FEASIBILITY STUDY ON ENVIRONMENTAL MONITORING OF PHENOXY HERBICIDE APPLICATIONS IN HUMBOLDT COUNTY, CALIFORNIA 1978

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INTRODUCION

The herbicide 2,4,5-Trichlorophenoxyacetic acid (2,4,5-T) has been an important tool in forest management to control unwanted brush and trees. Recently, it has been implicated as a possible nonpoint source of pollution to water. This project was intitiated to develop methods to monitor 2,4,5-T in aqueous media and to determine whether this material could be detected in insect samples after an aerial application for silvicultural resource management. This was one of a series of feasibility studies conducted by the California Department of Food and Agriculture to assess its current capabilities and to gather information to guide anticipated in-depth monitoring studies in the future.

Candidate streams in Humboldt County were identified during preapplication surveys of the project area. A cooperative effort with the Humboldt County Agricultural Commissioner's office was conducted during the spring and early summer of 1978.

MATERIALS AND METHODS

The project monitored weather, water, and air during aerial applications. Selected aquatic organisms were sampled to check for 2,4,5-T and TCDD.

Weather Monitoring

Weather monitoring consisted of measuring wind speed and direction, air temperature, relative humidity, barometric pressure, and rainfall. The wind sensing system consists of a low-threshold stainless steel cup anemometer and lightweight direction vane, both mounted on a prewired crossarm that is attached to the top of a 20-foot telescoping tower. Windspeeds from 0.6 to 50 mph can be recorded with an accuracy of $\pm$ 1% or 0.15 mph, whichever is greater. Temperature, relative humidity, and barometric pressure were measured and recorded with a meteorograph stored in a shelter. Rainfall was measured using a forester type rain gauge.

Air Monitoring

Staplex Model TF1A high volume air samplers (HiVols) were used for air monitoring. They were originally calibrated at 70 cubic feet per minute (cfm) when purchased, but were not recalibrated before use due to 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.). After each sample was drawn, the resin was transferred to a clean glass jar and placed on ice in chests for transport to the laboratory.

Water Monitoring

The stream flows were measured before the application using a pygmy current meter (W. & L. E. Gurley Co.). Water samples were collected before, during

and after the application. When possible, they were taken at the surface, from the center of each stream, using hexane-rinsed, one-gallon amber glass bottles with foil-lined screw caps. The water bottles were then placed in ice chests for transport to the laboratory.

Insect Samples

Aquatic insects were collected out of Tully Creek during this project. Nymphal caddisflies, dragonflies, and larvae of other small insects comprised samples taken on May 23 (38 grams) and May 25 (52 grams); a third sample was taken on June 22 (100 grams). The samples were dried, then frozen and sent to the laboratory for analysis.

Site Descriptions

Site 1.

An aerial application of 2,4-D and 2,4,5-T (1 lb of 2,4-D and 3 lbs of 2,4,5-T per acre) was proposed for approximately 1,700 acres of forest land in northern Humboldt County. In combination, these herbicides suppress competing hardwoods (madrone and tanoak) and encourage quicker growth of the conifers (Douglas firs). Unfavorable weather conditions curtailed much of the spraying effort and application was limited to 117 acres in Township 9N, Range 3E, Sections 8, 17, and 18 (Figure 1). One hundred-foot buffer zones from sensitive areas such as streams or neighboring property were required. The stream closest to the application was Robbers Gulch, which flows into Tully Creek.

Monitoring and sampling sites were selected during a preapplication site survey. Air monitoring station 2 was located near a logging road in the center of the proposed 1,700-acre spray area; station 3 was located on the edge of the spray area near a bridge across Robber8 Gulch; station 4 was located at the confluence of Robbers Gulch and Tully Creek, 1.25 miles east of the bridge across Robbers Gulch.

Spraying began at 0700 on April 18, 1978. Although the wind speed recorded on the ridgetop by Skookum Prairie ranged from 10 to 12 mph from the south during this time, the wind in the canyon varied from calm to gusts of 4 mph from the north measured at several sites below the ridge tops. The temperature was 4°C and the humidity 67%. Spraying was halted when wind conditions became a steady 3 mph from the north with gusts to 6 mph at 0740.

Water samples were taken at stations 3 and 4. At station 3 a prespray sample was taken at 0615, followed by post-spray sampling at 0755, 0900, 1015, and 1500. Both Tully Creek and Robbers Gulch were monitored at station 4 prior to the application, but no further water samples were taken from Tully Creek when further application was curtailed because of excessive wind. Post-spray sampling at station 4 began at 0830 and continued hourly through 1130, with the last sample that day taken at 1400. Follow-up samples at both stations were taken on April 22 and June 22.

Site 2.

Two hundred and twelve acre8 had been selected for this application site using 2,4-D (3 lbs 2,4-D per acre). The closest stream, Tully Creek, was 200 feet from the nearest part of the application site (Figure 2). Tully Creek flows into the Klamath River, approximately four miles away.

On May 23, 1978, the first day of the application, the weather recording equipment positioned inside the spray block at station 1 recorded a temperature of 5°C, 75% humidity, and wind speed of 2 to 4 mph from the southeast. Spraying began at 0715 on the northeast portion of the spray block in section 3. By 0804, 60 acres had been sprayed but further application was stopped because winds were beginning to gust above 5 mph. Water samples from Tully Creek were collected every half-hour beginning at 0745, with the last one taken at 1115.

The remaining 150 acres were not sprayed until May 25 because of .27 inches of rainfall on May 24. Weather conditions the morning of the 25th were: temperature 2°C; humidity 72%; and wind speed ranging from calm to 2 mph. Water monitoring began at 0500 and continued at half-hour interval8 until 0630, when sample8 were taken at hourly interval8 until noon.

Site 3.

A total of 91 acres of privately-owned rangeland were sprayed with a mixture of 2,4-D and 2,4,5-T (2 lbs 2,4-D and 1 lb 2,4,5-T per acre> on June 23,1978 in southwestern Humboldt County (Figure 3). A 69-acre block was sprayed first, beginning at 0510. Weather condition8 recorded at the north edge of the spray block were: temperature 8°C; humidity 98%; and wind speed 3.5 mph. The first block was finished at 0545, and two passes were made on the second block (22 acres) from 0555-0600. At 0605 it began to drizzle lightly. Measured precipitation between 1100 hours on June 22 and 0830 on June 23 was .01 inches. Water samples from Singley Creek were collected beginning at 0505 and every 15 minutes thereafter until 0550; then every 20 minutes from 0610 until 0650; and again at 0800, 0930, and 1300. Spraying on the 22-acre block began again at 0715, one half-hour after precipitation had stopped, and was completed at 0730. Water sample8 from the unnamed creek bordering the north edge of the block were collected at 0555, 0615, 0630, 0645, 0705, 0730, 0750, 0950, and 1300. In addition, water sample8 from below the confluence of the two creek8 were taken at 0635, 0645, 0700, 0730, and 0750.

RESULTS

Site 1.

Both 2,4-D and 2,4,5-T were detected in water samples taken from the Robbers Gulch sampling point immediately after the aerial application was concluded (Table 1). The levels were quite low, 1.0 ppb 2,4-D and 2.2 ppb 2,4,5-T respectively, and were only detected at the 0755 sampling time. Samples from the Tully Creek sampling point were negative for 2,4-D but did show low amounts of 2,4,5-T at 0830, 0930, and 1130. The earliest detection of 2,4,5-T occurred at 0830, 1.5 hours after the application was intitiated.

The Tully Creek sampling station was located 1.25 miles downstream of the aerial application site and the time frame for slug flow would appear to be realistic given the flow rate of Robbers Gulch, 0.7 mph. The data did not explain the apparent lack of dilution from the Robbers Gulch sampling point upstream; the dilution factor was only 1.2 in the 1.25 miles.

The air monitoring samples at all stations did not produce detectable levels of 2,4-D or 2,4,5-T.

Foliage samples taken on April 18, 1978 within the application area produced detectable levels of both herbicides (Table 4). Significant levels were also detected on samples on May 25, 1978. Further sampling on June 22, 1978 also produced appreciable levels of 2,4-D and 2,4,5-T on foliage from trees, but only 0.04 ppm 2,4,5-T in a soil sample and nothing on a shrub sample.

Site 2.

No detectable levels of 2,4-D were obtained in water samples or air monitoring despite the siting of a HiVol sampler within the application site.

Foliage samples taken within the application site did produce significant amounts of 2,4-D from both shrubs and trees (Table 4).

Site 3.

No herbicides were detected in water samples from Singley Creek which bordered the initial 69-acre spray application site until 0650, 45 minutes after a rain (Table 2). Low levels of both 2,4-D and 2,4,5-T were detected in the 0650 water sample but subsequent samples at 0800, 0930, and 1300 were negative. This pattern of detectable herbicide levels occurring after a rain persisted in monitoring the water from no name creek after the herbicide spray to the 22-acre application site. Herbicide levels were detected only after the rain (Table 2) and after the completion of the 2nd aerial application at 0730. No herbicides were detected in water samples from the sampling station below the confluence of Singley Creek and no name creek.

Air monitoring at stations 1A and 1B within the 69-acre application site detected widely divergent levels of 2,4-D both during application and for a one-hour period after the application ceased (Table 3). The divergent levels represent the difference between direct sampling and suspended particulate sampling. HiVol samples during the same period8 from station 2 also contained appreciable amounts of 2,4-D. No 2,4,5-T was detected in the air samples despite the fact that this material was present in the application formulation and was detected in the previously mentioned water samples.

The foliage samples taken on June 20, 1978 prior to the herbicide application were negative (Table 4). A broad range of herbicide levels was detected on foliage from trees and shrubs after the aerial application. Both 2,4-D and 2,4,5-T were detected on most samples both within the application site (station 1) and at the perimeter (station 2).

Insect Samples

No 2,4,5-T or TCDD (dioxin) was detected in the insect samples collected from Tully Creek.

DISCUSSION

Water Sampling

Both 2,4-D and 2,4,5-T were detected in low levels in water samples taken from stream8 adjacent to aerial application sites 1 and 3. Detection sensitivity was in the parts-per-billion (weight per volume) range. However, laboratory analyses were not evaluated for reproducibility and the error involved with the quantitative measurements was not documented.

Ratio8 of 2,4-D to 2,4,5-T detected in water were correlated to the formulated herbicide ratios at application sites 1 and 3. This would indicate some measure of confidence that relative level8 were comparable.

It was of concern that no 2,4-D was detectable in water samples from site 2 (Tully Creek). This may have been due to permit conditions requiring 200 ft buffer zones instead of 100 ft buffer zones used at site 1 and site 3.

Air Monitoring Samples

Levels of herbicides collected from HiVol samplers used in this project should not be used for further calculation. The HiVol samplers were not calibrated prior to use due to the lack of calibration equipment and facilities. The levels of pesticides reported at site 3, stations 1A and 1B, are examples of the potential error. Both stations 1A and 1B were within the application area and utilized exactly the same times for monitoring. The levels of 2,4-D detected were different by a factor of 6 during the 0500-0600 sampling period. The divergence between stations 1A and 1B was reduced to a factor of 2 during the 0615-0715 post-application sampling period. This would indicate that the amount of large droplets applied during the actual application period had settled and were not a source of pesticide during the post-application sampling period. Source8 of variation could also potentially include station location in relation to the fly-over aerial application, instrument calibration, recovery efficiency from the resin, and accuracy of the analytical procedures. It would be inappropriate to use the air monitoring samples as accurate estimate8 given these source8 of error.

The absence of detectable quantities of 2,4,5-T from the air samples taken at station8 1A and 1B within the application area at site 3 was especially disturbing since the application rate of herbicides was 2 lbs 2,4-D to 1 lb. 2,4,5-T per acre. The herbicide mixture was applied directly on the 1A and 1B sampling stations and 2,4,5-T should have been detected on the HiVol resin samples. It was detected in both water and foliage samples from the same application site.

Foliage Samples

Herbicides were detected on foliage sample8 from all application sites. The accuracy of the analyses are somewhat questionable, however, since the ratio of 2,4-D to 2,4,5-T varies considerably from sample-to-sample in relationship to the ratio of herbicides applied.

This feasibility study isolated several areas where improvement is needed before an in-depth monitoring study can be initiated:

1. Replication to ensure reproducibility and to define sampling error will be incorporated into experimental designs.

2. Analytical and sampling procedures for monitoring 2,4,5-T with XAD-4 resin will be reevaluated.

3. Instrument calibration equipment will be purchased and a regular schedule of calibrations will be initiated.

4. Procedures used in storing, processing, and analyzing foliage samples will be reviewed.

5. Experimental designs using sampling gradients of distance away from application sites and matrix designs for determining directionality will be developed.

Positive results stemming from the Humboldt County monitoring project were:

1. 2,4-D and 2,4,5-T were detectable in water samples in the parts-per-billion range. All samples were well within EPA water quality standards for the dates that monitoring was undertaken.

2. 2,4-D was detectable in the air using HiVol samplers and XAD-4 resin as a trapping medium.

3. Monitoring air, water, and foliage media for herbicides can be accomplished in extremely rugged terrain and under unfavorable weather conditions. A relatively small number of trained personnel could handle an in-depth study under more favorable conditions.

This feasibility study was successful in isolating the stated problem areas and confirming that future studies could be carried out by a relatively small monitoring team. The information gathered by this and other feasibility studies of MCPA, 2,4-D, 2,4,5-T, and DEF was extremely valuable in planning for full-scale monitoring efforts to be initiated in the 1979-80 fiscal year.

ACKNOWLEDGEMENTS

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Table 1. Herbicide levels in water samples taken at site 1 in Humboldt County, April 18, 1978.

Location	Time (PST)	2,4-D (ppb)[1]	2,4,5-T (ppb)
Robbers Gulch Station 3	0615	0.0[2]	0.0
	0755 (sprayed 0700-0740)	1.0	2.2
	0900	0.0	0.0
	1015 (rain 1050)	0.0	0.0
	1500	0.0	0.0
Tully Creek Station 4	0830	0.0	0.9
	0930	0.0	1.0
	1030	0.0	0.0
	1130	0.0	1.0
	1400	0.0	0.0

[1] parts-per-billion (ppb) concentrations were calculated on a weight per volume basis.

[2] a detection level of 0.5ppb was documented for the analytical analysis.

Table 2. Herbicide levels in water samples taken at site 3 in Humboldt County, June 23, 1978.

Location	Time (PST)	2,4-D (ppb)[1]	2,4,5-T (ppb)
Singley Creek	0505	0.0[2]	0.0
	0520 (sprayed 0510-0545)	0.0	0.0
	0535	0.0	0.0
	0550	0.0	0.0
	0610 (rained 0600-0630)	0.0	0.0
	0630	0.0	0.0
	0650	2.3	0.7
	0715	0.7	0.0
	0800	0.0	0.0
	0930	0.0	0.0
	1300	0.0	0.0
No Name Creek	0555 (sprayed 0555-0600)	0.0	0.0
	0615 (rained 0605-0645)	0.0	0.0
	0630	0.0	0.0
	0645	1.8	0.0
	0705	5.0	0.8
	0730 (sprayed 0715-0730)	1.5	0.0
	0750	9.0	1.0
	0930	0.0	0.0
	1300	0.0	0.0

[1] parts-per-billion (PPB) concentrations were calculated on a weight per volume basis.

[2] a detection level of 0.5ppb was documented for the analytical analysis.

Table 3. Herbicide levels monitored with high volume air samplers at site 3 in Humboldt Co.

Sampling Station	Time (PST)		2,4-D (µg)[1]	2,4,5-T (µg)
1A	0500-0610	(sprayed 0510-0545)	116.02	0.0
1A	0615-0715		27.5	0.0
1B[3]	0500-0610	(sprayed 0510-0545)	686.0	0.0
1B[3]	0610-0715		45.2	0.0
2	0505-0606	(sprayed 0510-0545)	8.5	0.0
2	0610-0710		2.4	0.0

[1]micrograms

[2]a detection limit of 0.5µg was documented for the analytical analysis.

[3]this sample was not housed in a weather shelter and received direct application.

Table 4. Herbicide levels on foliage samples taken in Humboldt County.

Location	Sampling Station	Date	Plant Type	2,4-D (ppm)[1]	2,4,5-T (ppm)
Site 1 Robbers Gulch	3	4/18/78	ground cover	0.80[2]	3.20
	3	4/18/78	ground cover	0.30	1.50
	3	5/25/78	not labelled	2.0	9.20
	3	6/22/78	tree	6.40	19.90
	3	6/22/78	tree	0.88	4.20
	3	6/22/78	shrub	0.0	0.00
	3	6/22/78	soil	0.0	0.04
Site 2 Tully Creek	1	5/25/78	shrub	3.10	not applicable
	1	5/25/78	tree	7.50	"
	1	6/21/78	shrub & tree	5.80	"
Site 3	1	6/20/78	combined shrubs & trees	0.00	0.00
	2	6/20/78	"	0.00	0.00
	2	6/23/78	shrub	0.00	0.00
	2	6/23/78	tree	0.02	0.00
	2	6/23/78	shrub	1.80	0.28
	1	6/23/78	shrub	25.50	1.70
	1	6/23/78	shrub	1.20	3.60
	1	6/23/78	tree	7.20	0.60
	1	6/23/78	shrub	0.28	0.84
	1	6/23/78	shrub	0.03	0.00

[1] parts-per-million (ppm) were calculated on a weight per weight basis.

[2] a detection limit of 0.01 ppm was documented for the analytical analysis.

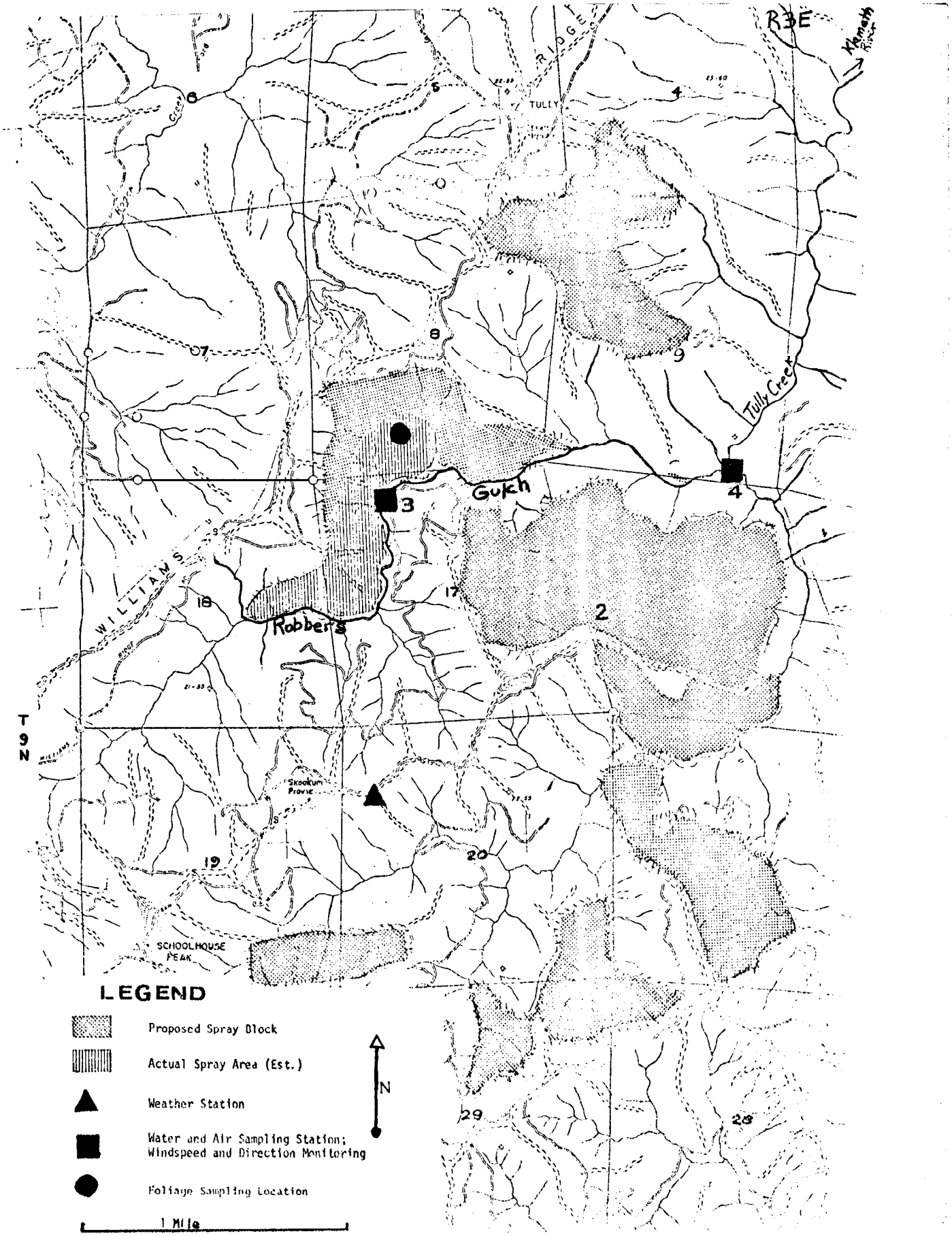

Figure 1. Application site 1 consisting of 2,4-D and 2,4,5-T aerial spraying and monitoring locations.

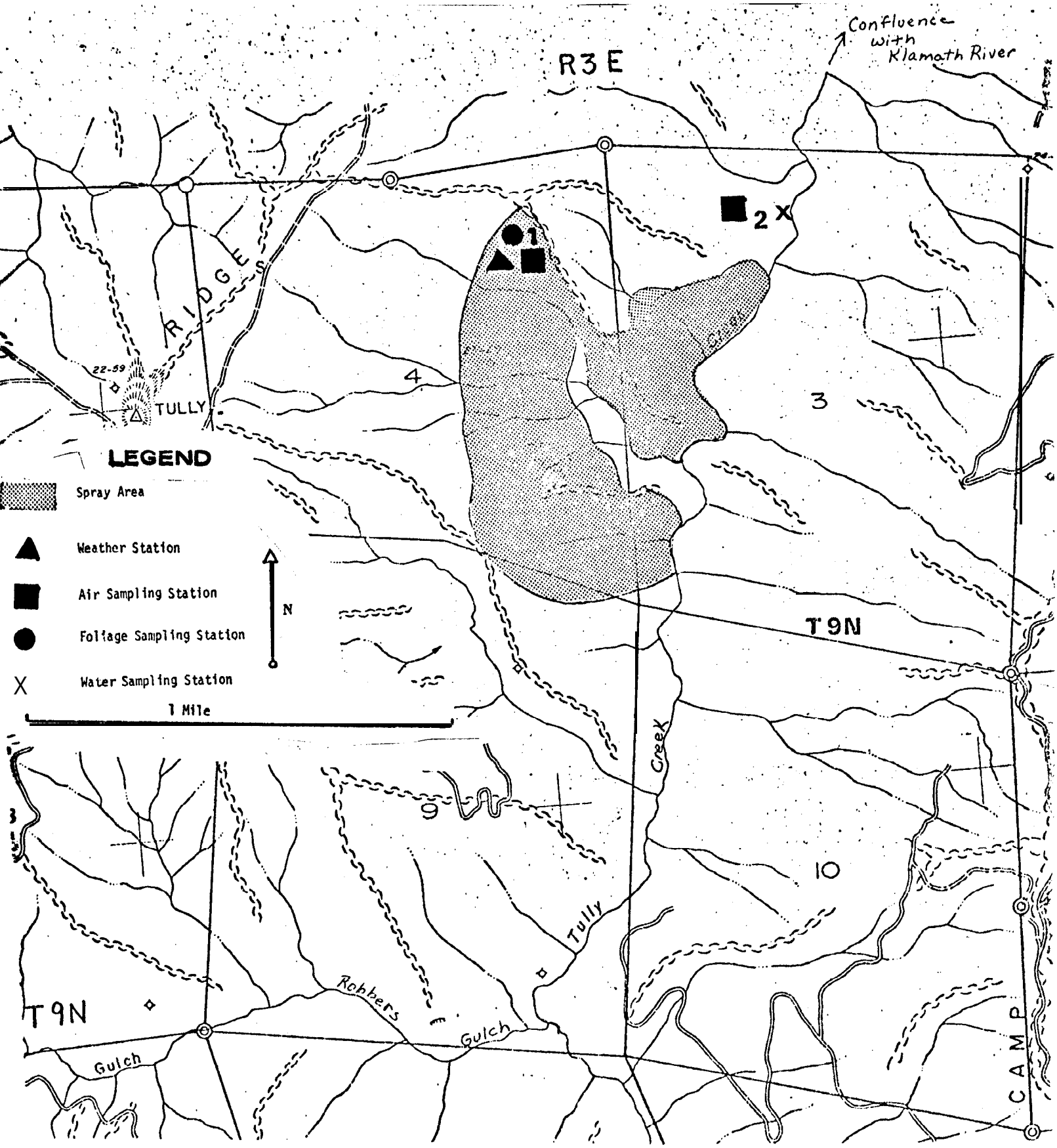

Figure 2. Application site 2 consisting of 2,4-D aerial spraying and monitoring locations.

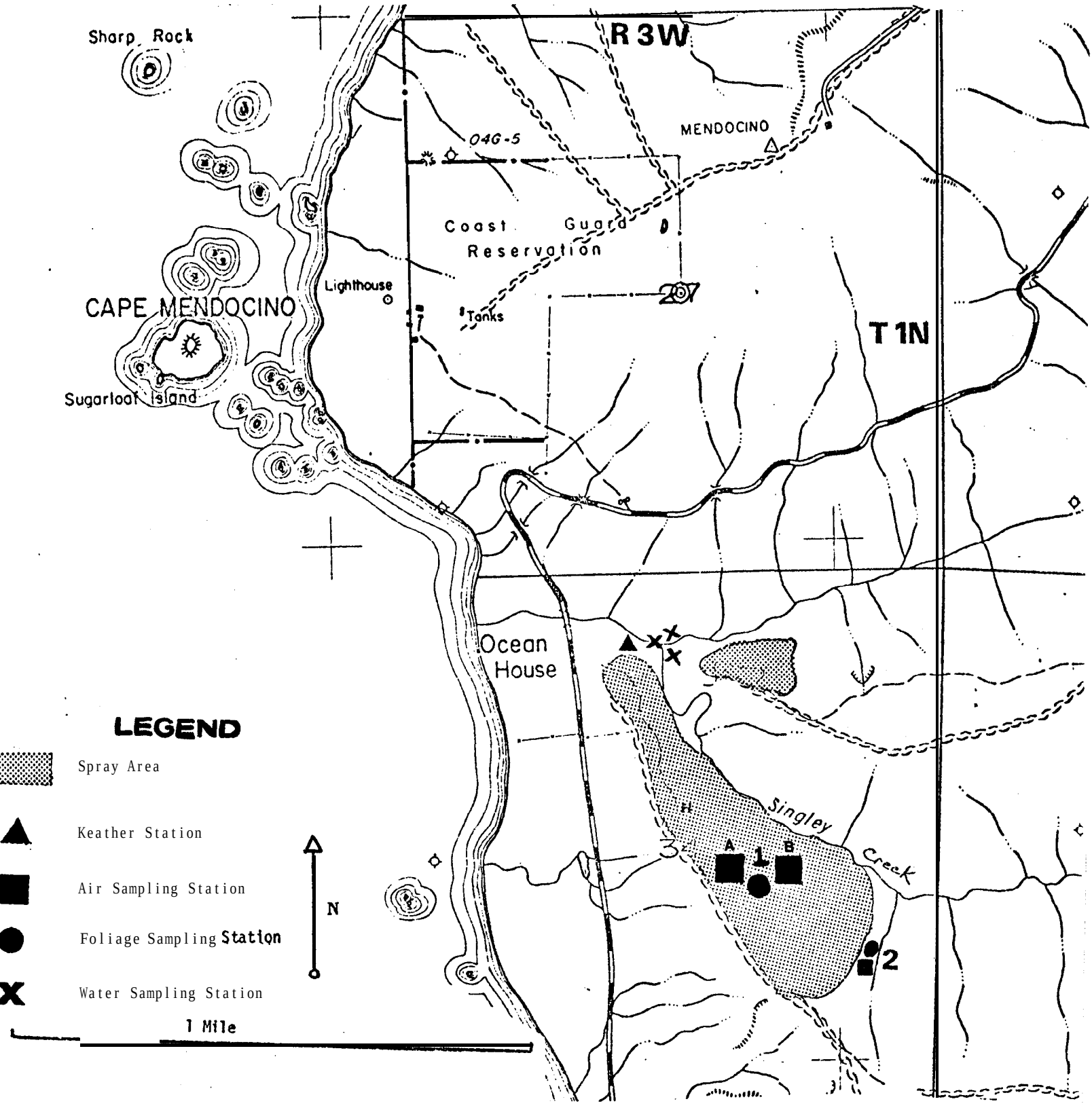

Figure 3. Application site 3 consisting of 2,4-D and 2,4,5-T aerial spraying and monitoring locations.