

Memorandum

To : Don Weaver, Ph.D.
Senior Environmental Research Scientist
Environmental Monitoring and
Pest Management

Date : March 13, 1996

Place :

From : Department of Pesticide Regulation - 1020 N Street, Room 161
Sacramento, California 95814-5624

Subject : Summary of Results for a Study to Monitor Diuron in a Tailwater
Recovery System in Yolo County, California:

SCOPE OF THIS MEMORANDUM

The purpose of this memorandum is to present results from the study entitled "Monitoring Diuron in a Tailwater Recovery System in Yolo County, California".

INTRODUCTION

A system of canals and sloughs have been developed to move agricultural runoff water from fields back to naturally draining concourses in California. Runoff water which is produced from winter rain and summer irrigation events can erode soil, carrying clay, silt, organic matter, and residues of agricultural chemicals from fields into the drainage system (Lal, 1988; Leonard, 1990). The Yolo County Resource Conservation District is promoting the construction of tailwater recovery systems as a management practice to prevent direct entry of runoff water from agricultural fields to sloughs.

Several tailwater recovery systems have been constructed on row crop production areas in Yolo County. In a tailwater recovery system, runoff water is collected onsite in excavated areas.



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Water captured in the tailwater recovery system is available for reapplication to fields or for other beneficial uses. Soil sediment may also be trapped by the system and the soil reapplied to fields. The Soil Conservation Service (1992) identifies the following potential beneficial functions of a tailwater recovery system:

- Eliminates sediment leaving field.
- Eliminates agricultural drainage.
- Conserves irrigation water.
- Potentially recycles all tailwater.
- Preserves down stream water quality.
- Reduces weed seeds and insects from moving down stream in the water supply.
- Recirculates silt.
- May eliminate the need for additional conservation practices to meet off-farm sediment standards.

DPR conducted a study in 1995 to evaluate the feasibility of using the tailwater recovery system as a reduced risk management practice for preventing surface and ground water contamination by a pesticide. The objectives of the study were:

1) to determine if herbicide residues were present in runoff water; and 2) to assess whether or not the tailwater recovery system would prevent movement of pesticide residues in water that either eventually drains to sloughs or potentially recharges ground water. Movement of diuron [N'-(3,4-dichlorophenyl)-N,N-dimethylurea], a preemergent herbicide, was monitored in runoff water collected from a row crop field planted with native grasses. Diuron is a systemic herbicide belonging to the urea family and acts primarily by inhibiting photosynthesis. This study was partially funded by the U.S. Environmental Protection Agency 1995 ground water grant #E009155-95.

MATERIALS AND METHODS

Site Description

The tailwater recovery system is located in Yolo County, California. It consists of two adjoining bodies of water; a sediment basin and a larger recharge pond area (Figure 1). Rain and irrigation runoff water is initially collected and stored in the sediment basin where soil particles are allowed to settle out of the water prior to discharge to the recharge pond. The recharge pond is used for storage, ground water recharge, and wildlife habitat. Water from the recharge pond is not redistributed back onto the fields.

The tailwater system in this study receives water from a nearby row crop field that is partitioned into 15 blocks planted with 14 native grasses and wheat. The soil is classified as a Capay Silty Clay (Soil Conservation Service, 1972). Textural analysis of the soil reported by the Soil Conservation Service (1972) is 46% clay, 46% silt, and 8% sand. The soil is listed as having a slight soil erosion potential, but water permeability is slow so production of water runoff from rain or irrigation events could be high.

Study Design

The original study objective was to obtain a preliminary assessment of the ability of the tailwater recovery system to prevent off-site movement of diuron to either surface or ground water. Initially, diuron concentrations were to be measured in soil and water throughout the growing season. Soil core samples were to be taken from dry areas at the edge of the recharge pond after irrigations were completed. Since the water level in the pond did not drop sufficiently to allow the soil to dry, no soil cores were collected and the study was limited to water sampling.

The presence and movement of residues from the field to the tailwater system was monitored by collecting runoff water samples

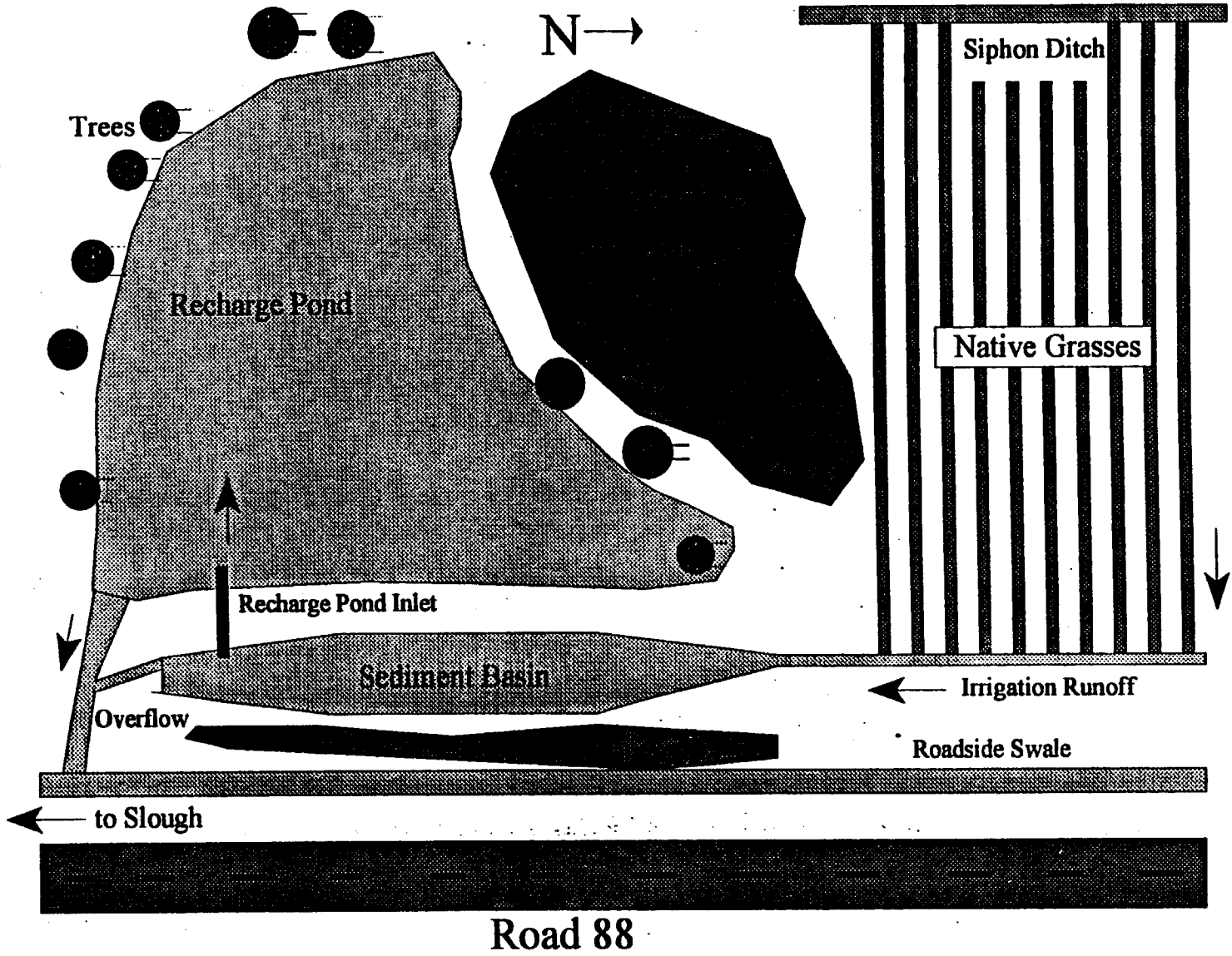


Figure 1. Diagram of Failwater Recovery System Site in Yolo County, CA.

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from the sediment basin and recharge pond after irrigation water had been applied. Diuron concentration was measured in unfiltered water samples and in split water samples that were filtered to remove soil particles from the water. The comparison between unfiltered and filtered water samples indicated whether or not pesticide residues were bound to soil particles that were eroded from the field. Water samples were collected from the sediment basin only after the first irrigation. Previous studies have shown that the first irrigation or rain event after application of a pesticide to soil has the greatest potential to move residues offsite (Leonard, 1990). Since soil particles should have been removed from the runoff water that was stored in the sediment basin, chemical analyses of water sampled from the recharge pond were only conducted on unfiltered samples. Sampling from the recharge pond was conducted throughout the growing season to determine the temporal pattern of potential movement of residues out of the sediment basin.

Diuron Applications and Irrigation Events

Diuron had been applied in the Fall of 1994 to the blocks of grasses served by the recovery system. On April 13, 1995 another application of diuron was made to three of the blocks served by the recovery system. Two of the blocks measured 1.82 acres each and the third at 9.52 acres. Diuron (Karmex[®] DF with 80% active ingredient (ai)) was applied with a boom power sprayer at a rate of 1.7 kg ai/ha (1.5 lb ai/acre) to the three blocks.

Four irrigation events followed the spring diuron application. The first irrigation occurred on May 25, about one month after the diuron application. The remaining irrigation events occurred at approximately one month intervals on June 20, July 19, and August 21. Only the first three irrigations were monitored because a peak in diuron concentration in the recharge pond was observed prior to the third irrigation.

Water Monitoring

All water samples were collected from the sediment basin and recharge pond using a hand pump to fill one-liter, narrow neck, amber glass bottles fitted with Teflon[®]-lined caps. Water samples were immediately stored on wet ice for transport and then maintained at +4°C until analyzed. Water collected from the sediment pond on March 16 was used by the laboratory for initial method validation and quality control analyses.

Sediment basin. Four replicate composite water samples were collected from the sediment basin directly after irrigation events. For each composite sample, the basin was divided into five equal sections with a random sample taken from each section and then all five samples pooled. Each replicate sample was split into two samples, one unfiltered to determine total diuron concentration and the other filtered to remove soil particles from solution. The difference between unfiltered and filtered samples indicated the amount of diuron dissolved in solution compared to the amount bound to soil that was removed during filtration. Split water samples were suction-filtered through pre-weighed filters, 0.45 μm in pore diameter (Acrodisc[®], Gelman Sciences) and then dried at 105° C until constant weight (Attachment A). The water in the sediment basin appeared cloudy and the samples were opaque indicating that some sediment was present in the runoff water.

Recharge pond. Water samples were first collected from the recharge pond after application of diuron but prior to the first irrigation event. Subsequent sampling occurred 3-5 days after runoff from each irrigation had entered the sediment basin. Theoretically, the delay would have allowed settling of the clay and soil particles from water in the sediment basin prior to release into the recharge basin. Releases of water from the sediment basin into the recharge pond did not follow a rigid schedule. At each sampling, four composite water samples were collected by dividing the recharge pond into eight equal sections. The recharge pond was divided into more sections

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because it is larger than the sediment basin. A random sample was taken from each section and then, all eight samples pooled.

Overflow water and irrigation supply. An overflow of water from the sediment basin into the adjacent slough was observed during the second irrigation. Two grab water samples were collected by holding a bottle in the overflow stream until the bottle was filled. Two grab water samples were also collected from the irrigation supply canal during the first and third irrigation events to determine diuron concentration in the input water.

Chemical Analyses and Quality Control

Chemical analyses for diuron in unfiltered and filtered water samples were conducted by the California Department of Food and Agriculture's (CDFA) Chemistry Laboratory Services in Sacramento, California (Attachment A). Methylene chloride was used to extract diuron from unfiltered water samples. The extract was then evaporated to dryness and exchanged to methanol for High Performance Liquid Chromatography (HPLC) analysis.

The filtrate from filtered water samples was passed through a conditioned C18 bond elute to retain diuron. The loaded bond elute was dried with nitrogen gas to eliminate water. Diuron was then eluted with methanol and detected by HPLC. The reporting limit for the determination of diuron in filtered and unfiltered surface water was 0.1 $\mu\text{g/L}$. The results from the method validation study were used to establish recovery control limits for the field study. Attachment B shows the laboratory's method detection limit data, method validation data, and continuous quality control data. For continuous quality control during the study, one matrix blank and one matrix spike sample were analyzed with each set of field samples. Spiked background filtered water showed an overall continuing quality control for diuron recovery of 98% (SD=1.1, CV=1.1%). The recovery for diuron in spiked background unfiltered surface water was 106% (SD=5.04, CV=4.74%).

Data Analysis

Mean concentration of diuron in the sediment basin on different sampling dates during the first irrigation were compared using an unpaired t-test. Since the unfiltered and filtered water samples were split from the same sample, paired t-tests were performed to test differences in diuron concentration between them. It was assumed that the variances of the means were equal for the t-tests. Data from the recharge pond were graphed to determine if a peak in concentration had been captured.

RESULTS

Background sampling. Raw data are reported in Attachment C. Diuron was detected at $0.3 \mu\text{g/L}$ in samples taken on March 16 from the sediment basin for method validation (Table 1). Similar levels were measured in the recharge pond in samples collected on April 17. This sample date was just after the spring diuron application but was prior to the first irrigation event. Apparently, low concentrations of diuron resulting from the fall application and winter runoff events persisted in the sediment basin and recharge pond.

Sediment basin. The first irrigation was staggered throughout the field resulting in two sampling opportunities in the sediment basin. Diuron was measured in unfiltered samples at a mean of $23 \mu\text{g/L}$ in samples taken on May 28 (Table 1). These levels were greater than the background concentrations, indicating movement of residues from the field in the runoff water. Mean diuron concentration in unfiltered water samples for the second sampling of the first irrigation on June 5 was $30 \mu\text{g/L}$. This concentration was significantly higher than the mean concentration of $23 \mu\text{g/L}$ in the May 28 unfiltered sample ($t=4.99$; $p=0.015$). Sediment measured in the samples averaged 0.029 g/L on May 28 and 0.018 g/L on June 5. Leonard (1990) stated that values below 5 g/L indicate a low transport of mass from the field.

Table 1. Concentration of diuron measured in replicate water samples taken from a tailwater recovery system at the sediment basin and recharge pond and from overflow water from the sediment basin to a drain. Amount of sediment was also measured in samples from sediment basin.

Chronology of Events	Sampling		Sediment Basin			Recharge Pond	Overflow
	Date	Replicate	Unfiltered Water (ug/L)	Filtered Water (ug/L)	Sediment (g/L)	Unfiltered Water (ug/L)	Unfiltered Water (ug/L)
Method Validation	3/16/95	1	0.3				
Diuron Application - 4/13/95							
Background	4/17/95	1				0.34	
		2				0.33	
		3				0.36	
		4				0.33	
		Mean				0.34	
		Standard Deviation				0.014	
1st Irrigation Begins - 5/25/95							
	5/28/95	1	23.2	23.3	.031	0.34	
		2	23.8	20.9	.030	0.33	
		3	22.1	22.1	.026	0.37	
		4	22.0	21.8	.027	0.29	
		Mean	22.8	22	0.029	0.33	
		Standard Deviation	0.87	0.98	0.003	0.030	
	6/5/95	1	31.6	27.9	.017	8.5	
		2	29.3	27.5	.018	7.8	
		3	32.8	27.6	.018	8.2	
		4	26.5	30.4	.019	8.3	
		Mean	30	28.4	0.018	8.2	
		Standard Deviation	2.78	1.37	0.001	0.28	
2nd Irrigation Begins - 6/20/95							
	6/21/95	1					14.3
		2					14.4
	6/23/95	1				20.8	
		2				22.9	
		3				24.2	
		4				22.3	
		Mean				22.5	
		Standard Deviation				1.41	
3rd Irrigation Begins - 7/19/95							
	7/24/95	1				7.8	
		2				9.	
		3				7.8	
		4				7.3	
		Mean				7.9	
		Standard Deviation				0.73	

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The mean diuron concentration was not significantly different between unfiltered or filtered samples. This result was consistent between the two sampling dates: for May 28 (t-value = 1.08 and p = 0.18) and for June 5 (t-value = 0.84 and p = 0.23). These results indicated that diuron was present as dissolved residue and not bound to soil particles in the sediment.

Recharge pond. Mean diuron concentrations plotted against sampling date indicated that a peak diuron concentration occurred after the second irrigation event on June 23 (Figure 2). The peak mean concentration of diuron in the recharge pond was at least 23 $\mu\text{g/L}$ which was the mean for the second irrigation. Actual peak concentration may have been higher because the sampling date may not have coincided exactly with the date of the peak concentration in the recharge pond.

Overflow water and irrigation supply. An overflow of water from the sediment basin directly to a drainage ditch was observed during the second irrigation event. Water samples collected from the overflow had a mean diuron concentration of 14.3 $\mu\text{g/L}$. Water samples collected from the irrigation supply canal had no detections of diuron.

DISCUSSION

Diuron's estimated physio-chemical properties are an aerobic $\frac{1}{2}$ -life of 90 days, water solubility value of 42 mg/L, and a K_{oc} of 480 ml/g. These properties indicated that it is long-lived with a low attraction to soil (Jenkins et al.). The National Resources Conservation Service ranks diuron as a high potential for surface runoff and medium potential for leaching through soil (Jenkins et al.). A possible explanation for the presence of residues in the runoff water is that the active ingredient was not fully incorporated into the soil after application. Residues would have been available for mixing and dissolution in the applied irrigation water.

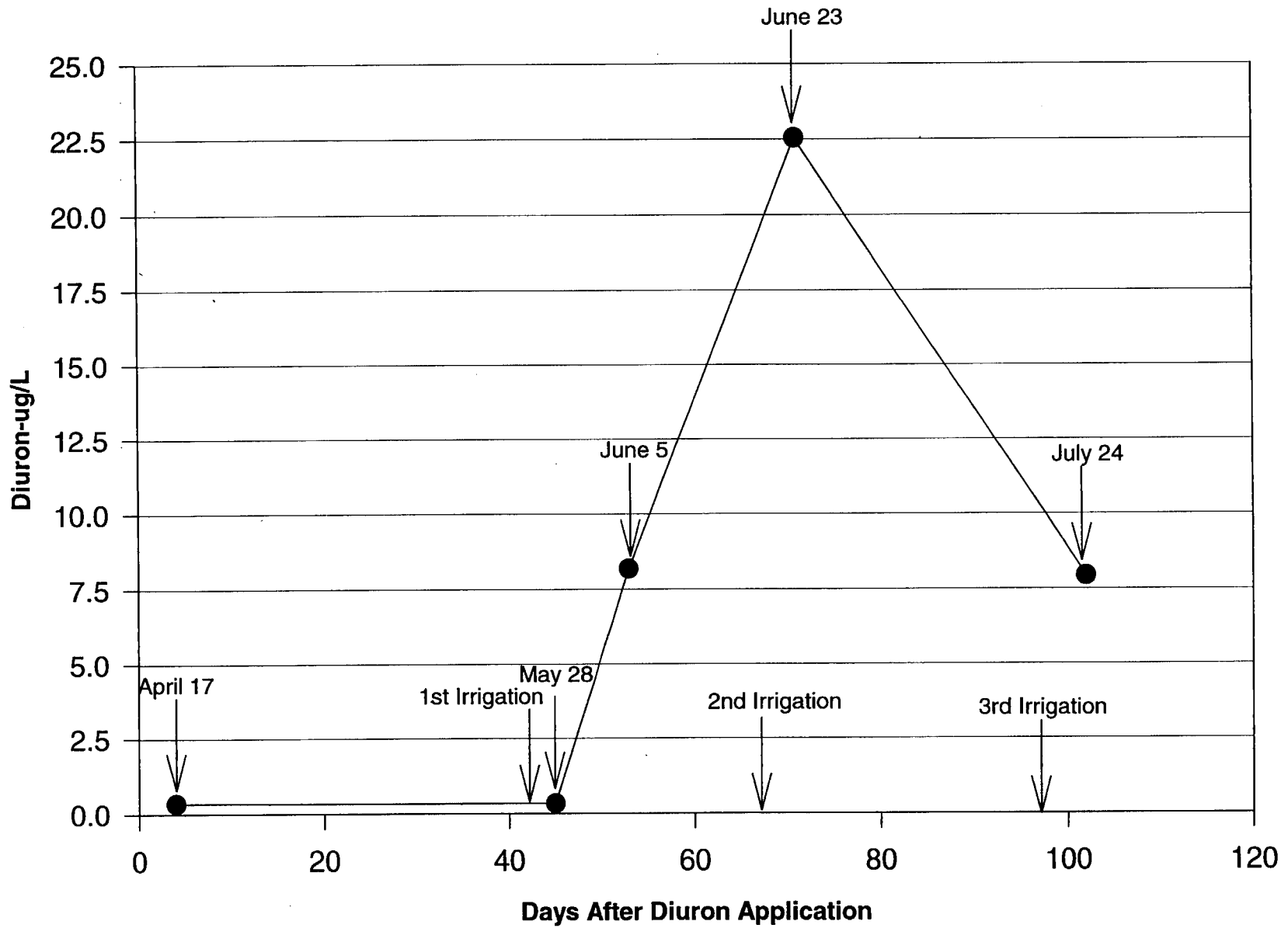


Figure 2. Diuron concentrations in recharge pond following diuron application (April 13 = Day 0).

Movement of residues in runoff water produced from either irrigation or rainfall events may be mitigated by further improvement in incorporation procedures.

CONCLUSIONS

Conclusion 1: Movement of diuron from the treated field was measured in irrigation runoff water captured by the tailwater recovery system.

Conclusion 2: Trapping soil sediment in the sediment basin does not prevent diuron from moving to the recharge pond or to overflow water because diuron residues were not bound to the sediment. Diuron concentration in the water sample was unaffected by filtering soil sediment out of the sample indicating that it was dissolved in the water.

Conclusion 3: The design of this tailwater recovery system allowed movement of diuron in overflow water directly entering the surface water drainage system.

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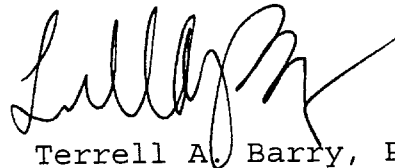
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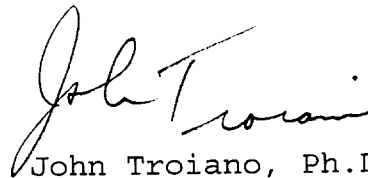
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ATTACHMENT A

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ORIGINAL DATE:03-29-1995
SUPERSEDES:
CURRENT DATE:04-12-1995
METHOD #: 29.1

DETERMINATION OF DIURON IN FILTERED AND UNFILTERED SURFACE WATER USING HPLC

SCOPE

This method is for the determination of Diuron in filtered and unfiltered surface water. CAS Registry Number for Diuron is 330-54-1.

PRINCIPLE

Diuron in unfiltered surface water is extracted with methylene chloride. The extract is evaporated to just dryness and exchanged to methanol for HPLC analysis. Filtered surface water is passed through a conditioned C18 bond elute to retain Diuron. The loaded bond elute is dried with nitrogen gas to eliminate water. Diuron is eluted with methanol and detected by HPLC.

REAGENTS AND EQUIPMENT

1. Solvents: Acetonitrile, methanol (HPLC Grade).
Methylene chloride (Pesticide quality or equivalent).
2. Rotary Evaporator.
3. Diuron stock standard solutions (1 mg/mL): Obtain standards from Standards Repository, California Department of Food and Agriculture, Center for Analytical Chemistry, 3292 Meadowview Rd. Sacramento, CA 95832.
4. Nitrogen evaporator, Organomation Model #12.
5. Test tube mixer.
6. Zymark® AutoTrace™ SPE workstation.
7. C18 bond elute®, 500 mg sorbent mass, Waters Division of Millipore.
8. Drying oven, for operation at $105 \pm 2^\circ\text{C}$.
9. Glass fiber paper type A/E 47 mm. Gelman Sciences.
10. Glassware
 - 10.1 Funnel - 75-cm.
 - 10.2 Boiling flask - 250-mL, with standard taper to fit rotary evaporator.
 - 10.3 Separatory funnel - 500-mL, with TFE stopcock
 - 10.4 Graduated test tube - 15-mL.
 - 10.5 Syringe - 5-mL.
 - 10.6 Beaker - 250-mL.
 - 10.7 Graduated cylinders - 1000-mL, 250-mL.
11. Desiccator.
12. Sodium sulfate- (ACS) Granular, anhydrous.

DETERMINATION OF DIURON IN FILTERED AND UNFILTERED SURFACE WATER USING HPLC

REAGENTS AND EQUIPMENT (continued)

13. Acrodisc[®], 0.2 μm filter. Gelman Sciences.
14. Balance - Analytical, capable of accurately weighing to the nearest 0.002 mg.
15. Filtration apparatus.

ANALYSIS

I. UNFILTERED SURFACE WATER

1. Remove sample from the refrigerator and bring the sample to room temperature. Record the temperature of the sample.
2. Mix the sample well and quantitatively transfer 250 mL of the sample into a 500-mL separatory funnel using a 250-mL graduated cylinder. Add 75 mL of methylene chloride and gently shake for two minutes with periodic venting to release excess pressure.
3. Allow the organic layer to separate from water layer for a minimum of 10 min. If the emulsion interface between layers occurs, the analyst must employ a mechanical technique such as stirring using a glass rod to complete the phase separation. Drain the bottom organic layer through a 75-cm funnel which contains glasswool and 40 g of sodium sulfate into a 250-mL round bottom flask.
4. Add a second 75 mL methylene chloride to the separatory funnel and repeat the extraction procedure a second time. Drain the bottom organic layer into the round bottom flask.
5. Evaporate the extract to just about dryness using a rotary evaporator set at 45°C.
6. Transfer the residue from the round bottom flask to a 15-mL graduated test tube using 10 mL of methanol.
7. Concentrate the extract from 10 mL to 1 mL using a Nitrogen evaporator set at 50°C.
8. Mix well and filter the extract through a 0.45 μm Acrodisc into two microvials. One is for HPLC analysis and the other stored for reanalysis or confirmation.

II. FILTERED SURFACE WATER

1. Filter preparation: Install a 47 mm glass fiber filter type A/E in a filtration apparatus. Wash three times with 2 mL of distilled water. Remove the filter and dry in 105°C oven for 1 hour. Cool in desiccator and record the weight. Repeat drying and weighing until weight is constant or weight loss is less than 0.5 mg between successive weighings. Store in desiccator. Weigh immediately before use.
2. Remove surface water sample from the refrigerator and bring the sample to room temperature. Record the temperature of the sample.
3. Measure and record the volume of the entire sample using a 1000-mL graduated cylinder.
4. Filtration: Wet the preweighed filter to seat with 2 mL of distilled water. Filter the measured amount of well-mixed sample through the filter (If the sample size is large and contains too much sediment, two preweighed filters are recommended for each sample). Continue suction for 3 minutes after filtration is completed. Dry the filter(s) in 105°C oven for at least 1 hour. Cool in desiccator and weigh. Repeat drying, cooling and weighing until weight is constant or weight loss is less than 0.5 mg between successive weighings.

DETERMINATION OF DIURON IN FILTERED AND UNFILTERED SURFACE WATER USING HPLC

ANALYSIS(continued)

II. FILTERED SURFACE WATER(continued)

5. Automated analysis steps: Measure exactly 250 mL of the well-mixed filtered surface water into a 250-mL beaker and use the following AutoTrace workstation procedure:
 - 5.1 Condition a C18 bond elute with 10 mL methanol into solvent waste at the flow rate of 10 mL/min.
 - 5.2 Condition the C18 bond elute with 20 mL distilled water into aqueous waste at the flow rate of 10 mL/min.
 - 5.3 Load 250 mL of sample onto the conditioned C18 bond elute at the flow rate of 10 mL/min.
 - 5.4 Rinse the loaded C18 bond elute with 10 mL distilled water at the flow rate of 10 mL /min.
 - 5.5 Dry the loaded bond elute with nitrogen gas for 10 minutes.
 - 5.6 Elute the compound with 8 mL methanol at the flow rate of 5 mL/min after soaking for 2 minutes.
 - 5.7 Elute the compound with 7 mL more methanol at the same flow rate.
6. Manual steps
 - 6.1 Remove the sample tube from the AutoTrace workstation.
 - 6.2 Concentrate the sample with Nitrogen evaporator at 50°C to 1 mL.
 - 6.3 Mix well and filter through a 0.45 µm Acrodisc into two microvials. One is for HPLC analysis and the other stored for reanalysis or confirmation.

EQUIPMENT CONDITIONS

Instrument: HPLC 1050 with a UV Variable Wavelength Detector.
Wavelength: 254 nm.
Column: Ultrasphere ODS 5 µm 4.6 mm x 25 cm.
Guard column: Ultrasphere ODS 5 µm 4.6 mm x 5 cm.
Mobile phase: 40% ACN, 60% Water.
Flow rate: 1 mL per minute.
Injected volume: 20 µL.
Retention time: 10.90 min.
Linearity range for the detector: 0.25 ng to 200 ng.

CALCULATIONS

The results of unfiltered surface and filtered surface water to be reported in µg/L:

$$\mu\text{g/L} = \frac{\text{Peak height of sample} \times \text{Amount of std (ng)} \times \text{Final volume } (\mu\text{L})}{\text{Peak height of Std} \times \text{Volume injected } (\mu\text{L}) \times \text{Sample Volume (mL)}}$$

For the filtered surface water, the suspended solid results to be reported in mg/L:

$$\text{Total suspended solid in mg/L} = \frac{(\text{A-B})}{\text{Sample volume, mL.}} \times 1000$$

DETERMINATION OF DIURON IN FILTERED AND UNFILTERED SURFACE WATER USING HPLC

CALCULATIONS(continued)

Where:

A = weight of dried residue + filter in mg.
 B = weight of filter in mg

METHOD PERFORMANCE

Quality Control

The laboratory that uses this method is required to operate a formal quality control program. The following are minimum requirements for quality control of this method.

Sample storage: All field samples shall be kept refrigerated at 4°C until extracted.

Sample extraction: All extracts shall be kept frozen at -10°C until analyzed.

Freezer, refrigerator and oven temperatures shall be monitored and recorded daily.

Temperature of samples shall be recorded before starting analysis.

A 4-point calibration curve (0.01 ng/μL, 0.1 ng/μL, 1 ng/μL and 10 ng/μL calibration standards) shall be obtained at the beginning and the end of each set of samples.

For each set of samples, one matrix blank and one matrix spike shall be included, and each set of samples shall not contain more than twelve samples.

Each sample shall be injected two times to determine reproducibility of the analysis.

To avoid contamination, all glasswares shall be rinsed with water several times and then with acetone before bringing to the washing area. Since a very high level of Diuron can be found in samples, a designated washing area is desirable to prevent contamination.

The AutoTrace Work station sample path lines shall be rinsed twice with 20 mL of distilled water each between runs to avoid contamination.

The AutoTrace Work station sample path lines shall be rinsed twice with 20 mL of distilled water each between runs to avoid contamination.

Recovery Data

The analytical method was validated by preparing five sets of sample for each matrix. Each set contained four different levels of spike and a reagent blank. Each set was processed through the entire analytical method at a different time and the following results were tabulated:

		<u>Unfiltered surface water</u>		
Chemical	Spike level	# Analysis	Mean Recovery	Std.Deviation
Diuron	μg/L	(n)	%	%
	1	5	105	7.4
	10	5	94.2	8.3
	100	5	99	1.4
	1000	5	106.7	2.2
		<u>Filtered surface water</u>		
Chemical	Spike level	# Analysis	Mean Recovery	Std.Deviation
Diuron	μg/L	(n)	%	%
	1	5	93.3	9.1
	10	5	102.3	1.9
	100	5	101.1	0.6
	1000	5	108.9	5.5

Method detection limit

The method detection limit (MDL) for both unfiltered and filtered surface water is 0.05 μg/L.

This is the minimum concentration of Diuron that can be measured with 99% confidence.

The MDL was computed based on the following procedure:

DETERMINATION OF DIURON IN FILTERED AND UNFILTERED SURFACE WATER USING HPLC

METHOD PERFORMANCE(continued)

Method detection limit(continued)

- a) Instrument detection limit (IDL) was estimated by using signal to noise ratio. IDL was 0.1 ng [equivalent to 0.005 ng/ μ L(the lowest standard) x 20 μ L(injected volume)] for both unfiltered and filtered surface water. The signal to noise ratio was about 3 to 1.
- b) The provided background matrix was checked to make sure it was interference free at the estimated IDL. When an interference was found, seven separate blank measurements were made. The average was obtained and subtracted from the respective sample measurements.
- c) Seven replicates of the analyte were prepared for each matrix at five times the IDL (5 x 0.1 ng = 0.5 ng) or equivalent to 0.1 μ g/L. The conversion from ng to μ g/L is:

$$\mu\text{g/L} = \frac{\text{Amount of analyte (ng)} \times \text{Final volume } (\mu\text{L})}{\text{Injected volume } (\mu\text{L}) \times \text{Sample volume (mL)}}$$

- d) Computed MDL as follows:

$$\text{MDL} = t_{(n-1, 1-\alpha = 0.99)} \times S$$

Where:

$t_{(n-1, 1-\alpha = 0.99)} = 3.143$ is the student t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom.

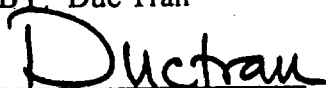
n = 7 is number of replicates for each matrix.

S = 0.018 for filtered surface water and 0.011 for unfiltered surface water were obtained from 7 replicate measurements for each matrix.

Reporting limit

The reporting limit (RL) for this method is 0.1 μ g/L. The reporting limit refers to the level at which quantitative results can be obtained. The MDL is used as a guide for determining the reporting limit. The relationship between these limits is MDL:RL:1:2

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TITLE: Agricultural Chemist II

APPROVED BY: Catherine Cooper



TITLE: Agricultural Chemist III

ATTACHMENT B

Table B1. CDFA Laboratory's Method Detection Limit Data (% recoveries) for the 1995 EPA Tailwater Study.

Chemical: Diuron
Date: 4/19/95

Laboratory: CDFA
Chemist: D. Tran

Matrix	Spike Level	Result	Recovery (%)	\bar{X}	SD	CV (%)
Unfiltered Water	0.1 ug/L	0.115	115	126	10.7	8.48
	0.1 ug/L	0.110	110			
	0.1 ug/L	0.130	130			
	0.1 ug/L	0.140	140			
	0.1 ug/L	0.124	124			
	0.1 ug/L	0.133	133			
	0.1 ug/L	0.133	133			
Filtered Water	0.1 ug/L	0.108	108	115	17.8	15.5
	0.1 ug/L	0.098	98.0			
	0.1 ug/L	0.092	92.0			
	0.1 ug/L	0.110	110			
	0.1 ug/L	0.139	139			
	0.1 ug/L	0.134	134			
	0.1 ug/L	0.123	123			
Soil	1.6 ppb	1.576	98.5	110	8.94	8.12
	1.6 ppb	1.613	100.8			
	1.6 ppb	1.768	110.5			
	1.6 ppb	1.728	108.0			
	1.6 ppb	1.972	123.3			
	1.6 ppb	1.904	119.0			
	1.6 ppb	1.764	110.3			

Table B2. CDFA Laboratory's Method Validation Data (% recoveries) for the 1995 EPA Tailwater Study.

Chemical:
 Date: 4/19/95
 Reporting Limit: 0.1 ug/

Laboratory: CDFA
 Matrix: Filtered Surface Water
 Chemist: D. Tran

Spike Level (ug/L)	Result (ug/L)	Recovery %	\bar{X}	SD	CV %	UCL	UWL	LWL	LCL
1	0.77	77							
1	1.05	105							
1	0.99	99							
1	0.83	83							
1	0.86	86	90	11.6	12.9	125	113	67	55
10	10.33	103.3							
10	10.19	101.9							
10	10.03	100.3							
10	10.51	105.1							
10	10.09	100.9	102	1.93	1.89	108	106	98	96
100	101.0	101.0							
100	101.9	101.9							
100	100.9	100.9							
100	101.5	101.5							
100	100.2	100.2	101	0.64	0.64	103	102	100	99
1000	1031.0	103.1							
1000	1101.8	110.2							
1000	1016.3	101.6							
1000	1146.7	114.7							
1000	1113.2	111.3	108	5.60	5.18	125	119	97	91
Overall:			100	9.02	8.98	127	118	82	73

UCL/LCL = mean +/- 3 SD
 UWL/LWL = mean +/- 2 SD

Table B3. CDFA Laboratory's Method Validation Data (% recoveries) for the 1995 EPA Tailwater Study.

Chemical:
 Date: 4/19/95
 Reporting Limit: 0.1 ug/

Laboratory: CDFA
 Matrix: Unfiltered Surface Water
 Chemist: D. Tran

Spike Level (ug/L)	Result (ug/L)	Recovery %	\bar{X}	SD	CV %	UCL	UWL	LWL	LCL
1	1.06	106							
1	1.02	102							
1	1.16	116							
1	0.96	96							
1	1.05	105	105	7.28	6.93	127	120	90	83
10	9.80	98.0							
10	8.37	83.7							
10	8.70	87.0							
10	10.34	103.4							
10	9.87	98.7	94.2	8.39	8.91	119	111	77	69
100	100.4	100.4							
100	100.0	100.0							
100	97.58	97.6							
100	99.63	99.6							
100	97.42	97.4	99.0	1.40	1.41	103	102	96	95
1000	1089.9	108.9							
1000	1067.7	106.7							
1000	1030.43	103.0							
1000	1080.2	108.0							
1000	1069.0	106.9	107	2.25	2.11	114	112	103	100
Overall:			101	7.32	7.23	123	116	86	79

UCL/LCL = mean +/- 3 SD
 UWL/LWL = mean +/- 2 SD

Table B4. CDFA Laboratory's Method Validation Data (% recoveries) for the 1995 EPA Tailwater Study.

Chemical:
 Date: 5/4/95
 Reporting Limit: 0.001 ug/g

Laboratory: CDFA
 Matrix: Soil
 Chemist: D. Tran

Spike Level (ug/g)	Result (ug/g)	Recovery %	\bar{X}	SD	CV %	UCL	UWL	LWL	LCL
0.25	0.213	85							
0.25	0.23	92							
0.25	0.23	92							
0.25	0.21	84							
0.25	0.21	84	87	4.19	4.79	100	95	79	74
0.50	0.421	84							
0.50	0.47	94							
0.50	0.40	80							
0.50	0.40	80							
0.50	0.307	61	80	12	15	116	104	56	44
5.00	4.35	87.0							
5.00	4.48	89.6							
5.00	3.83	76.6							
5.00	4.06	81.2							
5.00	4.43	88.6	84.6	5.53	6.54	101	96	74	68
50.0	47.28	94.6							
50.0	40.38	80.8							
50.0	41.34	82.7							
50.0	40.54	81.1							
50.0	40.62	81.2	84.1	5.93	7.05	102	96	72	66
Overall:			84	7.4	8.8	106	99	69	62

UCL/LCL = mean +/- 3 SD
 UWL/LWL = mean +/- 2 SD

Table B5. Continuing Quality Control (% recoveries) for the 1995 EPA Tailwater Study.

Study #: 137	UCL= 127	Sample Matrix: Filtered Surface Water
Chemical: Diuron	UWL= 118	Laboratory: CDFA
Date: 6/7/95	LWL= 82	Chemist: D. Tran
RL: 0.1 ug/L	LCL= 73	

Lab Sample #	Spike Level (ug/L)	Results (ug/L)	Recovery %	\bar{X}	SD	CV (%)
19, 22, 24, 26	10	9.868	99			
35, 37, 39, 42	10	9.72	97			
Overall:			98	1.1	1.1	

Table B6. Continuing Quality Control (% recoveries) for the 1995 EPA Tailwater Study.

Study #: 137	UCL= 123	Sample Matrix: Unfiltered Surface Water
Chemical: Diuron	UWL= 116	Laboratory: CDFA
Date: 6/7/95	LWL= 86	Chemist: D. Tran
RL: 0.1 ug/L	LCL= 79	

Lab Sample #	Spike Level (ug/L)	Results (ug/L)	Recovery %	\bar{X}	SD	CV (%)
	10	10.96	110			
15 - 18, 20 - 21 23, 25, 27 - 28	10	10.41	104			
30 - 34, 36, 38 40	10	11.14	111			
43, 44, 49, 50, 51, 52, 54	10	10.83	108			
55, 56, 57, 58	10	9.72	97			
59, 60	10	10.8	108			
Overall:			106	5.04	4.74	

ATTACHMENT C

Table 1
 Results of the Tailwater Pond Study, March-August 1995
 (numbers directly reported from Chain of Custodies)

Sample	Date	Replicate	Sample Source						
			Unfiltered Water ^a	Sediment Basin		Sediment ^b	Irrigation Supply		
				Filtered Water ^a	Recharge Pond		Canal	Overflow	
			Unfiltered Water ^a	Filtered Water ^a		Unfiltered Water ^a	Unfiltered Water ^a	Unfiltered Water ^a	
Method Validation	3/16/95	1	.3						
Application	4/13/95								
Background	4/17/95	1				0.34			
		2				0.33			
		3				0.36			
		4				<u>0.33</u>			
		Mean					0.34		
(1st Irrigation Begins)	5/25/95								
Sub-1st Irrigation ^c	5/28/95	1	23.230	23.308	0.0314	.340			
		2	23.760	20.946	0.0305	.325			
		3	22.116	22.072	0.0255	.365			
		4	<u>22.020</u>	<u>21.810</u>	<u>0.0272</u>	<u>.294</u>			
		Mean	22.782	22.034	0.0287	0.331			
1st Irrigation	5/30/95	1						ND	
		2						ND	
1st Irrigation	6/5/95	1	31.61	27.91	0.0168	8.46			
		2	29.32	27.53	0.0176	7.79			
		3	32.78	27.62	0.0177	8.18			
		4	<u>26.47</u>	<u>30.40</u>	<u>0.0187</u>	<u>8.29</u>			
		Mean	30.05	28.37	0.0177	8.18			
(2nd Irrigation Begins)	6/20/95								
2nd Irrigation Overflow	6/21/95	1						14.30	
		2						14.430	
2nd Irrigation	6/23/95	1				20.79			
		2				22.940			
		3				24.170			
		4				<u>22.280</u>			
		Mean				22.545			
(3rd Irrigation Begins)	7/19/95								
3rd Irrigation	7/24/95	1				7.770			
		2				8.970			
		3				7.770			
		4				<u>7.260</u>			
		Mean				7.943			
(4th Irrigation Begins)	8/21/95								
4th Irrigation	8/21/95	1						ND	
		2						ND	

^aConcentrations expressed in ug/L.

^bConcentrations expressed in g/L.

^cSamples collected due to suspicion that water had reached recharge pond. However, results indicate otherwise.