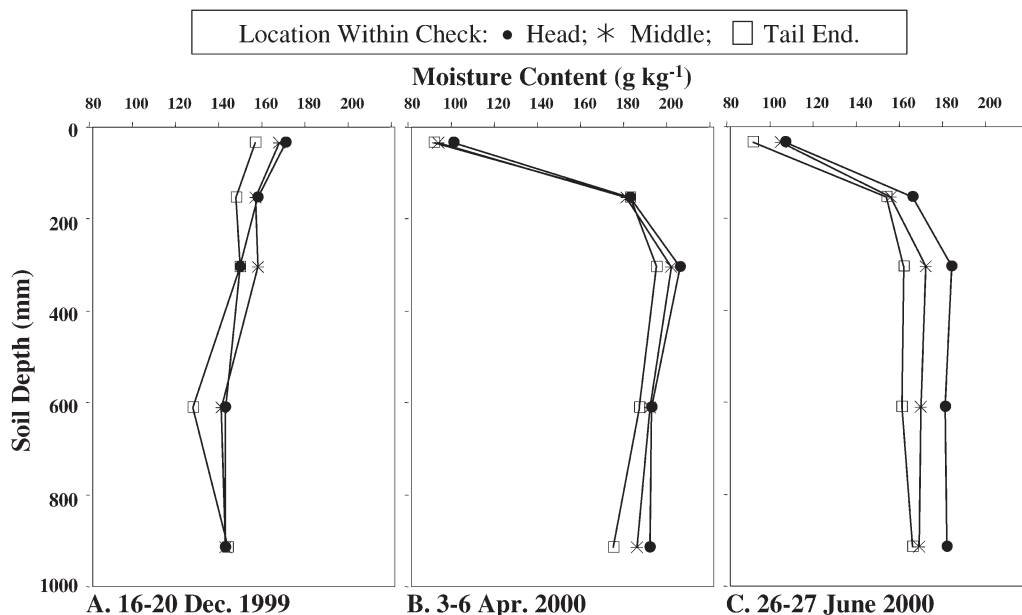

Fig. 4. Water distribution in soil cores obtained from: (A) background samples taken 16–20 Dec. 1999, (B) before initiation of border-check irrigation 3–6 Apr. 2000, and (C) after two border-check irrigations 26–27 June 2000.

colated down to the lowest soil depth sampled (Fig. 4B). There were no significant differences in water content due to treatment or location effects. Average estimated mass of water in the entire soil core was 239 ± 15 g, an increase of 39 g from the background sampling and based on the diameter of the soil core corresponded to an added depth of 44.5 mm of water. At 115 d after application the total amount of rainfall was 131 mm, whereas total ET_o was 217 mm. Although evapotranspiration was greater than rainfall, water was moved to the deepest soil segments.

Rainfall after Day 85 was minimal and owing to increasing solar radiation, the accumulation of ET_o began to accelerate. The two sharp upward spikes in accumulated rainfall plus irrigation illustrates the contribution of water from the two irrigations (Fig. 3). The irrigations supplied enough water to match the cumulative deficit in ET_o. Both irrigation events were similar in terms of total run time and onflow volumes, averaging 175 mm. Calculated runoff depth for the irrigations was 4.3 and 12.4 mm for the first and second irrigations, respectively. Differences between irrigations were caused by small differences in on-flow volumes, run times, and soil infiltration rate influenced by antecedent soil moisture content. The proportion of on-flow water volume occurring as runoff was 2.5% of the first and 7.1% of the second applied irrigation volumes. Runoff from the second irrigation was considered more reflective of typical conditions.

The moisture profile of the soil cores at the third sampling date, which was after two border-check irrigations, was reflective of a distribution caused by the dynamics of border-check irrigation (Fig. 4C). Within checks, there was a significant linear effect ($P = 0.02$) on total water content of the cores, which was a decrease in water content of soil cores from the head to tail ends— average estimated mass of water in cores was 228 ± 17,

213 ± 16, and 205 ± 12 g for head, middle, and tail end locations, respectively. Higher moisture at the head end of the border check is caused by greater opportunity time for water infiltration. More importantly, water content remained elevated at the lowest sampled depth, indicating that irrigation treatments caused drainage and provided a potential leaching environment.

Soil and Vegetation Sampling within the Alfalfa Field

Vegetation

Hexazinone was not detected in vegetation samples. Diuron was not detected in background samples but it was detected in 7 out of 24 samples obtained before the first irrigation event on 3–6 April. Detections were at or just above the reporting of $100 \mu g \ kg^{-1}$ with the average for detections at $118 \pm 18 \mu g \ kg^{-1}$ on a dry mass basis. Plant yield measured on 3 April was 2880 kg ha^{-1}, on a fresh mass basis. Assuming vegetative water content of 80%, dry mass would be estimated at 576 kg ha^{-1}, which at the average concentration of diuron would have sequestered diuron at a rate of 0.000068 kg ha^{-1}. Since presence in vegetation was a small portion of the total application rate (0.004%), the following discussion will focus on the fate of residues in soil and water samples.

Soil

Background Sampling. Diuron residues were detected in all samples centered at the 38-mm depth and only sporadically in the next lower depth centered at 114 mm (Table 4, please note that data at each depth were averaged over all locations). Hexazinone residues were essentially undetected, which was likely due to its lower application rate. Summation of the estimated mass re-

Table 4. Observed soil water content (T) and soil concentration of diuron and hexazinone compared with predicted values using the LEACHM model.

	Soil water content (T)		Pesticide soil conc.			
			Diuron		Hexazinone	
Soil depth	Observed†	LEACHM	Observed	LEACHM	Observed	LEACHM
mm	——— L L^{-1} ———		——————— μg kg^{-1} ———————			
	Background 15 Dec. 1999‡					
38	0.25 ± 0.02	–	115 ± 34	–	0.5 ± 3	–
114	0.23 ± 0.01	–	4 ± 9	–	0.3 ± 2	–
343	0.23 ± 0.02	–	0.5 ± 2	–	0 ± 0	–
645	0.21 ± 0.03	–	0 ± 0	–	0 ± 0	–
953	0.22 ± 0.03	–	0 ± 0	–	0 ± 0	–
	Before first irrigation April 2000					
38	0.14 ± 0.02	0.25	592 ± 175	800	45 ± 15	96
114	0.27 ± 0.02	0.24	13 ± 11	40	24 ± 13	54
343	0.30 ± 0.02	0.24	1 ± 3	0.2	0.5 ± 3	2
645	0.29 ± 0.02	0.23	0 ± 0	0	0 ± 0	0
953	0.28 ± 0.03	0.21	0 ± 0	0	0 ± 0	0
	After second irrigation June 2000					
38	0.15 ± 0.02	0.29	152 ± 57	319	11 ± 7	9
114	0.24 ± 0.02	0.29	9 ± 8	113	10 ± 5	9
343	0.26 ± 0.02	0.27	2 ± 5	0.3	0 ± 0	15
645	0.26 ± 0.03	0.26	0 ± 0	0	0 ± 0	3
953	0.26 ± 0.03	0.25	0 ± 0	0	0 ± 0	0.2

† Observed values are the average of data from 24 soil cores ±SD.
‡ Initial values used for LEACHM modeling.

covered from all depths indicated an average recovery corresponding to 0.12 kg ha^{-1} diuron, which was approximately an 8% carryover from the previous year's application. There were no significant differences in mass recovered between spatial locations within checks (Table 2).

Before First Irrigation. The plots received 130 mm of rainwater between pesticide application and commencement of soil sampling on 3 April. The distribution of residues in the soil profile differed between diuron and hexazinone (Table 4, see observed values). The bulk of diuron residue was located in the first soil segment centered at the 38-mm depth with very low concentrations in the next depth—average concentration in the second soil segment was only 2% of the concentration measured in the first segment. In comparison, hexazinone concentration in the second soil segment was 50% of that measured in the first segment, which in relation to application rates represented a greater portion of mass moved below the first segment.

For total mass recovered per core, a test for the main effect of surfactant indicated greater total amount of diuron recovered in treatments with added surfactant, but when deposition data were used as a covariate in the ANOVA, the effect was nonsignificant (Table 2). The test for a linear effect between the head to tail location was significant with or without the addition of the covariate, which appeared to be caused by lower recovery of diuron in the head portion of the minus surfactant plot. When tested within treatments, the linear effect was significant for the minus surfactant treatment but not in the plus surfactant treatment. Although statistical tests were not significant, the pattern for hexazinone appeared similar to diuron where the head end of the minus surfactant treatment appeared lower than the rest of the data, but the residues were more evenly distributed in the plus surfactant treatment. Since deposition data indicated very even application from the head to tail portion of each treatment (Table 2), this pattern could indicate that the surfactant was effective at minimizing redistribution of residues within the field.

Mass of residues recovered from the total soil core length averaged over both treatments was 0.59 kg ha^{-1} for diuron and 0.11 kg ha^{-1} for hexazinone. These represented a decrease from the application day values of 65% for diuron and 74% for hexazinone. Based on first-order exponential dissipation and a sampling interval of 106 d, estimated half-life values were 70 and 55 d for diuron and hexazinone, respectively.

After Second Irrigation. The alfalfa field received two border-check irrigations before soil sampling on 26 June, resulting in a cumulative total application of 498 mm of water. Distribution of diuron and hexazinone residues were similar to the April sampling where diuron residues were mainly located in the first soil segment and with hexazinone residues split nearly evenly between the first two soil segment depths (Table 4). Although the head end of the plots received greater water infiltration and percolation as observed in Fig. 4, soil distribution was the same between locations, indicating similarity in downward movement of residue between head and tail locations (data not shown).

For total mass recovered per core, the overall linear effect for location of checks was significant for both diuron and hexazinone where the concentrations were lowest at the head end when compared with the tail end (Table 2). With border-check irrigation, water flows from the head to the tail and this pattern could indicate movement of residues with the irrigation water. In this case the surfactant was not adequate to minimize redistribution of residues in the irrigation water.

Mass of residue recovered from the total soil core length averaged over both treatments was 0.18 kg ha^{-1} for diuron and 0.04 kg ha^{-1} for hexazinone. These represented a decrease from the application day values of 90% for diuron and 91% for hexazinone. Based on first-order exponential dissipation and a sampling interval of 198 d, estimated half-life values were 62 and 56 d for diuron and hexazinone, respectively. These estimates do not include residue lost in tailwater.

Soil LEACHM Model Predictions

LEACHM model predictions for water content and herbicide concentration in the soil profile were compared to observed data at each sampled depth (Table 4). The comparisons were made only to determine whether preferential movement had a great effect on soil distribution of residues in relation to a situation where flow would have been dominated by convection–dispersion theory. At the April soil sampling before the first irrigation, LEACHM predicted slightly lower water content for the deepest soil segment. In contrast, measured water contents indicated much drier soil conditions in the first 76-mm segment and wetter conditions in the remaining profile. The observed data could be reflective of the influence of macropore flow where water preferentially flowed through surface cracks wetting subsurface soil. The pattern was similar at the June sampling, which was after two surface irrigations. In addition to soil structure effects on water flow, plant transpiration is another process that would produce a drier surface soil condition. Although LEACHM modeled approximately 45 mm of water lost to evaporation and 155 mm to plant uptake between the first and second soil coring, relatively high water content was maintained in the first soil segment. LEACHM allows upward movement of water, which may be a cause of the overestimation for this soil.

Surprisingly good agreement was observed between predicted and observed soil concentrations for both pesticides at the April and June sampling dates (Table 4). The agreement between concentrations indicated that the bulk of the residues were confined to the upper layers of soil even though the soil water distribution indicated an effect of macropore flow early in the season. LEACHM predicted deeper movement for hexazinone, an effect that was observed in the field data.

Runoff Water Sampling

A significant difference in diuron concentration was measured between irrigations where the concentration measured in runoff from the first irrigation was approxi-

Table 5. Concentration of diuron and hexazinone measured in runoff water and respective mass recovered averaged across treatments and irrigations.

Treatment or irrigation event	Conc.		Mass recovered	
	Diuron	Hexazinone	Diuron	Hexazinone
	$\mu g\ L^{-1}$		$kg\ ha^{-1}$	
Treatment				
Minus surfactant	13.27	0.42	1.06	0.03
Plus surfactant	17.37	0.70	0.91	0.03
Probability	0.20	0.28	0.61	0.63
Irrigation event				
Irrigation 1	20.53	0.95	0.77	0.03
Irrigation 2	10.08	0.26	1.20	0.03
Probability	0.02	0.07	0.19	0.90

mately twice the concentration of the second irrigation runoff event (Table 5). Although hexazinone concentrations also appeared greater at the first irrigation, the level of probability indicated only a trend ($P = 0.07$). Significant differences in mass of herbicide leaving the field were not detected between treatments or irrigations. The concentration of diuron herbicide was reduced by 50% from the first irrigation but 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. Addition of the surfactant did not affect the concentration of herbicides in runoff water (Table 5).

Holding Pond Sampling

Measure of Infiltrated Water and Ground Water Levels

The holding pond captured runoff water generated from the entire field, which received the grower standard treatment without added surfactant. At full capacity, the pond held a volume of 420 m³ water. The pattern of water collection and disappearance indicated a small amount of water was collected in the pond due to winter rain, which most likely originated from runoff generated near the pond and not from the entire field (Fig. 5A). The pond was nearly empty before each irrigation with less runoff measured in the first irrigation than in the second irrigation event when maximum pond capacity was reached.

There was no pond water-recycling pump so water was lost either to evaporation or infiltration that eventually percolated. Each irrigation event consisted of a sequencing of sets from one end of the field to the other. Thus, infiltration occurred during the surges of runoff that was captured from each of the daily irrigation sets. Average daily pond water volume was calculated and adjusted for evaporative loss based on surface area and gain from precipitation. The volume difference between days was considered to be the volume of water infiltrated within the 24-h period. The amount of water infiltrated was estimated at 235 m³ for the first irrigation and at 615 m³ for the second irrigation. Total volume of runoff water infiltrated by the pond as a result of both irrigations was 850 m³. The majority of the pond water volume was infiltrated in just a few days (Fig. 5A). The highest rate of infiltration was estimated at 17.2 cm

d⁻¹ (0.72 cm h⁻¹) at a pond depth of 995 mm. Infiltration rates decreased as the wetted area of the pond decreased.

Comparison of the simultaneous measurements between pond water depth and ground water depth measured in a borehole near the pond indicated that the shallow ground water was relatively constant until the first irrigation, at which time the depth from the surface decreased sharply (Fig. 5B). A similar response was measured for the second irrigation; the rise in ground water elevation corresponded to the loss of water from the pond. The quick response in the ground water level indicated a short travel time for pond water to recharge nearby ground water.

Soil Sampling

Presence of residues in the soil profile of the pond was determined when the pond was dry, which was at the background and before the first irrigation soil sampling dates. For the background sampling, diuron residues at $45 \pm 18\ \mu g\ kg^{-1}$ were detected down to the fourth deepest sample, which was centered at 645 mm below the bottom of the pond. Although these soil concentrations were low, they were indicative of movement of diuron residues from the field during the previous season. In addition, the pond was excavated to between 2500 and 3000 mm so residues were much deeper in the soil than measured within the field. Diuron residues were also detected in soil samples taken before the first irrigation and they were located at the third deepest sample centered at 345 mm below the bottom of the pond. The average concentration was slightly greater at $69 \pm 49\ \mu g\ kg^{-1}$. Hexazinone was not detected at either sampling date.

Water Sampling

Herbicide residues were measured in filtered pond water samples collected after rain runoff water at 2.2 $\mu g\ L^{-1}$ for diuron and 0.6 $\mu g\ L^{-1}$ for hexazinone. As noted earlier, the pattern of rainfall did not generate significant runoff from the field; therefore, these samples were probably reflective of conditions near the pond and not the entire field. Samples collected after the inflow to the pond had ceased from the first irrigation contained diuron at 12.4 $\mu g\ L^{-1}$ and hexazinone at 1.0 $\mu g\ L^{-1}$. The concentrations in samples collected after the second irrigation were similar to the first irrigation runoff samples with diuron at 11.8 $\mu g\ L^{-1}$ and hexazinone at 0.9 $\mu g\ L^{-1}$. The concentration of diuron in the pond in the first irrigation was about twice that of the average treatment runoff, but hexazinone concentrations in the runoff water were similar. The cause for these variable differences is not apparent but may be due to a combination of variability in spray deposition and in application of irrigation water throughout the entire field: irrigation of the entire field required seven individual irrigation sets applied sequentially. Runoff volumes between sets were variable as measured by pond inflow volumes.
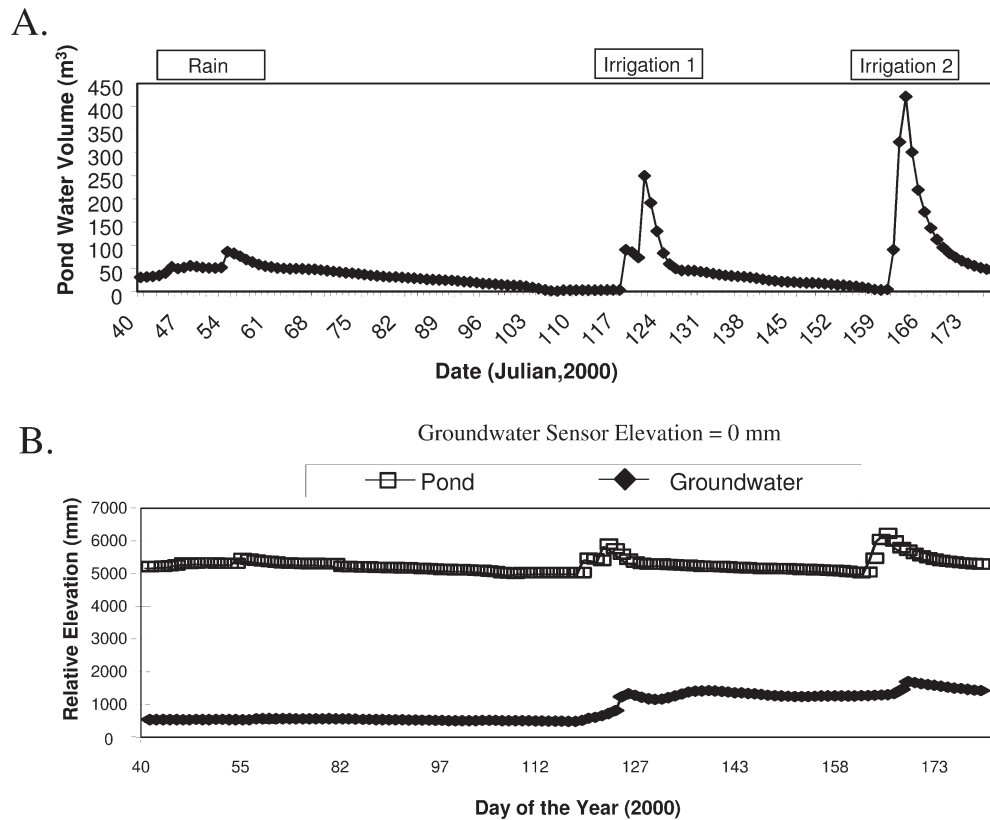
A.

B.

Fig. 5. Water gain and loss in the holding pond in relation to changes in ground water depth: (A) daily changes in holding pond water volume and (B) changes in pond volume in relation to elevation in ground water depth measured below the pond where the scale is graded so that the deepest measure is initiated at 0.

Groundwater Depth and Herbicide Concentration

Samples of ground water obtained from boreholes near the pond on 24 October were located on a transect at 3, 6, 12, and 48 m from the pond. At this time, the last irrigation had occurred >40 d before this measurement; therefore, the pond was nearly empty for about 25 d. Depth to ground water ranged from 3080 to 3140 mm with little hydraulic gradient measured between boreholes. Herbicide residues were detected with the concentration of diuron in the water, decreasing with distance from the pond water; the concentration was near 2.5 μg L^{-1} near the pond and nondetectable at 12 m and further (Fig. 6). The hexazinone concentrations found in the boreholes were similar at all sampling distances at about 0.5 μg L^{-1}. The cause of the difference in pattern of detections is unclear.

DISCUSSION

Even though this investigation was only 1 yr in scope, the results clearly implicated percolation of water collected in the pond as the predominant pathway for entrance of herbicide residues into ground water at this site. Within the field, hexazinone and diuron residues were not detected below the 152-mm soil depth. The reporting limit in soil was 8 μg kg^{-1}. It is possible that residues below these limits were moved deeper into the soil profile. In addition, the soil sampling design may

have not adequately detected all residue movement. However, a number of lines of evidence tend to indicate that residue movement was restricted. First, many studies measuring the significance of macropore flow have been conducted in other cracking clay soils where the soils were modified with drainage systems to alleviate shallow water table conditions (Harris et al., 1994; Beck et al., 1995; Brown et al., 1995; Traub-Eberhard et al., 1995). We acknowledge that these previous studies have shown macropore flow as a significant pathway to shallow drains at those sites. However, in a model of vulnerable areas that contained cracking clay soils in the Netherlands, Oostindie and Bronswijk (1995) identified thickness of the clay layer and depth to ground water as important factors that determine residence time of
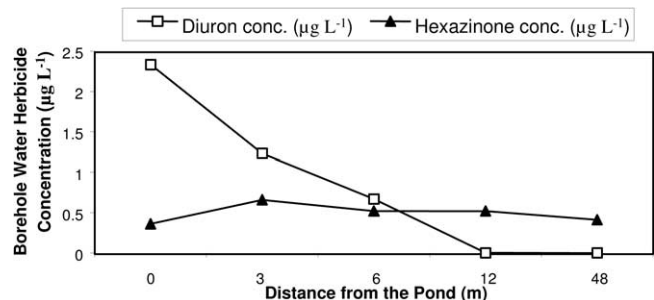

Fig. 6. Concentration of diuron and hexazinone measured in ground water samples obtained along a transect at increasing distances from the holding pond.

water within the soil profile and subsequently ground water vulnerability. For the conditions they modeled, depth to the water table was shallow, beginning at the bottom of the cracks—water table depth was around 500 mm in wet conditions and deeper than 1200 mm in dry conditions. The conditions at the Tracy site provide a contrast to these studies, because the Capay soil at our site was a thick clay soil at least 1520 mm in depth and it changed from a structured to a structureless soil in the lower horizon. One other important feature of the Capay clay is that it does not have an inherent shallow water table because it is classified as having no apparent water table above 1520 mm during the winter, rainy season. These soil properties would have tended to dead end macropores, allowing water and pesticide to infiltrate first into the soil matrix instead of flowing directly into the water table. Gish et al. (1991) concluded that after movement into soil by preferential flow, residues diffuse into the soil matrix, limiting further movement. Even if residues below our detection limits moved deeper into the soil, the time for travel time to the ground water located at around the 4500-mm depth would have allowed for further residue degradation.

Deeper soil movement observed for hexazinone was another indication of intimate interaction between pesticide residues and the soil matrix because the difference reflected their respective physical and chemical properties. The K_{oc} for diuron is greater than for hexazinone, which should result in greater soil retention and less potential for downward movement. Dissipation rates are relatively long for both diuron and hexazinone, so soil adsorption would be the major determinant for differences in soil distribution (Jury et al., 1987; Gustafson, 1989). In a previous comparison between diuron and cyanazine, less soil movement of diuron was attributed to greater soil adsorption (Majka and Lavy, 1977). The concurrence between LEACHM modeled and observed soil concentrations of diuron and hexazinone and their relative soil distribution indicated a close association between the pesticide residues and the soil matrix. We are not suggesting that the primary mechanism of water movement was through convection–dispersion, only that the similarity in results between the modeled and observed data indicated that effects of preferential flow in macropores were localized to a shallow layer of the soil. In contrast, Tindall and Vencill (1995) noted similar anomalous high concentrations of atrazine [6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine], dicamba (3,6-dichloro-2-methoxybenzoic acid), and 2,4-D [(2,4-dichlorophenoxy)acetic acid] deeper in a cracking-soil profile and ascribed the similarity in movement to bypass due to preferential flow. The presence of the alfalfa root system in our study could have provided additional sources for pesticide adsorption, further emphasizing their differences in K_{oc}.

Another factor lessening the influence of soil macropores was the typical pattern of rainfall. Dry conditions at the onset of the study would have promoted surface cracking. Then, winter rains would have filled the cracks causing swelling of the clay soil before the crop irrigations. Hourly rainfall data indicated that 154 h of measured rainfall occurred at the site between the herbicide application and the April soil sampling. The rainfall intensity of 70% of events was 1 mm h^{-1} or less. For the first 62 d after pesticide application, the maximum hourly intensity measured in a 24-h period was 3.3 mm h^{-1} and at only six times were intensities >1 mm h^{-1}. After 15 Feb. 2000, a few rains were recorded with a maximum intensity at 7.62 mm h^{-1}. Macropore flow was shown to be a major pathway for solute movement under high intensity rainfall (Júnior et al., 2004). However, the low intensity rain events typical for this site would have tended to swell the clay soil, thereby minimizing effect of larger water applications on rapid downward movement. Lin et al. (1998) reported temporal changes in infiltration rates of Vertisol soils where rainfall events decreased macroporosity, resulting in associated decreases in infiltration rates. Decreased velocity in the downward movement of water would have also contributed to greater interaction between herbicide residues and the soil matrix.

In contrast, data collected for the pond indicated fast movement of water to shallow ground water where water infiltrated from the pond within a few days after collection, elevating the level of nearby shallow ground water. This route provided a direct conduit for residues dissolved in runoff water to enter ground water. The major route of water loss was apparently through the sides of the pond because over time fine soil particles collected and formed a sediment on the bottom of the pond. Even though the herbicide concentrations measured in runoff water were low, they were about an order of magnitude greater than the concentrations measured in nearby domestic wells. Based on the rapid injection of pond water and herbicide residues into the ground water, we concluded that the pond was the most likely source for contamination. It should be noted that the specific volumes of water or herbicide concentrations generated in other years or from other sites could be larger or smaller depending on nuances in irrigation management and subsequent runoff management. As part of the Nebraska Management Systems Evaluation Area study, Spalding et al. (2003) monitored concentrations of pre-emergence herbicides in ground water using multilevel samplers located up-gradient, within, and down-gradient of the experimental site. Seasonal peaks in detections of pre-emergence herbicides in samplers located down-gradient of the plot were attributed to recharge that originated from ditches that collected runoff water from surge irrigation treatments.

Ground water sampled near the pond later in the season indicated similar concentration of hexazinone along a transect that radiated outward from the pond. Diuron concentration, however, decreased with increase in distance from the pond. It may be serendipity but results from the domestic well sampling that resulted in this investigation detected only hexazinone residues in the well located adjacent to this field, mimicking the pattern measured along the transect. Another well situated at the opposite end of this section of land, at around a distance of 1609 m, contained residues of atrazine and bromacil [5-bromo-6-methyl-3-(1-methylpropyl)-2,4(1H,

3*H*)pyrimidinedione]. And as indicated in the introduction, simazine and other combinations of residues had been detected in wells within the original six-section study area. This indicates a complex scenario for pesticide movement to ground water that is determined by a combination of localized cropping patterns, which dictate specific pesticide use, and the specifics of water application and subsequent capture and flow of water from the ponds to ground water.

Lastly, the addition of surfactant to the spray mixture produced mixed results. Before irrigation events, the surfactant appeared to maintain an even distribution of residues throughout the check. After two irrigation events, residues appeared greater at the tail end of the checks, indicating that the volume of water supplied in irrigation washed out potential for surfactant to retain residues. Previous studies with surfactants have indicated variable effects. For example, increased mobility was not observed for lindane (γ-1,2,3,4,5,6-hexachlorocyclohexane), diuron, or atrazine (Huggenberger et al., 1973), whereas increased mobility into soil was observed for trifluralin [2,6-dinitro-*N,N*-dipropyl-4-(trifluoromethyl)benzenamine] and oryzalin [4-(dipropylamino)-3,5-dinitrobenzenesulfonamide] (Koren, 1972) and for lindane (Sanchez-Camazano et al., 2000). Effects of surfactant are complex and depend on the physicochemical properties of pesticides, the properties of the soil, and the modification of the surfactant on both. The lack of a consistent surfactant effect in this study indicated that it would not be an effective mitigation measure for this soil, crop, and irrigation combination. Instead, mitigation effects will focus on management of water infiltration rates observed in the pond.

CONCLUSION

An investigation was conducted to determine the predominant source for pesticide residues detected in domestic wells located in an area where the predominant soil was a cracking clay. Although preferential flow through macropores within the field was a potential pathway, residues within the field were maintained above the surface 152-mm soil depth (RL 8 μg kg^{-1}). In addition, the thickness of the soil and distance to ground water would have resulted in long residence times, allowing for degradation of residues that may have moved undetected past the 152-mm depth. Measurements of water balance in an adjacent holding pond indicated that infiltration of water collected in the pond provided a more direct route to ground water. Runoff water containing pesticide residues was collected in the pond and subsequently infiltrated within a few days, directly recharging and raising localized ground water levels. The most practical mitigation measure at this site where alfalfa crops were present would be to manage the runoff water that contains herbicide residues rather than management of the soil–herbicide interface. Pumping the water out of the pond for reuse in the same or adjacent field would reduce the volume of water available for infiltration and decrease the total time for infiltration.

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