



# Department of Pesticide Regulation



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## MEMORANDUM

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SUBJECT: PRELIMINARY MONITORING RESULTS OF THE SIXTH AND SEVENTH  
 SPINOSAD AERIAL APPLICATIONS FOR MEXICAN FRUIT FLY  
 ERADICATION IN VALLEY CENTER, SAN DIEGO COUNTY (STUDY 216)

The Department of Pesticide Regulation (DPR) conducted the sixth and seventh monitoring in a series of spinosad aerial applications to eradicate the Mexican fruit fly in Valley Center on March 18-20 and 27-28, 2003. During these two applications, DPR staff collected deposition, surface water, fruit (only for the sixth application), and tank mix (from mixing tanks and aircraft) samples. Deposition samples taken at nine sites ranged from trace amount to 1.43  $\mu\text{g}/\text{ft}^2$  with an average of 0.70  $\mu\text{g}/\text{ft}^2$  spinosad concentration in the sixth application. The average was 22% of the 3.26  $\mu\text{g}/\text{ft}^2$  target application rate, much lower than the 54% average of the previous five applications. Deposition samples were also collected at two sites within the Keys Creek buffer zone and spinosad was below quantifiable levels in these two sites. None of the surface water samples contained detectable spinosad residues. Background fruit samples from one site contained 0.005 to 0.067 parts per billion (ppb) spinosad residues, and none detected (ND) on the other site. Three of the four fruit samples collected after the application contained 0.005 to 0.028 ppb spinosad residues. Six tank mix samples were collected during the sixth application and spinosad concentrations ranged from 0.0079% to 0.0099% which were 97% to 123% of the target concentration (0.0080%). One tank mix sample was collected for the seventh application and concentration was 0.0076%, 95% of the target concentration. No organophosphates, carbamates, and chlorinated hydrocarbons were detected in these samples. However, prior to the sixth application, when all three aircraft were sampled for screening contaminants, one aircraft contained 1.9 to 5.6 ppm of malathion and other contaminants. Therefore, this aircraft was not used during the sixth application, and all contaminated parts were replaced or decontaminated prior to the seventh application.

### Introduction

The California Department of Food and Agriculture (CDFA) is conducting aerial applications with spinosad to eradicate the Mexican fruit fly infestation in the Valley Center area of San Diego County. The application area consists of 28 square miles ( $\text{mi}^2$ ), of which 23  $\text{mi}^2$  are treated using



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aerial applications and five square miles are treated using ground applications. CDFA plans to aerially apply spinosad once every two weeks, and as the temperature increases, reduce the application interval to effectuate eradication. The sixth and seventh applications were conducted two weeks and eight days, respectively, after the previous applications.

Starting with the sixth application, DPR has changed monitoring sites and media. Deposition, surface water, and tank mix samples will be collected for each application. The deposition samples will be reduced from 26 to 11 sites. For even numbered applications (6<sup>th</sup>, 8<sup>th</sup>, 10<sup>th</sup>, etc), all collected samples will be analyzed. For odd numbered applications, tank mix and water samples will be analyzed, but deposition samples will only be analyzed if the tank mix samples show unusual results. Fruit samples and aircraft rinsate samples were collected and analyzed during the sixth application, but will no longer be collected. In addition, composite spinosad concentrate samples will be collected and analyzed prior to each application by the Los Angeles County Department of Agriculture.

### **Materials and Methods**

The pesticide applications were similar to the previous applications, using GF-120 NF Naturalyte Fruit Fly Bait (U.S. Environmental Protection Agency Registration Number 62719-498), containing 0.020% spinosad by weight (mixture of spinosyn A and spinosyn D) as the active ingredient. For application, GF-120 NF was diluted with water to a tank mix target concentration of 0.0080% (by weight) of spinosad or 0.363 grams per gallon. The spinosad target application rate was 3.26  $\mu\text{g}/\text{ft}^2$  (0.005 oz/acre). The application was made using fixed-wing aircraft with a swath width of 100 feet, sprayed in east and west directions at a height of approximately 500 feet. The sixth application was conducted using only two aircraft over two nights on March 18-19. The seventh application was conducted using three aircraft on March 27 at 8:00 p.m. and finished on March 28 at 5:00 a.m. CDFA established buffer zones around several water bodies that are excluded from the aerial application.

Spinosad residues were measured in deposition, surface water, fruit, and spray tank mix samples. Deposition samples were collected using one  $\text{ft}^2$  mass deposition sheets. Deposition sheets were set at nine sampling sites dispersed throughout the treatment area (Figure 1 and 2, attached). In addition, two deposition sites were sampled within the buffer zone around Keys Creek (Figure 1 and 2). The sheets were set at sampling sites before application and collected after each application.

Surface water samples were collected before (background) and after each application. For both background and application, three water samples, two primary and one backup, were taken from Keys Creek (Figure 1 and 2).

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Fruit samples were collected from two orchards (Figure 1). At each sampling site, two grapefruit trees were randomly picked (the same trees are being used for the duration of the treatment program) and two samples were collected, one from the upper and the other from the lower portions of the trees at randomly chosen compass directions. For each sample, two grapefruit were collected from each of the two trees placed into a stainless steel bucket, and covered with a stainless steel lid. Background fruit samples were collected prior to application and application samples were collected 4-5 hours after application.

Prior to the sixth application, rinsate samples were collected on March 12 from the three aircraft used for aerial applications. An organophosphate, carbamate, and chlorinated hydrocarbon screen was performed on these samples due to contamination concerns (Segawa, R., et al. 2003). The rinsate sample from aircraft N7136M was collected as a composite of the five spray nozzles. The samples for aircraft N70Y and N7198Y were collected from the loading valve, due to the inability to prime the spray pumps on these aircraft. Additional samples were collected from the aircraft N7198Y on March 17 due to continued contamination.

For the sixth application, six tank mix samples were collected, two directly from the mixing tanks and four from the two aircraft. The mixing tank samples were collected from the tank loading valves. Each aircraft sample was a composite of five subsamples collected from five nozzles on each aircraft at each application day. For the seventh application, DPR staff collected one tank sample from the mixing tank loading manifold outlet, and Los Angeles County Agriculture Commissioner staff collected samples from the aircraft nozzles.

The samples for deposition, surface water, and fruit were stored on dry ice; surface water duplicates and tank mix samples were stored on ice until delivery to the CDFA Center for Analytical Chemistry for analysis. All samples were analyzed for spinosyns A and D, as well as the breakdown product spinosyn B. The deposition samples were extracted with methanol and analyzed using a liquid chromatograph with a tandem mass spectrometer detector (LC/MS/MS), providing a reporting limit of 0.1  $\mu\text{g}/\text{ft}^2$ . The water samples were extracted with methylene chloride and analyzed using LC/MS/MS, providing a reporting limit of 0.05 ppb. Grapefruit samples were extracted with acetonitrile and water, and analyzed using LC/MS/MS providing a reporting limit of 1 ppb. Outer-surface of fruit and inner surface of sample containers were rinsed with methanol and analyzed using LC/MS/MS providing a reporting limit of approximately 0.0037 ppb (ng/g fruit). The tank mix sample was extracted with acetone and analyzed using a high-performance liquid chromatograph and ultraviolet detector, providing a reporting limit of one ppm (0.0001%). The tank mixture sample was also screened for organophosphates, carbamates, and chlorinated hydrocarbons.

## Results

Deposition samples for the sixth application contained trace amount to  $1.425 \mu\text{g}/\text{ft}^2$  (Table 1, attached). Average concentration was  $0.70 \mu\text{g}/\text{ft}^2$ , 22% of the  $3.26 \mu\text{g}/\text{ft}^2$  target application rate. This result was much lower than the 54% average of the previous five applications (Figure 3, attached). The deposition samples were collected between 4:36 and 7:03 am on March 19 and 20, and four samples were collected in direct sunlight, after sunrise.

None of buffer zone deposition samples contained quantifiable amount and one was detected trace amount of spinosad (Table 2, attached). For all previous five applications, quantifiable amounts of spinosad were detected in buffer zone samples.

Spinosad was not detected in any of the surface water samples collected during the six and seventh applications. These results were the same as the previous five applications.

Background fruit samples collected from one orchard contained no detectable spinosad residue and those from the other orchard contained 0.067 and 0.005 ppb (ng/g) on the upper and lower portions, respectively, of the sampled trees. Three of the four fruit samples collected after application contained 0.005 to 0.028 ppb spinosad residues (Table 3, attached). These results were comparable to those in the previous applications. The grapefruit samples collected for this application were not mature and, therefore, are unsuitable for determining legal compliance with the tolerance, although all application samples were less than the 300 ppb tolerance level for mature fruit.

Rinsate samples from aircraft N70U and N7136M showed no detectable organophosphate, carbamate, or chlorinated hydrocarbon pesticides. Malathion, d-phenothrin and piperonyl butoxide residues were found in aircraft N7198Y at the following concentrations: malathion 1.9-6.1 ppm, d-phenothrin 1.7-4.6 ppm and piperonyl butoxide 8.4-22 ppm (Table 4, attached). Aircraft N7198Y was not used in the sixth application, and was decontaminated prior to the seventh application.

The tank mix samples collected for the sixth application contained 0.0079% to 0.0099% , spinosad, which were 97% to 123% of target concentration, 0.0080% (Table 5, attached). The tank sample concentration for the seventh application was 0.0076%, 95% of the target concentration (Table 5). In the sixth and seventh applications, 5860 and 5852 gallons of spinosad mix were applied over 15001 and 14981 acres for a nominal application rate of  $3.26 \mu\text{g}/\text{ft}^2$  and  $3.26 \mu\text{g}/\text{ft}^2$ , respectively. These were 100% of the target application rate assuming the tank mix contained the target concentration. Screening tests showed no detectable organophosphate, carbamate, or chlorinated hydrocarbon pesticides in the application tank mix/load samples.

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The sixth application occurred on two clear nights with temperature 35-47° F, relative humidity 75-97%, and wind speed 0-1 miles per hour (mph). The seventh application also occurred during a clear night with temperature 48-63° F. Before midnight, wind speed was 0-1 mph and relative humidity 83-94%. However, at the turning into a new day, the wind speed increased to 4 mph for three hours and relative humidity dropped to 18-28%. Between 3:00-5:00 a.m. on March 28, the wind speed was up to 10-12 mph and relative humidity down to 15-16% (<<http://cdec.water.ca.gov/queryCSV.html>>). Results reported here are also available at DPR's Web site at <<http://www.cdpr.ca.gov/docs/mexfly/>>.

### **References**

Segawa, R., D. Kim, P. Wofford. 2003. Malathion Contamination in the Spray Material Used For Mexican Fruit Fly Eradication in Valley Center, San Diego County. Memo to John Sanders. California Environmental Protection Agency, Department of Pesticide Regulation, Environmental Monitoring Branch, Sacramento, California.

<<http://cdec.water.ca.gov/queryCSV.html>>. California Department of Water Resources, Division of Flood Management, Sacramento, California.

Attachments

bcc: Fan Surname File (w/Attachments)

Table 1. Monitoring results for deposition samples. The amount of spinosad is sum of the individual spinosyns (A, D, and B). The target amount is 3.26  $\mu\text{g}/\text{ft}^2$ .

Site Code	Spinosad ( $\mu\text{g}/\text{ft}^2$ )		
	Application Day 1	Application Day 2	Sum of Two Days
1	0.202 <sup>a</sup>	0.455	0.657
3	Tr <sup>b</sup>	0.655	0.709
4	0.657	Tr	0.711
7	1.425	Not Sampled	1.425
13	ND <sup>c</sup>	0.475	0.475
15	Tr	Not Sampled	Tr
17	1.169	Not Sampled	1.169
19	Tr	0.430	0.484
25	0.295	0.328	0.623
<b>Average</b>	<b>0.434</b>	<b>0.400</b>	<b>0.701</b>
<b>Std. Dev.</b>	<b>0.532</b>	<b>0.200</b>	<b>0.398</b>
<b>Std. Error</b>	<b>0.177</b>	<b>0.067</b>	<b>0.085</b>
<b>Minimum</b>	<b>ND</b>	<b>Tr</b>	<b>0.054</b>
<b>Maximum</b>	<b>1.425</b>	<b>0.655</b>	<b>1.425</b>

<sup>a</sup> Sum of detected spinosyns (A, D, and B), wherever none detected (less than a detection limit of 0.008, 0.020, and 0.028  $\mu\text{g}/\text{ft}^2$  for spinosyn A, D, and B, respectively) the quantity of 0  $\mu\text{g}/\text{ft}^2$  was used, and wherever trace amount (less than a reporting limit 0.1  $\mu\text{g}/\text{ft}^2$  for each individual spinosyn A, D, and B) was detected, the quantity of (reporting limit + detection limit)/2  $\mu\text{g}/\text{ft}^2$  was used to calculate the sum of spinosyns in this report.

<sup>b</sup> Trace amount was detected.

<sup>c</sup> None detected.

Table 2. Monitoring results for buffer zone deposition samples. The amount of spinosad is sum of the individual spinosyns (A, D, and B).

Site Code	Spinosad ( $\mu\text{g}/\text{ft}^2$ )		
	Application Day 1	Application Day 2	Sum of Two Days
12	Tr <sup>a</sup>	ND <sup>b</sup>	Tr
24	ND	ND	ND

<sup>a</sup> Trace amount (less than a reporting limit 0.1  $\mu\text{g}/\text{ft}^2$  for each individual spinosyn A, D, and B) was detected.

<sup>b</sup> None detected with a detection limit of 0.008, 0.020, and 0.028  $\mu\text{g}/\text{ft}^2$  for spinosyn A, D, and B, respectively.

Table 3. Monitoring results for fruit samples. The spinosad is sum of spinosyns (A, D, and B)

Site Code	Sampling Portion	Spinosad (ppb)	
		Background	Application
3	Upper	0.067 <sup>a</sup>	0.028
3	Lower	0.005	0.005
27	Upper	ND <sup>b</sup>	0.006
27	Lower	ND	ND

<sup>a</sup> Sum of detected spinosyns in fruit and rinse of fruit and container, wherever trace amount was detected in the rinse, the quantity of half reporting limit was used to calculate the sum in this report.

<sup>b</sup> None Detected, with a detection limit for fruit samples at 0.903, 0.716, and 0.959 ppb spinosyn A, D, and B, respectively, and a reporting limit at 0.0037 ppb for rinse of fruit and container. Detection limit for rinse was not available.

Table 4. Monitoring results for aircraft rinsate samples.

Sampling Location (Date)	Malathion (ppm)	d-Phenothrin (ppm)	Piperonyl Butoxide (ppm)
Aircraft N70U <sup>a</sup> (3/12)	ND	ND	ND
Aircraft N7136M <sup>b</sup> (3/12)	ND	ND	ND
Aircraft N7198Y <sup>a</sup> (3/12)	1.9	2.8	8.4
Aircraft N7198Y <sup>a</sup> (3/17)	4.1	1.7	12
Aircraft N7198Y <sup>b</sup> (3/17)	6.1	4.6	22

<sup>a</sup> Sample collected from aircraft loading valve.

<sup>b</sup> Composite sample collected from 5 spray nozzles.

Table 5. Monitoring results for tank samples. The amount of total spinosad is sum of the individual spinosyns (A, D, and B). The target tank mix concentration is 0.008%.

Sampling Location (Date)	Spinosad (%)	% of Target
<b>sixth application:</b>		
Tank 1 (3/18)	0.0078	97
Tank 2 (3/18)	0.0099	123
Aircraft N70U <sup>a</sup> (3/18)	0.0079	98
Aircraft N70U <sup>b</sup> (3/19)	0.0080	99
Aircraft N7136M <sup>a</sup> (3/18)	0.0080	100
Aircraft N7136M <sup>b</sup> (3/19)	0.0080	100
<b>seventh application:</b>		
loading manifold <sup>a</sup> (3/27)	0.0076	95

<sup>a</sup> Aircraft and manifold loaded from tank 1.

<sup>b</sup> Aircraft loaded from tank 2.

Figure 1. Sampling sites for the sixth aerial spinosad application (March 18-19 and 19-20, 2003)

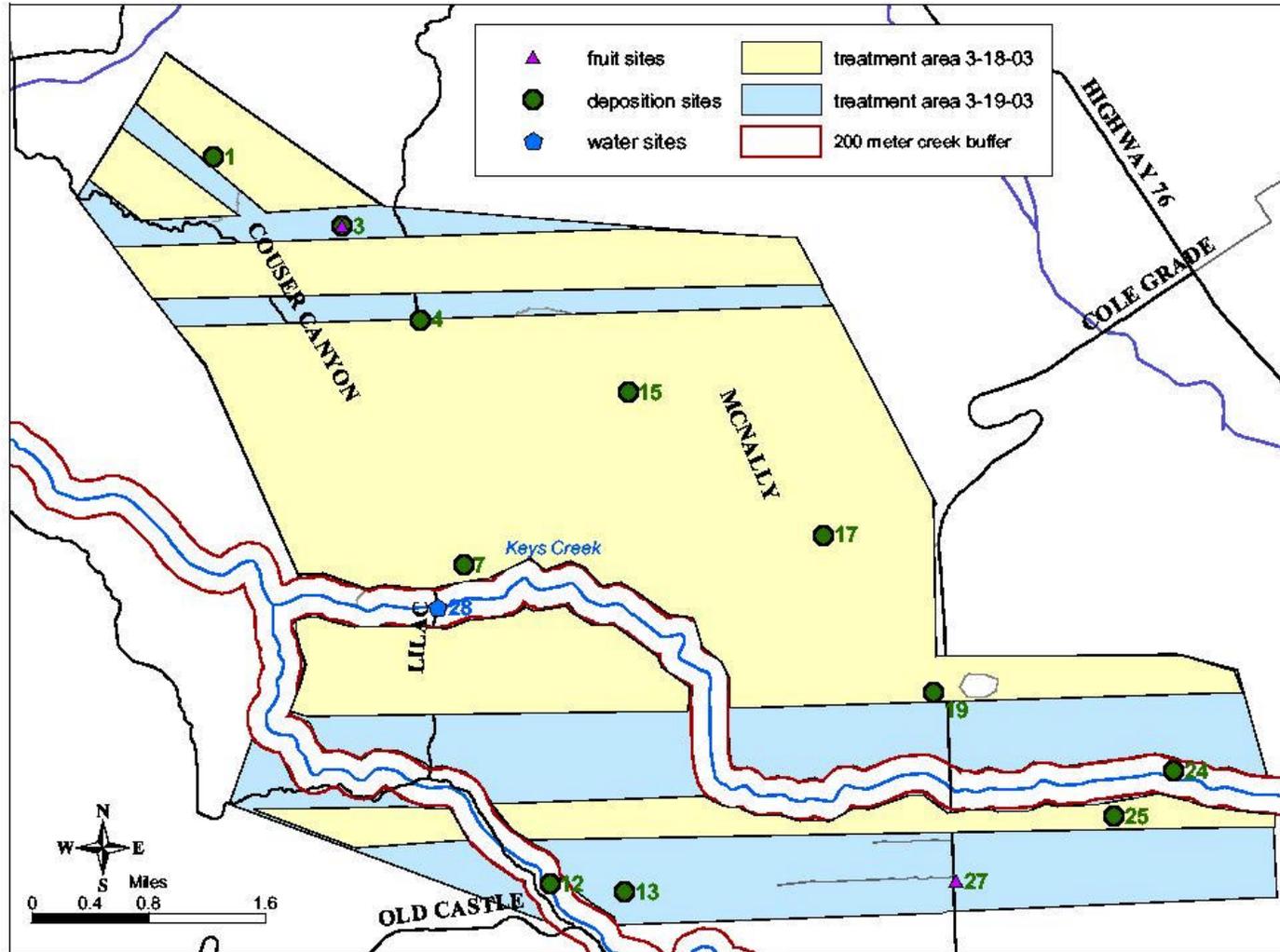


Figure 2. Sampling sites for the seventh aerial spinosad application  
(March 27-28, 2003)

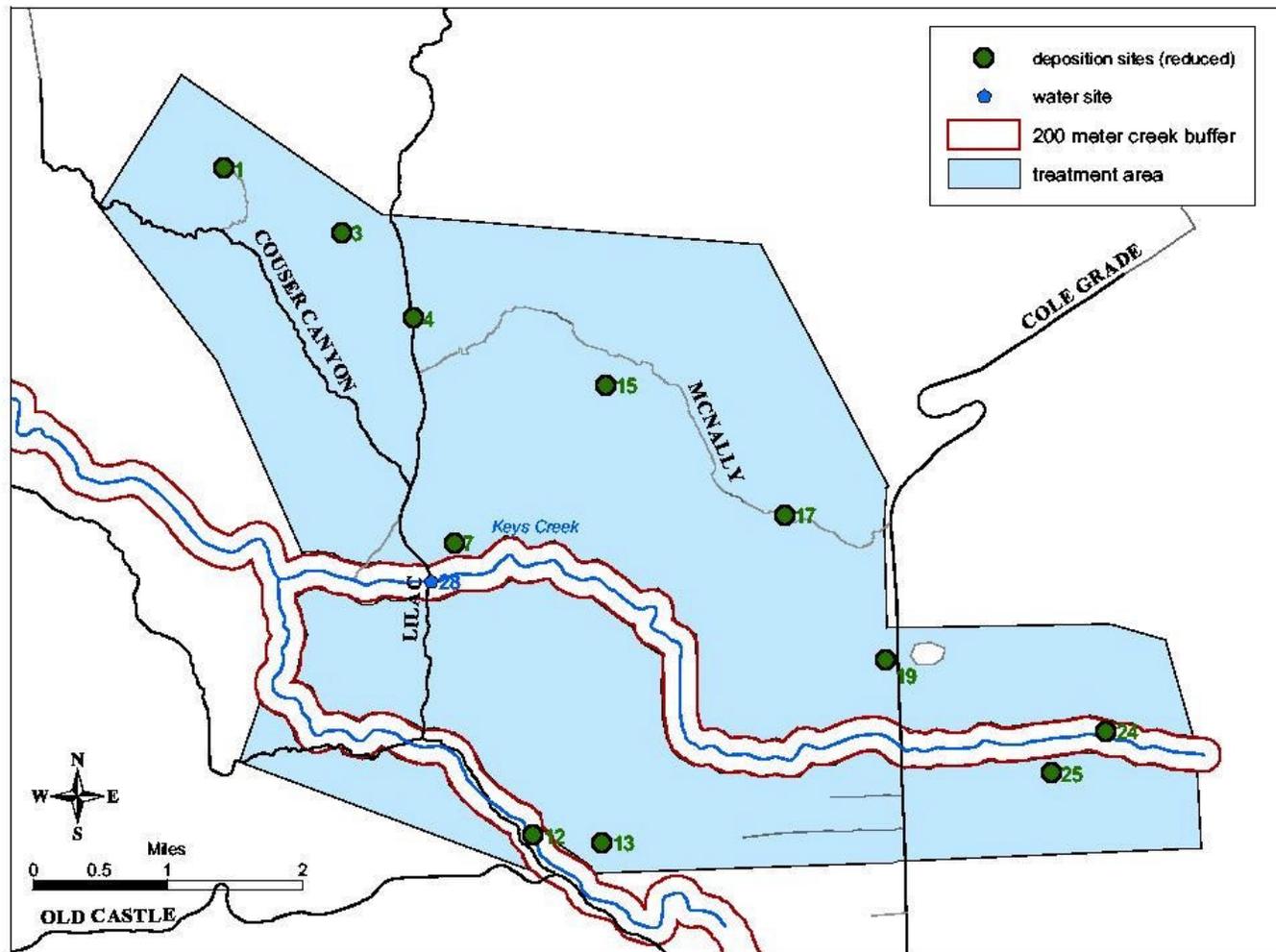


Figure 3. Comparison of average ( $\pm 1$  standard error) deposition spinosad.

