Impact of 2,4,5-T on Blodgett Forest

I. Description of an Experimental Aerial Application of 2,4,5-T

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INTRODUCTION

2,4,5-Trichlorophenoxyacetic acid (2,4,5-T) contains a contaminant. 2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD) in minute amounts (less than 0.1 ppm). The bioaccumulation of 2,4,5-T and TCDD in deer flesh is a major concern because of the probability of human consumption.

The California Department of Food and Agriculture (CDFA) participatedina cooperative study titled "The Blodgett Forest Environmental Monitoring Project". The University of California at Berkeley provided the II-acre site at the Blodgett Forest Research Station. Dr. Barrett of U.C. Berkeley studied the impact of 2,4,5-T on the small animal population on the site. The United States Forest Service (Dr. Hugh Black) supplied the funds necessary for fencing the site, contracted with the company who applied the material to the application site, and coordinated the performance of the high resolution analysis for TCDD by Dr. Gross at the University of Nebraska. Dr. Black arranged for the preparation of the samples for analyses by the Environmental Protection Agency Laboratory at Bay St. Louis, Missouri and an assessment of the spray distribution on the site using spray cards placed by the U.S.F.S. F'orest Insect and Disease Management Unit in Davis. The California Department of Fish and Game participated in the study and were partly reimbursed by contractual funds supplied by the CDFA. They collected and transported the deer used in the project, studied their habits on the site, and collected the tissue samples at prescribed times. The CDFA also contracted with a private laboratory, Cal Analytical Laboratory in Sacramento, California, to perform TCDG analysis on plant tissue, herbicide formulation, and mylar panels. The mylar panels were used by Dr. Don Crosby

of the University of California at Davis in a collateral study on photo-degradation of TCDD in pesticide formulations when sprayed on a forest site.

This report will be limited to results of analyses of air, water, soil and vegetation by the Department's Chemistry Laboratory Services Unit and the methods used by the Department in collecting the samples. A supplementary report on the levels of 2,4,5-T in deer tissue will be completed at a later date.

METHODS AND MATERIALS

Site Description

The Blodget Forest is 12.1 miles east of Georgetown, California on the Wentworth Spring6 Road. The site consists of an II-acre plot in Township 12N, Range 12E, Section 16, Mount Diablo Base Meridian, in the Blodgett Forest Research Station, El Dorado County. The site is at an elevation of 4,350 feet. It is a ten-year-old clear cut which was replanted to white fir (Abies concolor) and giant sequoia (Sequoiadendron giganteum).

These crop trees have been suppressed by an overstory of brush consisting of deer brush (Ceanothus integerrimus), snow bush (Ceanothus cordulatus), bitter cherry (Prunus emarginata), black oak (Quercus kelloggii), greenleaf manzanita (Arctostaphylos patula), whiteleaf manzanita (Arctostaphylos viscida), sierra gooseberry (Ribes koezlii) wood rose (Rosa gymnocarpa), giant chinquapin (Castanopsis chrysophylla), white alder (Alnus rhombifolia), azalea (Rhododendron occidentale). The major portion of the flora is made up of deer brush, 6now bush, greenleaf manzanita, and whiteleaf manzanita. The brush ranges to eight feet high and the crop trees average 18 inches high.

The site (figure 1) is rectangular in shape with the north-south axis being the long dimension. The site was subdivided into a sprayed (northern) section and a non-sprayed (southern) section. A road exists along the west side of the plot and a small spring is located at the southeast corner of the rectangle. A small watering trough was located in the northeastern corner of the rectangle for use by the deer. The rectangle is surrounded on four sides by second growth conifers which average 80 to 100 feet in height. The site has been enclosed with an eight to ten foot high hog wire fence.

The sampling stations for all media were established by dividing the length of the rectangular site into eighths and the width into fourths. The division points were then drawn into lines at 90 degree angles from the lines representing the length and width. These lines produced 21 intersections which were then numbered 1 to 21 starting at the northwest corner and proceeding to the southeast corner. A random number table was utilized to select required sample stations from the 21 possible.

The CDFA study was conducted during the six week period beginning 25 September 1978 through 2 November 1978. Pre-application control samples were taken one week before the herbicide spray. The control samples consisted of one high-volume air sample from the site using XAD-4 resin as the sample media, one sample from each foliage sample station, one soil sample from each soil sample station, and one water sample from the spring in the southeast corner of the site.

Soil Sampling

All soil samples were taken from four randomly selected sample stations marked with an annotated wooden stake. Collected samples include the

prespray control sample and soil samples taken on post-application day 1, 2, 4, 8, 15, 21, 32 and 228. These samples were submitted to Chemistry Laboratory Services for analysis for residues of 2,4,5-T.

Foliage Sampling

Four foliage sample stations were also randomly selected from the 21 intersections and marked with annotated wooden stakes. Two samples were taken from each station during each sampling period. The first sample was taken on the southern side of the sample station at approximately chest height. The second sample was taken on the northern side of the sample station at approximately knee height. Only the foliage of deer brush (Ceanothus integerrimus) was utilized, with each sample consisting of a combination of leaves and tender tips of twigs weighing approximately 20 grams. The foliage sampling periods were post-application day 1, 2, 4, 8, 15, 21, 32 and 228. These samples were submitted to Chemistry Laboratory Services for analysis for residues of 2,4,5-T.

An additional series of foliage samples were taken using a one inch leaf punch. These were taken from the four established foliage sample stations. Each sample consisted of 200 one-inch leaf punches and each site was sampled on post-application day 1, 2, 4, and 8. Only greenleaf manzanita (Arctostaphylos patula) was sampled with this technique because of the need for a leaf large enough to obtain a one inch punch. These samples were submitted to Cal Analytical Laboratories for analysis for TCDD.

Air Sampling

Air samples were obtained using both high and low volume air samplers. The high volume samplers (Staplex Model TF1A) were powered by portable gasoline generators located downwind of the instruments. High volume samplers were originally calibrated at 70 cubic feet per minute (cfm) at the factory but were not recalibrated before use because of a lack of calibration equipment and facilities. Air was drawn through 30 gram beds of Amberlite XAD-4 (polystyrene, divinylbenzene copolymer) macroreticular polymer resin beads (20/50 mesh Rohm and Haas, Philadelphia, PA) for two hours. After the samples were drawn, the resin was transferred to a clean glass jar and placed on ice in chests for transport to the laboratory. The XAD-4 resin used as the capture media was cleaned before use by the 'Environmental Toxicology Department at U.C. Davis. This procedure involves washing the resin beads with hydrochloric acid and water, then extracting with acetone in a soxhlet for eight hours and finally drying the beads overnight in an oven.

The most intensive air sampling occurred on the day of the herbicide application. Three low volume air samplers were placed within the site along with two high volume air samplers. Three additional high volume air samplers were operated during this period. One was at the downwind edge of the site and the remaining two located 100 and 200 feet downwind of the site.

All air samplers were operated for two hours beginning with the starting of the application. Resin samplers were removed and the air samplers recharged with fresh XAD-4. A second air sampling run of two hours commenced within 15 minutes producing an additional six air samples.

Ten post-spray air samples were taken. The post-spray samples were taken on day 2, 4, 8, 15, 21 and 32. The air sampler was located at the intersection of the axis of the long and short sides of the rectangular spray site (sample station II) and was operated for two hours from 7-9 AM and from 12-1 PM providing two samples of XAD-4 resin per sample day.

Water Sampling

All water samples were collected using one-gallon Amber glass jars with foil lined caps. Each jar was filled just below the surface level of the water. All samples consisted of one jar with the exception of these from 2 November 1978, when three jars were collected at both the spring and trough.

RESULTS

Pre-spray control samples showed no detectable level of 2,4,5-T herbicide for all mediums and techniques.

The 2,4,5-T ester was applied on the morning of 2 October 1978 between 0950 and 1020 in a temperature of 22°C and a relative humidity of 33%.

Foliage Samples

No TCDD was detected in any foliage samples of Arctostaphylos sp. sampled.

All samples of Ceanothus sp. foliage collected from the area of application (sites 5 & 6a) were contaminated with appreciable levels of 2,4,5-T on all

sampling dates (Table 1). The detected levels of the ester form on 2 November 1978 at both sites 5 & 6 represent a 98% reduction from 2 October 1978 levels, whereas the levels of the acid form present in 2 November 1978 samples represent an approximate 61% loss from 2 October 1978 levels at both sites 5 and 6. The 2,4,5-T levels on vegetation from the non-sprayed section of the application site were extremely low and virtually disappeared after 10 October 1978 (Table 1).

Water Samples

At the trough location, only the first two post-application sampling dates showed the presence of the ester form of 2,4,5-T (Table 2). A sharp drop from the relatively high value of 364 ppb ester to a level below detection limits occurred between the 3 October 1978 and 5 October 1978 samplings. This drop in the ester form occurred concurrently to an increase from 85 ppb to 249 ppb in the acid form. The acid was detected at high levels in the trough throughout the study period.

No ester form of the herbicide was detected in samples taken from the spring within the control area. Low levels of the acid were detected in spring water samples collected on the 2nd and 3rd of October, with all other sampling dates yielding no detectable herbicide present.

Soil Samples

No detectable levels of either ester or ester forms of 2,4,5-T were detected at the two sampling stations (numbers 16 and 19) located within the control area (Table 3).

Detectable levels of both forms of the herbicide were recorded on all sampling dates at one or both stations (numbers 8 and 11) within the application area. The one exception was 17 October 1978 when none of the acid form was detected.

Air Samples

Air samples were taken during a 2-hour period (1000 - 1200 PST) which included the aerial application. A gradient of decreasing amounts of 2,4,5-T ester was monitored at 1, 100, and 200 feet downwind and a total of 43 µg of material was collected just upwind at station 15 (Table 4). These results were almost duplicated during an additional monitoring period from 1200 to 1400 in the afternoon despite no further aerial application. Low volume samplers were also used at stations 5 and 11 and produced detectable levels of 2,4,.5-T. The high volume sampler at station 11 within the application area did not produce the expected high levels of 2,4,5-T.

During the post-application air monitoring, widely separated morning and afternoon levels of 2,4,.5-T ester were detected on all but the 17 October 1978 sampling date (Table 5). Afternoon levels were consistently higher than the morning level, with the overall levels decreasing until no detectable herbicide was present on 2 November 1978.

DISCUSSION

The Ceanothue sp. foliage samples from within the application site contained significant levels of 2,4,5-T but no detectable TCDD throughout

the one month post-application sampling period. It can be assumed that the deer enclosed within the application site ingested a significant amount of 2,4,5-T herbicide since the Ceanothus sp. is a preferred food plant for deer and the study animals were observed foraging on the Ceanothus sp. during the post-application period. Sample6 taken from the control end of the site produced drift residues of 2,4,5-T that did not exceed one half of a part per million. These sample sites were 65 feet (sample station 15) and 171 feet (sample station 16) from the nearest border of the application portion of the site.

The levels of 2,4,5-T ester collected from high volume sampler6 should not be used for further calculations. The flow rate and resin breakthrough times for the high volume samples were not calibrated prior to use due to the lack of calibration equipment. The discrepancy between high volume and low volume sampler results at station 11 on the morning of the application is an example of the potential problem. A value of only 3 µg 2,4,5-T ester was detected on the high volume sampler versus a 115 µg level from the low volume sampler located at the same site. The herbicide had been applied directly overhead and the high volume with a flow rate of about 70 cubic feet per minute should have contained a large amount of 2,4,5-T. It is possible that the breakthrough time for the resin in the high volume sampler had been exceeded for the high aerial concentrations and significant levels of herbicide had been drawn completely through. This, however, would not explain why only a 3 µg sample was collected. Without data on herbicide recovery efficiency from the sorbent, and instrument calibration, it would be inappropriate to use the air monitoring samples as accurate estimates of the levels of 2,4,5-T present.

The study did show significant levels of the herbicide to have drifted at least 200 feet downwind of the application site during the morning hours following the application.

During the post-application period, the herbicide was detected in decreasing amounts at station 11 over time. After one month, no herbicide was detected in the air during either morning or afternoon samples.

Herbicide levels were detected in soil samples taken within the application area during all seven sampling days after application. The levels of the ester form remained in the upper soil layer throughout the post-application period with no indication of conversion to the acid form except for samples at station 8 and 11 on 2 November 1978. Herbicide levels of the ester form decreased with time.

Although detectable levels of herbicide were found in air and foliage samples from the control area, the soil samples from the same control sampling stations did not produce detectable levels throughout the study period.

The high levels of ester form detected in the water trough samples in the application area on the date of application and following day seem reasonable considering the direct impact of the herbicide onto the water surface. The sharp drop in ester levels and concurrent rise in acid form levels may be accounted for through the metabolic action of microorganisms.

Since the trough was a stagnant source of water established by study personnel for the enclosed deer population, a rapid growth in the population of microorganisms would be expected.

The detected levels of herbicide from the existing spring in the control area were very low indicating little contamination on this water source. Except for the 1.0 ppb acid form detected on the application date and the 0.3 ppb acid form on the following day, no other post-application sample produced detectable levels.

In summary, the 2,4,5-T ester application produced appreciable levels of the ester over the exposed surfaces in the treated area. Foliage, soil, and water from the trough all contained detectable levels of the ester on the day of application. With the exception of the acid form in the trough, herbicide levels in the other substrates decreased with time. The 2,4,5-T ester conversion to acid was only documented in soil and in water from the trough.

Both foliage samples in the non-treated area and downwind drift levels off the application site did not produce appreciable residues with an extended residence time. Only substrates within the application area appeared to retain significant levels of herbicide.

This report was designed to produce an accurate description of 2,4,5-T impact on the substrates within a conifer release application site. It documents herbicide levels present immediately after application and during a 30-day post-treatment period and compares them with an untreated area immediately adjacent to the sprayed location.

A report on the levels of 2,4,.5-T and TCDD in captive deer on the study area will be produced. This document will describe contamination of various tissues from exposure to the application and ingestion of contaminated vegetation and water.

FIGURE 1. LOCATION MAP

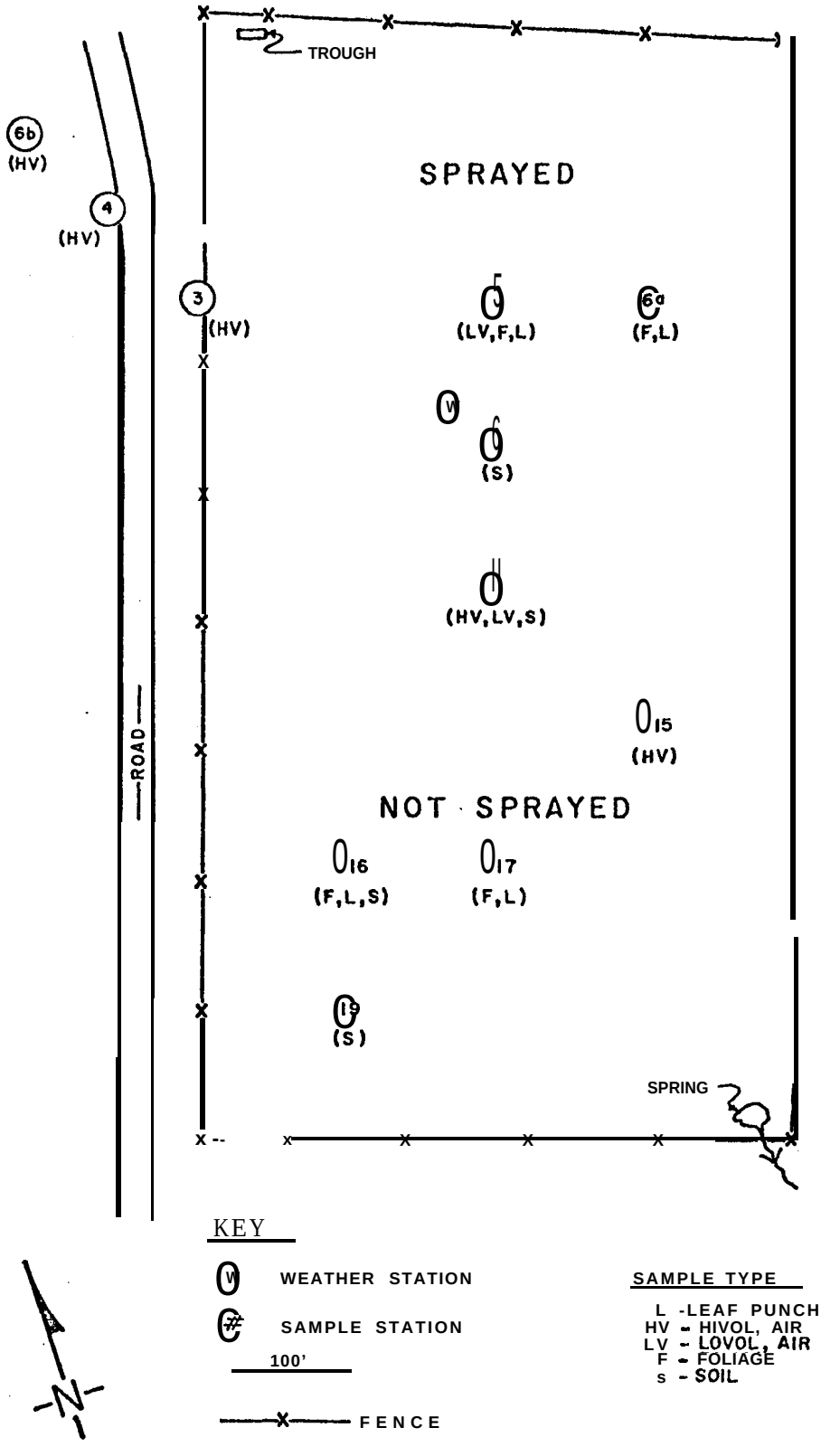

Table 1. Levels of 2,4,.5-T on Ceanothus sp. Foliage, Blodgett Forest 1978.

Sampling Station	Date	2,4,5-T	
		Ester (ppm)[1]	Acid (ppm)
5	10/2/78	105.60[2]	10.90[3]
	10/3/78	105.61	11.20
	10/5/78	79.30	2.00
	10/10/78	46.35	4.10
	10/17/78	5.80	3.45
	10/23/78	2.50	1.35
	11/2/78	2.40	4.35
	5/18/79	0.00	0.62
6a	10/2/78	158.50	19.35
	10/3/78	179.30	12.50
	10/5/78	100.90	8.10
	10/10/78	55.82	4.00
	10/17/78	6.90	5.00
	10/23/78	3.50	2.20
	11/2/78	3.10	7.20
	5/18/79	0.00	1.20
15	10/2/78	0.45	0.20
	10/3/78	0.07	0.00
	10/5/78	0.03	0.03
	10/10/78	0.00	0.01
	10/17/78	0.00	0.00
	10/23/78	0.00	0.04
	11/2/78	0.00	0.00
	5/18/79	0.00	0.00
16	10/2/78	0.05	0.01
	10/3/78	0.04	0.01
	10/5/78	0.17	0.05
	10/10/78	0.00	0.01
	10/17/78	0.00	0.00
	10/23/78	0.00	0.00
	11/2/78	0.00	0.00
	5/18/79	0.00	0.00

[1] Parts per million calculated on a weight per weight basis.

[2] Mean of 2 samples analyzed with an instrument sensitivity of .04 ppm 2,4,5-T ester.

[3] Mean of 2 samples analyzed with an instrument sensitivity of .01 ppm 2,4,5-T acid.

Table 2. Level6 o 2,4,5-T in Water Samples from Blodgett Forest.

Sampling Station	Date	2,4,5-T	
		Ester (ppb)[1]	Acid (ppb)
Trough	10/2/78[2]	26.0[3]	19.0[4]
	10/3/78	364.0	85.0
	10/5/78	0.0	249.0
	10/10/78	0.0	185.1
	10/17/78	0.0	128.9
	10/23/78	0.0	156.2
	11/2/78	0.0	132.7[5]
	5/18/79	0.0	2.2
Spring	10/2/78	0.0	1.0
	10/3/78	0.0	0.3
	10/5/78	0.0	0.0
	10/10/78	0.0	0.0
	10/17/78	0.0	0.0
	10/23/78	0.0	0.0
	11/2/78	0.0	0.0[5]
	5/18/79	0.0	0.0

[1]Parts per billion calculated on a weight per volume basis.

'Application date, 10/2/78 (0950 - 1020 PST).

[3]A detection limit of 1.3 ppb was documented for the 2,4,5-T ester analysis.

[4]A detection limit of 0.3 ppb was documented for the 2,4,5-T acid analysis.

[5]Mean of 3 samples, all other6 are single sample values.

Table 3. Level6 of 2,4,5-T in Soil Sample6 From Blodgett Forest.

Station No.	Date	2,4,5-T	
		Ester (ppm)[1]	Acid (ppm)
8	10/2/78	9.20[2]	0.02[3]
11		0.70	0.00
16		0.00	0.00
19		0.00	0.00
8	10/3/78	8.80	0.02
11		2.10	0.00
16		0.00	0.00
'9		0.00	0.00
8	10/5/78	1.60	0.02
11		6.70	0.10
16		0.00	0.00
19		0.00	0.00
8	10/10/78	1.80	0.07
11		1.20	0.00
16		0.00	0.00
'9		0.00	0.00
8	10/17/78	1.10	0.00
11		0.74	0.00
16		0.00	0.00
19		0.00	0.00
8	10/23/78	1.70	0.04
11		0.48	0.00
16		0.00	0.00
19		0.00	0.00
a	11/2/78	0.00	1.10
11		0.37	1.90
16		0.00	0.00
19		0.00	0.00
a	5/18/79	0.00	0.00
11		0.00	0.00
19		0.00	0.00

'Part6 per million calculated on a weight per volume basis.

[2]A detection level of .04 ppm was documented for 2,4,5-T ester analysis.

[3]A detection level of .01 ppm was documented for 2,4,5-T acid analysis.

Table 4. Levels of 2,4,5-T Ester from Air Samplers at Blodgett Forest on 10/2/78.

Station No.	Distance[1] (ft.)	Time (PST)	Sample Type: HiVol[2]	Sample Type: LoVol[3] (µg)
5	0	1000-1200	Not sampled	71
11	0		34	115
3	1		294	Not Sampled
4	100		122	"
6b	200		10	"
15	(upwind)		43	"
5	0	1200-1400	Not Sampled	21
11	0		163	Not Sampled
3	1		294	"
4	100		143	"
6b	200		33	"
15	(upwind)		0	"

[1]Distance downwind of application site.

[2]High Volume Air Sampler.

[3]Low Volume Air Sampler.

[4]A detection limit of 2 µg was documented for the 2,4,5-T ester analysis.

Table 5. Levels of 2,4,5-T Ester in Post Application Air Monitoring at Station 11, Blodgett Forest.

Date	Time (PST)	2,4,5-T Ester (µg)
10/2/78	1000-1200 (application period)	3[1]
	1200-1400	163
10/3/78	0700-0900	28
	1200-1330	161
10/5/78	0650-0850	8
	1200-1400	42
10/10/78	0700-0900	3
	1200-1400	7
10/17/78	0700-0900	4
	1200-1400	4
10/23/78	0700-0900	0
	1200-1400	13
11/2/78	0700-0900	0
	1200-1400	0

'A detection limit of 2 µg was documented for the 2,4,5-T ester analysis.