Assessing the Runoff Potential of Diuron Following Application to Irrigation Canal Access Roads in Fresno County

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ABSTRACT

Diuron is a pre emergent soil herbicide that is widely used in agricultural production and on rights-of way (ROW) to control weed growth in Fresno and Tulare counties. ROW applications generally occur in the fall-winter season to comply with label recommendations for incorporation of residues into the soil by rainfall. A field study was conducted in Riverdale, Fresno County, California to evaluate the potential for off-site movement of diuron caused by rainfall after a ROW application. The study was conducted in cooperation with the Riverdale Irrigation District, (RID) and the study site was located on an access road that straddled an irrigation canal in Riverdale. Soil at the site was classified as a sandy loam with 2.9% slope and it was compacted due to vehicular traffic. Diuron (Diuron 80DF) was applied at a rate of 21.1 kg ai/ha, corresponding to 1474 mg ai applied to the experimental plot. Simulated rain events were applied at 0, 14, and 28 days after application and run-off water samples were collected from each event. Intensity of simulated rainfall was set to 38 mm per hour to represent a worst-case scenario and the average total runtime was 78 minutes. For the first simulated rain event, 125 mg of diuron was removed, which represented 8.5% of the total amount of diuron applied on the plot. The second and third events resulted in an additional removal of 73 and 28 mg of diuron, respectively. Total amount of diruon removed in runoff from all three events accounted for 15.3% of the initial applied amount. The amount of diuron measured in the runoff water generated from the compacted access road in this study was similar to the mass measured in runoff investigations conducted for ROW applications made to strips of land located adjacent to major highways that also were compacted. Incorporation by rainfall on compacted soil could result in runoff of a significant portion of the application, potentially affecting nearby ecological systems, contaminating surface or ground water, or causing crop injury.

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The mention of commercial products, their sources or use in connection with material reported herein is not to be construed as either an actual or an implied endorsement of such products.

Acknowledgment

Our thanks to Murray Clayton and Lisa Quagliaroli for their review of the report.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

I. INTRODUCTION

Diuron and simazine are two pre-emergent soil herbicides widely used in agricultural production and on rights-of way (ROW) to control weed growth in Fresno and Tulare counties. ROW applications encompass noncrop pesticide application to railway tracks, county and state roadside shoulders, medians, recharge basins, canal, ditch banks, and their associated roads along with other uses. ROW applications are generally made in the fall-winter season per label recommendation for incorporation of residues into the soil by rainfall.

Diuron and simazine are also frequently detected in domestic drinking water wells sampled in Fresno and Tulare Counties (Nordmark et al., 2007). The Department of Pesticide Regulation (DPR) issues annual reports on statewide pesticide use. Normally location of pesticide applications are identified by the associated location of the crop application, reported by meridian/township/range/section (MTRS) convention (Davis and Foote, 1966). Typically, pesticide applications on ROW are applied as a narrow band over extended distances, so ROW applicators are not required to report the type of application, pesticide treatment date, or application location using the MTRS convention. Lack of location information hinders a spatial analysis for potential contribution of movement from ROW applications of herbicides to ground water. Based on total amount applied within a county, application to ROW can represent a significant portion of the total applied. Data obtained from DPR's Pesticide Use Reports indicate that use of diuron for ROW applications in Fresno and Tulare counties was 328,706 pounds, summed for years from 1996 to 1999. This value corresponded to 24% of the total reported use of diuron used in both counties. Simazine ROW applications were a smaller portion of total use where for the same period reported ROW use was at 45,575 pounds, corresponding to 3.7% of total reported use in these two counties.

Previous studies on ROW applications have measured pre-emergent herbicide residues in runoff water collected from applications made to the shoulders of highways (Simmons and Leyva, 1994; Powell et al., 1996). Application to compact agricultural soils also resulted in large amounts of simazine and diuron moved offsite in rain runoff water collected from citrus groves (Braun and Hawkins, 1991; Spurlock et al., 1997; Troiano and Garretson, 1998). The objectives of the first phase of this study was to gather more information on ROW use by identifying predominant ROW users of diuron and simazine, determine the types of application and rates used, find innovative practices, and define the locations of ROW applications in Fresno and Tulare Counties. This report contains the results of the second phase of the study, which was to conduct a field study to characterize the potential for off-site movement of a soil-applied herbicide at selected major ROW application sites. Owing to the larger ROW use, diuron was selected for further investigation of potential off-site movement after application. Diuron was applied to an access road where the soil was compacted. The site on the access road straddled an irrigation canal in Riverdale, Fresno County, California. In order to characterize the movement of residues from the site of application, runoff water samples were collected during simulated rain events applied after initial application of diuron to the site.

II. MATERIALS AND METHODS

2.1. Site description

The field study was conducted in Riverdale, California (Fresno County), in cooperation with the RID, where the objective was to evaluate the potential for off-site movement of diuron caused by rainfall. The study site was located 20 miles south of Fresno on an access road adjacent to an irrigation canal. Runoff water was captured from a narrow rectangular area that was delimited by a metallic frame and that was 1.5 m long by 0.45 m wide and 15 cm high. Total plot area was 0.675 square meters (Figure 1). The frame was driven six inches into the ground and it channeled simulated rainfall runoff within the plot to a single collection point. The experimental plot was oriented perpendicular to the length of the access road and the inside of the plot was neither disturbed nor leveled. The soil was sandy loam in texture with 2.9% slope.

2.2. Treatment

Diuron 80 DF (EPA Reg. 9779-318-AA), which contains 80% diuron by weight, is a soil-applied preemergent herbicide that was selected for this study because it is commonly used for weed control on ROW in Fresno County. On November 14, 2002, RID staff applied Diuron 80 DF to the study plot using a tractor-pulled ground spray rig (Figure 2). The applicator made a single pass with a 0.37 m swath over the study plot at stated rate of application between 8.9 to 13.5 kg ai/ha diuron. DPR staff monitored the application rate, provided the simulated rain treatments and sampled runoff water during each event. The triangular "nose" of the steel frame was covered with a plastic sheet during diuron application to the soil to prevent overspray of pesticide residue into the water collection area. The second plot, which is visible in Figure 3, was intended as a backup that was not used in the study.

The amount of pesticide deposited onto the plot was estimated by placing mass deposition sheets on each side of the plot (Figure 3). Each deposition sheet measured 35.6 by 26.2 cm, providing an area of 0.09 square meters. Deposition sheets were collected immediately following the application. Each sheet was folded and placed into a glass quart jar and tightly sealed with an aluminum foil lined lid. Samples were stored in a cooler with wet ice and kept frozen in the freezer until extracted in the laboratory. The experimental plot was covered with a loosely fitting plastic sheet in between the scheduled application of simulated rain events to prevent confounding of runoff by natural rain events.

2.3. Rainfall Simulation

The rainfall simulator was constructed by the Center for Irrigation and Technology at California State University, Fresno, using pieces of metal bar. The base of the frame had a "U" shape and the legs on the open side of the frame had a screw that was used to level the simulator (Figure 1). The screws could be moved up or down depending on the soil surface. A seven-foot vertical bar welded at the base of the "U" frame provided support for the water delivery system and it was used to set the height of the nozzles at 4.5 feet above the ground level. The water delivery system was composed of a hose, pressure regulator, pressure gauge, and four nozzles located on two parallel wands that were situated two feet apart. A garden hose connected the simulator to a 500-gallon water tank pressurized by a portable generator. Four nozzles were positioned in an upward direction so that water leaving the nozzles would simulate rainfall. The simulator was calibrated to deliver 38 mm-inches of rainfall per hour. Wind, soil and air temperature were collected prior to each simulation event. Wind speed and air temperature were measured with a Mini Thermo Anemometer. Soil temperature was recorded by inserting a thermometer into the first-inch of soil. Tarps were constructed around the rain simulator to diminish the effect of wind on the pattern of rainfall deposition.

2.4. Water Runoff and Soil Samples

Simulated rain events were applied on 0, 14, and 28 days after diuron treatment, corresponding to November 14, November 28, 2010, and December 12, 2002, respectively. The 0-day rainfall event occurred 2 hours after the diuron application to emulate the worst-case scenario. Nozzle pressure was checked and adjusted, if necessary, to deliver simulated rain at a rate of 38 mm/hour. Background water samples were collected directly from a nozzle. At each event, simulated rain was applied until 20 consecutive one-liter samples were collected. The length of time for collection of each one-liter sampled was recorded. Each sample was a one-liter amber glass bottle that was filled directly at the collection port (Figure 1), tightly capped with Teflon-lined lids, and placed on wet ice in a storage container. All samples remained chilled at 4ûC until extracted in the laboratory.

The runoff collection area was washed and rinsed with de-ionized water just prior to each runoff event to minimize contamination (Figure 1). Prior to each runoff simulation event, a soil moisture sample was collected just outside of the plot at a depth of between 0 and 0.15 m and analyzed by DPR staff at CSU Fresno/DPR Lab in accordance with SOP METH001.00 (Garretson, 1999).

2.5. Chemical analysis

The California Department of Food and Agriculture (CDFA) Center for Analytical Chemistry analyzed water samples and mass deposition sheets for diuron (CDFA 2000 and CDFA 2001). Blind spikes (quality control samples containing known amounts of diuron and disguised as actual samples), were prepared and analyzed in accordance with SOP QAQC001.00 (Segawa, 1995). Background water samples were collected from the rainfall simulator prior to application to determine potential concentration of diuron in the water source. The water samples were analyzed with Hewlett Packard High Performance Liquid Chromatography 1050 with a UV Variable Wavelength Detector. Pesticide residues were extracted from the mass deposition sheets with methanol and were analyzed using both gas and liquid chromatography equipped with TSD and UV detectors, respectively. The reporting limits for diuron were 0.5 mg/km and 0.1 μg/L for mass deposition and water samples, respectively. One matrix blank and one matrix spike were analyzed with each extraction set.

2.6. Data Analysis

According to the initial study design, all runoff water samples were to be analyzed. However, owing to budgetary constraints, only every other serially collected water sample collected during each runoff event was analyzed. Estimated concentrations for samples not sent to the laboratory were calculated from regression of the concentration for analyzed samples (Y value) on cumulative collection time expressed as minutes (X-value). Since runoff was not immediately observed, X-axis values were adjusted by the observed time at which the first water ran off the treated plot. This resulted in an adjustment of 7, 9, and 5 minutes for the first, second, and third events, respectively (Tables 1, 2, and 3). Furthermore, since the measured diuron concentrations approximated the value at the midpoint of the sampling interval, the associated X-values were plotted as the mid-point of the sampling interval (Figures 4, 5 and 6). Table Curve 2D v5.0[1] was used to determine a simple function that provided a consistent fit for the simulated runoff events. A 3-parameter exponential decay curve with a term for an intercept (EQ 1) provided a good fit to the data:

$$\text{EQ 1} \qquad Y = a + b\,\exp(-X/c)$$

where Y is the observed diuron concentration (ug/L); X is the cumulative time interval; a is the value of the plateau; b represents the difference between the value at the y-intercept and the plateau; and c is the estimated rate constant for decay over time. A comparison of curve fit between 2- and 3- parameter exponential decay functions is illustrated in Figure 4. Results for curve fits indicated that the adjusted r-square value for the 3-parameter curve (Figure 4A) was 0.97 compared to 0.68 for the 2-parameter curve (Figure 4B). The better fit of the 3-parameter curve is due to the apparent presence of a plateau in the data over time, i.e. a decline to zero concentration is not evident for this data set. Comparisons between the 2- and 3- parameter curves were similar for events 2 and 3. Estimated concentrations for samples that were not sent to the laboratory for analysis were interpolated from the fit of the 3-parameter exponential decay equation. The mass of diuron collected at each sampling interval was calculated as the product of the predicted concentration (µg/L) and the estimated amount of runoff water (L) produced for each sampling event (Tables 1, 2, and 3). The mass of diuron was then summed over the entire sampling period to determine the cumulative amount washed-off from the site of application during each runoff event.

III. RESULTS

3.1. Environmental Information

The wind speed at application time was calm, ranging from zero to 2 mph, and the air temperature was 13.8° C. The soil temperature during each simulated event ranged from 9.4 to 12.4° C and the soil moisture ranged from 8.9 to 10% (Appendix 1). It did not rain for the duration of the study.

[1] Software program information is available at: <www.systat.com>.

3. 2. Mass Deposition and Application Rate

The amount of diuron deposited on each mass deposition sheet was 191 mg and 202 mg, respectively (Appendix 2). The average deposition of 196.5 mg ai per sheet corresponded to 1474 mg ai deposited in the plot, or an application rate of 21.1 kg ai /ha, which indicates that the plot received approximately 57% more diuron than the intended application rate of 13.5 kg ai/ha. The cause of this over-application is not known; however, it is likely that the operator slowed down by the plot area because of the presence of the metallic frame, causing greater deposition. The excess diuron did not affect our objective which was to characterize the lateral off-site movement of a soil-applied herbicide.

3. 3. Control (Blank) Water Samples

Prior to each simulation event, a blank sample was collected from the simulator. Blank samples were used to confirm that the simulated rain did not contain residues of diuron and that the plot was the only source of diuron. Blank water samples collected on November 14 and November 28, 2010 did not contain detectable levels of diuron; however, the sample collected on December 12, 1910 contained 0.2 ppb of diuron (Appendix 2). Relative to the concentrations measured for the runoff samples, the amount of diuron found in the blank sample corresponded to 0.0149% to 0.035% of the highest and the lowest concentrations, respectively. Since this value was extremely low compared to the actual runoff water samples, there was no need to adjust the runoff values because the effect on total mass calculations would have been small. The exact cause for the presence of residues in the background sample is unknown.

3. 4. Diuron in runoff water

Runoff water samples were collected approximately every 2.4 minutes for a total of 20 samples collected at each event. Because of budgetary constraints, only every other sample analyzed. Application of the 3-paramenter exponential decay curve provided a good fit to the data to all three events, as determined by visual observation and high R-square values of 0.98, 0.84, and 0.98 for the first, second, and third events, respectively (Figures 4, 5, and 6). The values for the intercept declined between each event, reflecting decreases in initial available concentration over time: 13,217, 4718, and 1986 ug/L for the first, second, and third events, respectively. Decreases in initial concentration over time have previously been reported due to combined dissipation processes of movement into the soil and degradation (Powell et al. 1996). Even though the shapes of the curves appeared similar between the events, the slope for amount washed-off was greater for the first simulated rain event on November 14 than for the two succeeding events (Table 4). Greater availability of residues early in the first event caused a rapid decline in the wash-off curve. The slope of the curve was the same for the second and third events indicating similar availability of surface residues for wash-off during these events. The good fit of EQ. 1 to the observed values indicated an associated high level of confidence for using the curve to estimate concentrations for samples that were not sent to the laboratory, enabling an estimate of total mass removed in sampled runoff water (Tables 1, 2, and 3 and Appendix 3).

The first runoff event took place immediately after the application of diuron on November 14, 2002. Collection of the first runoff sample commenced at 7 minutes after the simulated rainfall began (Table 1). The event lasted 72 minutes and generated a total of 29.4 liters of runoff. Only the first

20 liters were collected and eleven of these 20 samples were analyzed. During the first runoff event, 125 mg of diuron was removed from the plot. This corresponded to 8.5% of the initial application of 1474 mg of diuron.

The second runoff event occurred on November 28, 2002, 14 days after the application. Collection of runoff water commenced at nine minutes after the simulator was turned on, just slightly longer than observed for the first runoff event (Table 2). The event lasted 79 minutes, generating a total of 31.8 liters. During the second runoff event, 73 mg of diuron was removed from the plot which corresponded to 5.0% of the initial amount applied.

At the third runoff event, on December 12, 2002, 28 days after the application, collection of runoff water commenced at 5 minutes after the simulator was turned on (Table 3). The simulation lasted 83 minutes and generated 33.4 liters of runoff. Although the volume of runoff water was slightly greater than observed for the two previous runoff events, only 28 mg of diuron was removed from the plot during sample collection period, which corresponded to 1.9% of the initial amount of diuron applied.

The runoff curves for all three simulated runoff events are compared in Figure 7. As observed for previous studies, concentrations decreased with increased time between events, indicating less pesticide available at the surface for dissolution in runoff water (Powell et al., 1996). The shallow shape of the curve for the third event reflects the limited amount of diuron residues present on the soil surface. The total mass of diuron collected in the runoff water for all three events was estimated at 226 mg, corresponding to 15.3% of the amount initially applied to the plot. Complete results for statistical analysis of the fit of EQ 1 to each event are given in (Appendix 3).

IV. DISCUSSION

The results of this study were similar to that observed in Powell et al. (1996) where runoff of diuron from an engineered rights-of-way on Interstate 5 in California was investigated. Both studies used simulated rainfall events to generate runoff water and both were conducted on a compacted soil condition. The Powell et al. (1996) study was located on a shoulder of a major highway, whereas, this study was located on an access road of an irrigation canal. These sites are designed intentionally to shed water away from the highway in Powell et al. (1996) or from the canal in this study. Even though this study used a higher rate of applied diuron, 21 kg ai/ha versus 3.59 kg/ha in Powell et al. (1996), and a higher simulated intensity of rainfall (38 mm/hour versus 13 mm/hour in Powell et al. (1996), the overall response was similar. Slope and soil compaction at both study sites in combination with the application of a persistent, soluble herbicide were the primary causes of the high concentration of diuron measured in simulated rain runoff. Powell et al. (1996) measured 5.4% of the applied amount of diuron removed in runoff water after one hour of simulated rainfall. In this study, with much higher simulated rain intensity than Powell et al study, an estimated 8.5% of diuron was displaced after 73 minutes of the first simulated rain event.

Compaction of soil has been shown as an important factor that increases the amount of runoff water generated from a site (Heathman et al., 1985). For engineered ROWs at highway sites, the intent is to remove water away from the highway in order to reduce flooding hazards. For the canal, a constant traffic on the road causes the soil to compact. Pre-emergent herbicide applications at both study sites reflect typical use practices that rely upon rainfall to incorporate the herbicide residues into the soil. A previous study by Troiano and Garretson (1998) illustrated that slight disturbance of compacted soil in citrus row middles reduced not only the amount of runoff water but also the mass of simazine that left the treatment site. Mechanical incorporation is not required or suggested in the labels of currently registered pesticide products that contain diuron for ROW. The label for the product used in this study indicates the use of a shallow mechanical incorporation if the weather is dry but this statement is only found for uses on cotton crops. Although shallow mechanical incorporation on canal or ditch banks may reduce the amount of diuron that runs off application sites, the practice may hinder the original construction purpose to shed water. Further investigation is needed to prove that mechanical incorporation can be useful at ROW application sites.

V. CONCLUSION

This study confirmed the findings of Powell et al. (1996) where compacted soil was also found to result in significant loss of herbicide mass in rain runoff generated from applications made to roadsides. In 2004, DPR adopted mandatory mitigation measures for the use of pesticides listed in the Title 3, California Code of Regulations (3CCR) section 6800(a) in areas deemed sensitive to ground water contamination. In general, pesticide users may not apply these pesticides, including diuron, below the high water line inside artificial recharge basins or unlined canals and ditches unless applications occur at least six months before the basin is used to recharge ground water or water is run in the canals or ditches (3CCR sections 6487.1 and 6487.2, respectively). For engineered ROWs in leaching or runoff Ground Water Protection Areas, pesticide users must obtain a permit from the county agricultural commissioner and comply with the mitigation measures stated on the permit, which could include mechanical incorporation (3CCR sections 6487.3 and 6487.4). Although shallow mechanical incorporation on certain ROW sites could effectively reduce the potential for diuron, or similar pre-emergent herbicides, to move offsite in measurable concentrations and potentially increase effectiveness of applications, further investigation is needed to prove the potential for adoption of shallow mechanical incorporation by ROW pesticide users.

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for references not available email GWPP@cdpr.ca.gov

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VII. FIGURES

Figure 1. Photograph of the construction of the rainfall simulator.

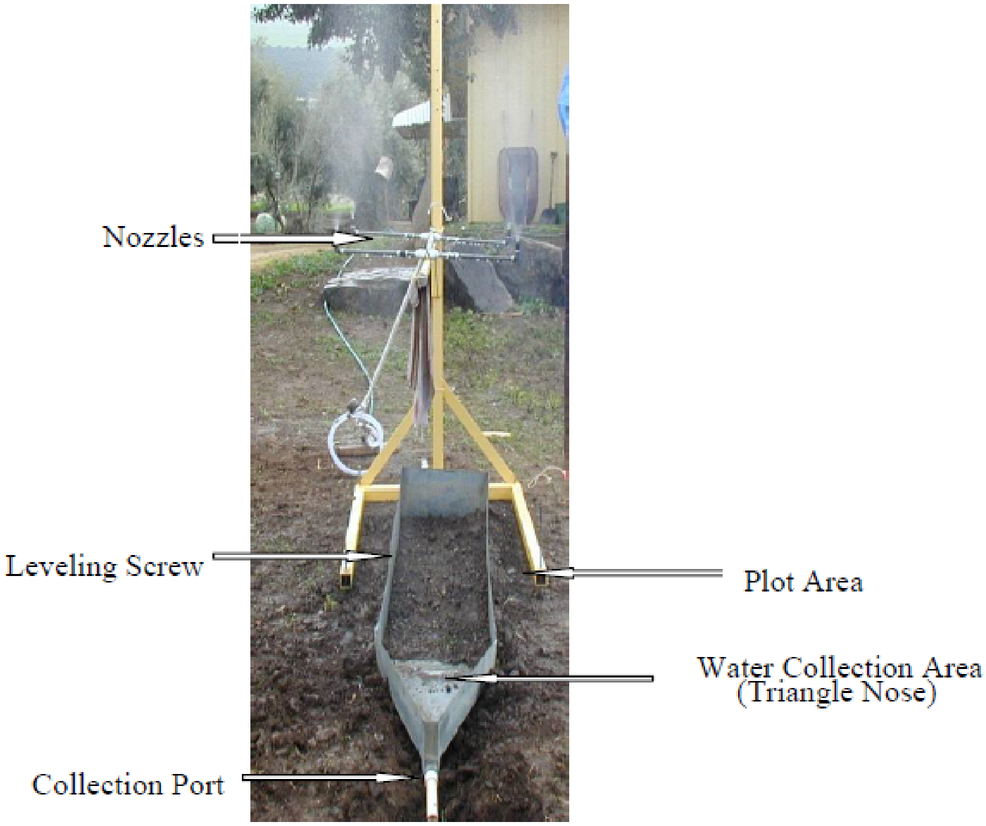
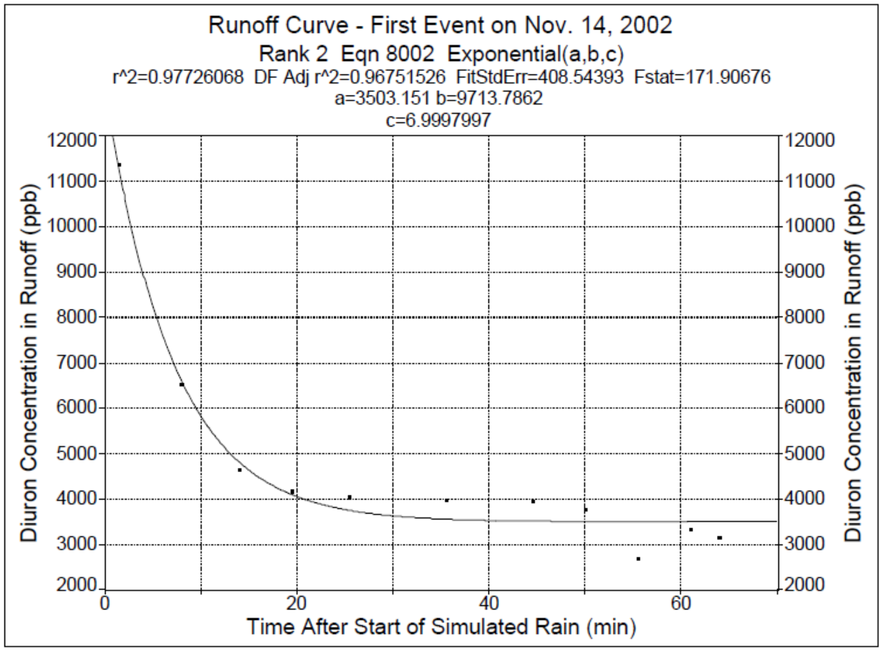


Figure 2. Riverdale Irrigation District staff conducting ground application spray.

Figure 3. Location of mass deposition sheets to measure application rate of diuron. Two plots were constructed where the second plot was used as a backup.

Figure 4. Comparison of 3- (4A) and 2 (4B) parameter exponential decay curves for the fit of diuron concentration in runoff water generated from the first simulated rainfall event applied on November 14, 2002.

4A - Fit of 3-Parameter Exponential Decay Curve



4B - Fit of 2-Parameter Exponential Decay Curve

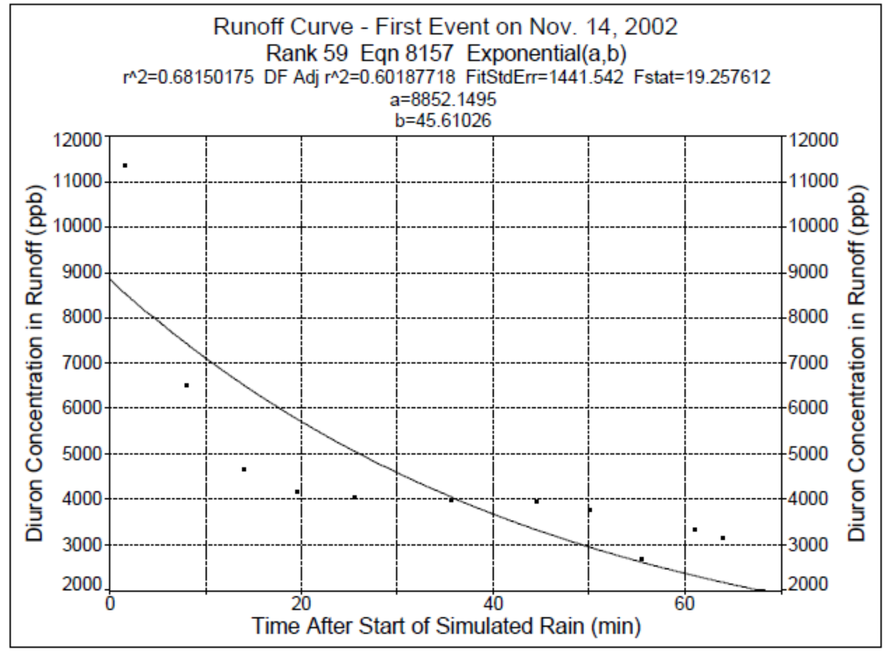


Figure 5. Fit of the 3-parameter exponential decay curve to diuron concentration in runoff water generated from the second simulated rainfall event applied on November 28, 2002

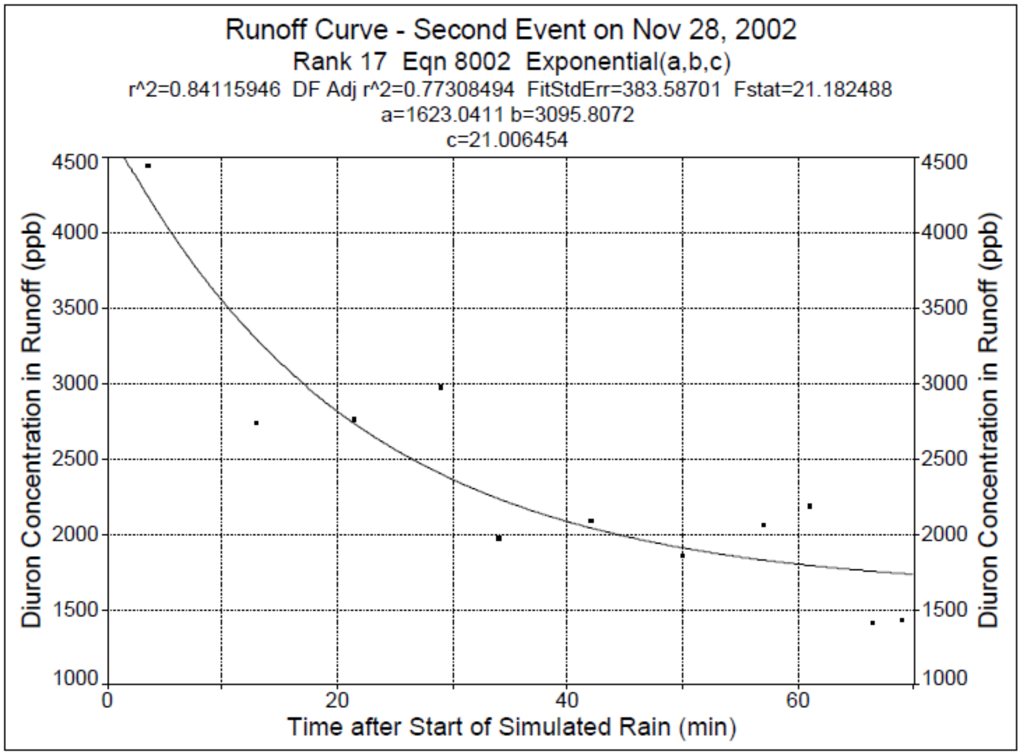


Figure 6. **Fit of the 3-parameter exponential decay curve to diuron concentration in runoff water generated from the second simulated rainfall event applied on December 12, 2002.**

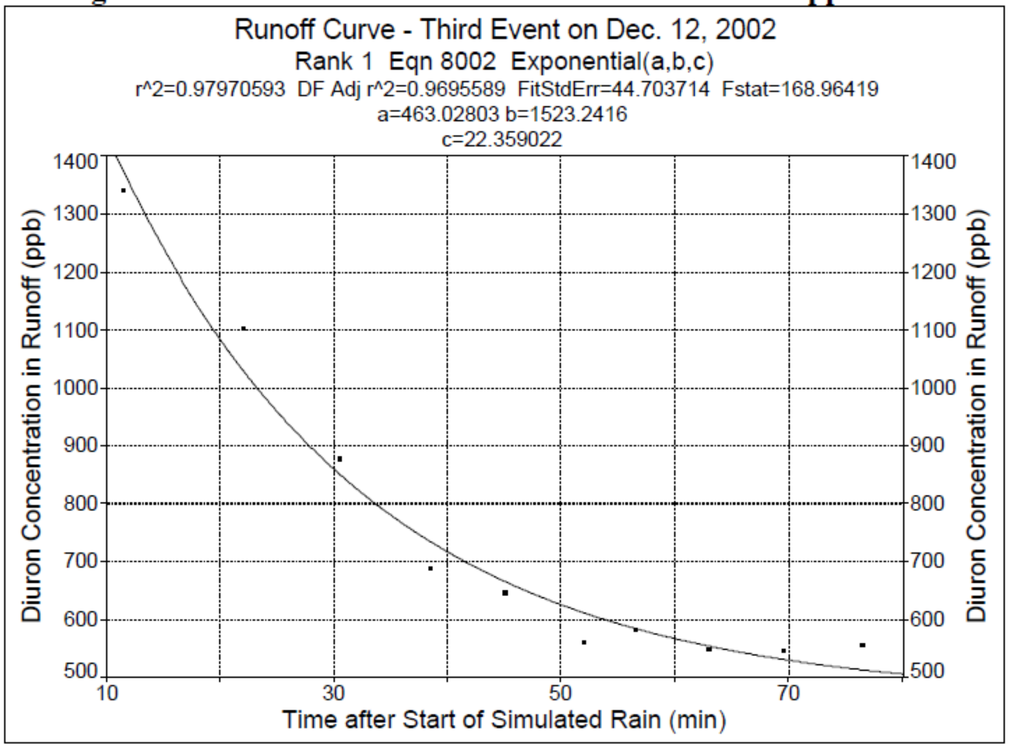
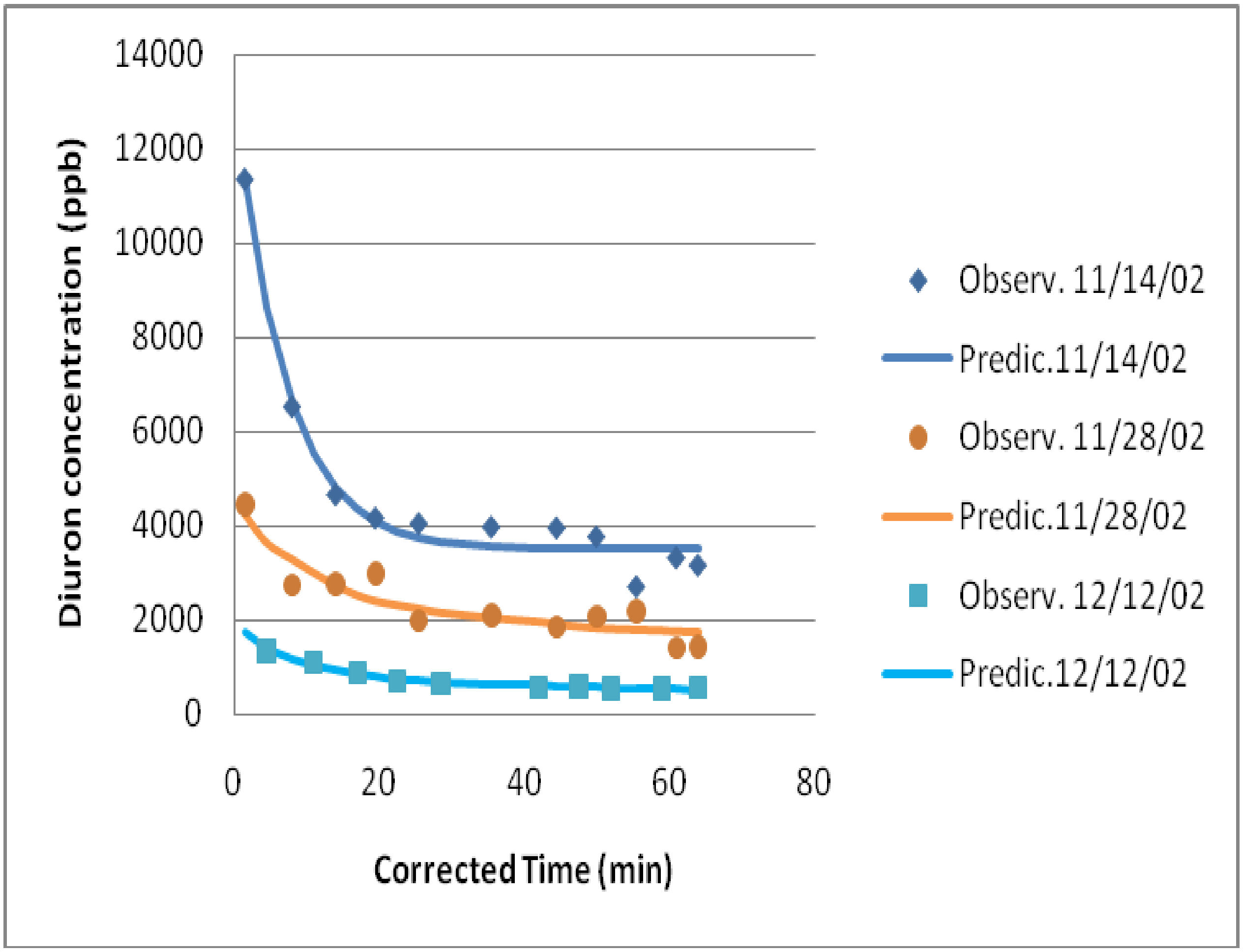


Figure 7. Diuron concentration on each of the three runoff events (from analyzed samples).



VIII. TABLES

Table 1. **Results from first simulated runoff event on 11/14/2002 and calculated amount of diuron**.

Field sample (#)	Time: Collected (min)	Time: Corrected (min.)	Rainfall on plot (L)	Runoff between samples (L)	Diuron: Measured Concentration (ppb)	Diuron: Predicted Concentration from Equation 1 (ppb)	Diuron: Removed by total runoff based equation 1 (mg)	Diuron: Cumulative removed by rainfall runoff (mg)
	7*		2.82	0.00		13217		
4	10	1.50	4.03	1.20	11373	11340	13.61	13.61
5	13	4.50	5.20	1.20	**N/A****	8610	10.33	23.94
6	17	8.00	6.80	1.60	6541	6601	10.56	34.50
7	19	11.00	7.60	1.00	**N/A****	5521	5.52	40.02
8	23	14.00	9.30	1.70	4668	4818	8.19	48.21
9	25	17.00	10.10	1.00	**N/A****	4359	4.36	52.57
10	28	19.50	11.30	1.20	4172	4102	4.92	57.49
11	31	22.50	12.50	1.20	**N/A****	3893	4.67	62.17
12	34	25.50	13.70	1.20	4056	3757	4.51	66.67
13	37	28.50	14.90	1.20	**N/A****	3669	4.40	71.08
14	48	35.50	19.30	4.40	3980	3565	15.69	86.76
15	50	42.00	20.10	1.00	**N/A****	3527	3.53	90.29
16	53	44.50	21.30	1.20	3962	3520	4.22	94.51
17	56	47.50	22.50	1.20	**N/A****	3514	4.22	98.73
18	58	50.00	23.30	1.00	3774	3511	3.51	102.24
19	60	52.00	24.10	0.80	**N/A****	3509	2.81	105.05
20	65	55.50	26.20	2.10	2712	3507	7.36	112.41
21	67	59.00	27.00	1.00	**N/A****	3505	3.13	115.55
22	69	61.00	27.80	1.00	3327	3505	3.51	119.05
23	73	64.00	29.40	1.60	3167	3504	5.61	124.66

* = The first runoff drip into the bottle was at seven minutes
** N/A = Sample not analyzed

Table 2. Results from second simulated runoff event on 11/28/2002 and calculated amount of diuron.

Field sample (#)	Time: Collected (min)	Time: Corrected (min.)	Rainfall on plot (L)	Runoff between samples (L)	Diuron: Measured Concentration (ppb)	Diuron: Predicted Concentration from Equation 1 (ppb)	Diuron: Removed by total runoff based equation 1 (mg)	Diuron: Cumulative removed by rainfall runoff (mg)
	9*		3.6			4719		
31	16	3.50	6.44	2.82	4454	4244	11.96	11.96
32	20	9.00	8.10	1.61	**N/A****	3640	5.86	17.82
33	24	13.00	9.70	1.61	2741	3290	5.30	23.12
34	28	17.00	11.30	1.61	**N/A****	3001	4.83	27.95
35	33	21.50	13.30	2.01	2764	2735	5.50	33.45
36	37	26.00	14.90	1.61	**N/A****	2521	4.06	37.51
37	39	29.00	15.70	1.00	2979	2401	2.40	39.91
38	42	31.50	16.90	1.21	**N/A****	2314	2.80	42.71
39	44	34.00	17.70	1.00	1974	2237	2.24	44.94
40	48	37.00	19.30	1.61	**N/A****	2155	3.47	48.41
41	54	42.00	21.70	2.41	2097	2042	4.92	53.34
42	57	46.50	22.90	1.21	**N/A****	1961	2.37	55.71
43	61	50.00	24.50	1.61	1855	1909	3.07	58.78
44	65	54.00	26.20	1.61	**N/A****	1860	2.99	61.78
45	67	57.00	27.00	1.00	2067	1828	1.83	63.60
46	69	59.00	27.80	1.00	**N/A****	1810	1.81	65.41
47	71	61.00	28.60	1.00	2191	1793	1.79	67.21
48	74	63.50	29.80	1.21	**N/A****	1774	2.15	69.35
49	77	66.50	31.00	1.21	1418	1754	2.12	71.48
50	79	69.00	31.80	1.00	1433	1739	1.74	73.22

*= The first runoff drip into the bottle was at 9 minutes
** N/A = Sample not analyzed

Table 3. **Results from third simulated runoff event on 12/12/2002 and calculated amount of diuron.**

Field sample (#)	Time Collected (min)	Time Corrected (min.)	Rainfall on plot (L)	Runoff between samples (L)	Diuron Measured Concentration (ppb)	Diuron Predicted Concentration from Equation 1 (ppb)	Diuron Removed by total runoff based equation 1 (mg)	Diuron Cumulative removed by rainfall runoff (mg)
	5*		2.01			1986		
52	13	4.00	5.20	3.00	N/A**	1737	5.21	5.21
53	20	11.50	8.00	2.80	1342	1374	3.85	9.06
54	24	17.00	9.70	1.60	N/A**	1175	1.88	10.94
55	30	22.00	12.10	2.40	1104	1032	2.48	13.42
56	34	27.00	13.70	1.60	N/A**	918	1.47	14.88
57	37	30.50	14.90	1.20	878	852	1.02	15.91
58	42	34.50	16.90	2.00	N/A**	789	1.58	17.48
59	45	38.50	18.10	1.20	689	735	0.88	18.37
60	48	41.50	19.30	1.20	N/A**	701	0.84	19.21
61	52	45.00	20.90	1.60	646	667	1.07	20.27
62	56	49.00	22.50	1.60	N/A**	633	1.01	21.29
63	58	52.00	23.30	1.00	562	612	0.61	21.90
64	60	54.00	24.10	1.00	N/A**	599	0.60	22.50
65	63	56.50	25.30	1.20	582	585	0.70	23.20
66	67	60.00	27.00	1.60	N/A**	567	0.91	24.11
67	69	63.00	27.80	1.00	549	554	0.55	24.66
68	73	66.00	29.40	1.60	N/A**	543	0.87	25.53
69	76	69.50	30.60	1.20	547	531	0.64	26.17
70	80	73.00	32.20	1.60	N/A**	521	0.83	27.00
71	83	76.50	33.40	1.20	556	513	0.62	27.62

*= The first runoff drip into the bottle was at 5 minutes
** N/A = Sample not analyzed

Table 4. **Comparison of the slope (c-parameter value) for the 3-parameter wash-off curve and corresponding 95% confidence intervals among the 3-simulated rain events (Appendix 3)**.

Simulated Rain Event	C-Parameter Value	95% Confidence Limits Low	95% Confidence Limits High
14-Nov-02	7.00	4.99	9.01
28-Nov-02	21.01	0.44	41.57
12-Dec-02	22.36	13.82	30.90

APPENDIX 1. Weather and Soil Moisture Data

Weather data at time of simulation events

Date of Event	Temperature (°F)		Wind Speed (mph)	Soil Moisture (%)
	Air	Soil		
11-14-2002	56.8	54.3	0	10.05
11-28-2002	52.0	49.3	0 to 2	8.94
12-12-2002	48.7	48.9	0 to 5	9.72

Note: It did not rain during the study.

APPENDIX 2. Sample Analytical Results

Laboratory results from Center for Analytical Chemistry of CDFA

EHAP No.	CDFA No.	Date Collected	Sample Type	Date Extracted	Date Analyzed	Results	Comment / Method / Blind Spike Recovery	MDL ug/L
2	855	11/14/2002	*Kimbie	12/23/2002	12/26/2002	202mg/kim[2]	Kimbie Rep1	.5mg/kim
3	856	11/14/2002	*Kimbie	12/23/2002	12/26/2002	191mg/kim	Kimbie Rep2	.5mg/kim
1	854	11/14/2002	Water	12/5/2002	12/9/2002	Nd	Control Water	0.1
4	857	11/14/2002	Water	12/5/2002	12/9/2002	11373[3]	Immediately after application	0.1
6	858	11/14/2002	Water	12/5/2002	12/9/2002	6541	Immediately after application	0.1
8	859	11/14/2002	Water	12/5/2002	12/9/2002	4668	Immediately after application	0.1
10	860	11/14/2002	Water	12/5/2002	12/9/2002	4172	Immediately after application	0.1
12	861	11/14/2002	Water	12/5/2002	12/9/2002	4056	Immediately after application	0.1
14	862	11/14/2002	Water	12/5/2002	12/9/2002	3980	Immediately after application	0.1
16	863	11/14/2002	Water	12/5/2002	12/9/2002	3962	Immediately after application	0.1
18	864	11/14/2002	Water	12/6/2002	12/10/2002	3774	Immediately after application	0.1
20	865	11/14/2002	Water	12/6/2002	12/10/2002	2712	Immediately after application	0.1
22	866	11/14/2002	Water	12/6/2002	12/10/2002	3327	Immediately after application	0.1
23	867	11/14/2002	Water	12/6/2002	12/10/2002	3167	Immediately after application	0.1
30	868	11/28/2002	Water	12/6/2002	12/10/2002	Nd	Control Water	0.1
31	869	11/28/2002	Water	12/6/2002	12/10/2002	4454	2 wks post application	0.1
33	870	11/28/2002	Water	12/6/2002	12/10/2002	2741	2 wks post application	0.1
35	871	11/28/2002	Water	12/6/2002	12/10/2002	2764	2 wks post application	0.1
37	872	11/28/2002	Water	12/17/2002	12/18/2002	2979	2 wks post application	0.1
39	873	11/28/2002	Water	12/17/2002	12/18/2002	1974	2 wks post application	0.1
41	874	11/28/2002	Water	12/17/2002	12/18/2002	2097	2 wks post application	0.1
43	875	11/28/2002	Water	12/17/2002	12/18/2002	1855	2 wks post application	0.1
45	876	11/28/2002	Water	12/17/2002	12/18/2002	2067	2 wks post application	0.1
47	877	11/28/2002	Water	12/17/2002	12/18/2002	2191	2 wks post application	0.1
49	878	11/28/2002	Water	12/17/2002	12/18/2002	1418	2 wks post application	0.1
50	879	11/28/2002	Water	12/17/2002	12/18/2002	1433	2 wks post application	0.1
51	945	12/12/2002	Water	12/26/2002	12/27/2002	0.242	Control Water	0.1
53	946	12/12/2002	Water	12/26/2002	12/27/2002	1342	4 wks post application	0.1
55	947	12/12/2002	Water	12/26/2002	12/27/2002	1104	4 wks post app.	0.1
57	948	12/12/2002	Water	12/26/2002	12/27/2002	878	4 wks post app.	0.1
59	949	12/12/2002	Water	12/26/2002	12/27/2002	689	4 wks post app.	0.1
61	950	12/12/2002	Water	12/26/2002	12/27/2002	646	4 wks post app.	0.1
63	951	12/12/2002	Water	12/26/2002	12/27/2002	562	4 wks post app.	0.1
65	952	12/12/2002	Water	12/26/2002	12/27/2002	582	4 wks post app.	0.1
67	953	12/12/2002	Water	12/26/2002	12/27/2002	549	4 wks post app.	0.1
69	954	12/12/2002	Water	12/26/2002	12/27/2002	547	4 wks post app.	0.1
71	955	12/12/2002	Water	12/26/2002	12/27/2002	556	4 wks post app.	0.1

[2] Kim = Kimbie wipe.
[3] Measured in parts per billion.

APPENDIX 3. Statistical Analysis for Fit of 3 – Parameter Exponential Decay Curve to Runoff Data.

A 3.1: **Statistics for Fit of Data from Runoff Event on November 14, 2002 to 3 Parameter Exponential Decay Curve**.

Rank 2 Eqn 8002 Exponential(a,b,c)

r^2 Coef Det	DF Adj r^2	Fit Std Err	F-value
0.9772606808	0.9675152582	408.54393442	171.90676127

Parm	Value	Std Error	t-value	95% Confidence Limits		P>|t|
a	3503.150972	162.0985043	21.61124797	3129.351151	3876.950792	0.00000
b	9713.786215	619.3013503	15.68507191	8285.674742	11141.89769	0.00000
c	6.999799666	0.870277596	8.043180356	4.992935933	9.006663398	0.00004

Area Xmin-Xmax	Area Precision		
273818.94098	7.504107e-10		
Function min	**X-Value**	**Function max**	**X-Value**
3504.1898926	64.000000000	11343.269090	1.5000027177
1st Deriv min	**X-Value**	**1st Deriv max**	**X-Value**
-1120.048929	1.5000027177	-0.148421523	64.000000000
2nd Deriv min	**X-Value**	**2nd Deriv max**	**X-Value**
0.0212036815	64.000000000	160.01156925	1.5000027177

Procedure	Minimization	Iterations	
LevMarqdt	Least Squares	8	
r^2 Coef Det	**DF Adj r^2**	**Fit Std Err**	**Max Abs Err**
0.9772606808	0.9675152582	408.54393442	794.65006215

Source	Sum of Squares	DF	Mean Square	F Statistic	P>F
Regr	57385278	2	28692639	171.907	0.00000
Error	1335265.2	8	166908.15		
Total	58720543	10			

A 3.2: **Statistics for Fit of Data from Runoff Event on November 28, 2002 to 3 Parameter Exponential Decay Curve.**

Rank 17 Eqn 8002 Exponential(a,b,c)

r^2 Coef Det	DF Adj r^2	Fit Std Err	F-value
0.8411594578	0.7730849397	383.58700509	21.182487702

Parm	Value	Std Error	t-value	95% Confidence Limits		P>|t|
a	1623.041084	328.5018392	4.940736674	865.5144856	2380.567683	0.00113
b	3095.807233	486.5462915	6.362821559	1973.829474	4217.784992	0.00022
c	21.00645442	8.917302236	2.355696136	0.443118611	41.56979022	0.04627

Area Xmin-Xmax	Area Precision		
158924.80067	3.182413e-16		
Function min	**X-Value**	**Function max**	**X-Value**
1738.9841488	69.000000000	4243.7190384	3.5000039566
1st Deriv min	**X-Value**	**1st Deriv max**	**X-Value**
-124.7558442	3.5000039566	-5.519401910	69.000000000
2nd Deriv min	**X-Value**	**2nd Deriv max**	**X-Value**
0.2627479060	69.000000000	5.9389291356	3.5000039566

Procedure	Minimization	Iterations	
LevMarqdt	Least Squares	7	
r^2 Coef Det	**DF Adj r^2**	**Fit Std Err**	**Max Abs Err**
0.8411594578	0.7730849397	383.58700509	577.53138518

Source	Sum of Squares	DF	Mean Square	F Statistic	P>F
Regr	6233539.7	2	3116769.9	21.1825	0.00064
Error	1177111.9	8	147138.99		
Total	7410651.6	10			

A 3.3: **Statistics for Fit of Data from Runoff Event on December 12, 2002 to 3 Parameter Exponential Decay Curve.**

Rank 1 Eqn 8002 Exponential(a,b,c)

r^2 Coef Det	**DF Adj r^2**	**Fit Std Err**	**F-value**
0.9797059324	0.9695588986	44.703714246	168.96419343

Parm	**Value**	**Std Error**	**t-value**	**95% Confidence Limits**		**P>|t|**
a	463.0280320	48.42538142	9.561680639	348.5202009	577.5358631	0.00003
b	1523.241626	121.7690531	12.50926724	1235.303571	1811.179682	0.00000
c	22.35902231	3.610740771	6.192364317	13.82097713	30.89706749	0.00045

Area Xmin-Xmax	**Area Precision**		
49347.649422	1.273566e-16		
Function min	**X-Value**	**Function max**	**X-Value**
512.78539112	76.500000000	1373.7715932	11.500019373
1st Deriv min	**X-Value**	**1st Deriv max**	**X-Value**
-40.73270954	11.500019373	-2.225381703	76.500000000
2nd Deriv min	**X-Value**	**2nd Deriv max**	**X-Value**
0.0995294728	76.500000000	1.8217571848	11.500019373

Procedure	Minimization	Iterations	
LevMarqdt	Least Squares	9	
r^2 Coef Det	DF Adj r^2	Fit Std Err	Max Abs Err
0.9797059324	0.9695588986	44.703714246	71.532123952

Source	**Sum of Squares**	**DF**	**Mean Square**	**F Statistic**	**P>F**
Regr	675323.55	2	337661.77	168.964	0.00000
Error	13988.954	7	1998.4221		
Total	689312.5	9			