Cranberry Sampling for Anvil 10+10
Southeastern Massachusetts

March 2011

Massachusetts Department of Public Health
Bureau of Environmental Health
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Boston, Massachusetts 02108

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I. BACKGROUND AND STATEMENT OF ISSUES

In response to a public health threat from mosquitoes carrying Eastern equine encephalitis virus (EEE), Massachusetts moved forward with wide-area aerial pesticide application (ultra-low volume, or ULV) in parts of southeastern Massachusetts where numerous cranberry bogs are located. Aerial applications were conducted the nights of August 5 – 7, 2010. The active ingredient of the pesticide used (Anvil 10+10; EPA registration #1021-1688-8329) is sumithrin, a synthetic pyrethroid compound, which has a federal food tolerance of 0.01 ppm (US EPA, 2008a, b, c). Thus, the Massachusetts Department of Public Health (MDPH) undertook a sampling and analysis effort to ensure that sumithrin residues, if any, would not exceed the food tolerance. This report presents the results of cranberry testing before and after the aerial application of pesticides over southeastern Massachusetts.

II. METHODS

MDPH/BEH Environmental Toxicology Program (ETP) developed a sampling and analysis plan and coordinated with the Cape Cod Cranberry Growers Association (CCCGA) to conduct the sampling of selected bogs in southeastern Massachusetts. Sampling of cranberries was conducted both before (August 4) and after (August 10) the aerial application on August 5-7, 2010 (application occurred from approximately 7:50 PM to 3:00 AM each day). Cranberries from a control bog (i.e., not geographically near or beneath the area sprayed with Anvil 10+10 aerially for mosquito control) and from six bogs beneath the spray area (before and after spraying) were collected.

Sample Locations

MDPH/BEH worked with representatives of the CCCGA to identify cranberry bogs located within the aerial application zone (see Figure 1), as well as one bog located outside of the application zone to serve as a control or background. In addition to sampling at the control bog, six different cranberry bogs throughout the aerial application zone were identified for sampling. The locations of these bogs were as follows (note, location code in parenthesis):

1. Pickens Street, Lakeville (HBB)
2. West Grove Street, Middleborough (WG)
3. Ward Street, Carver (WARD)
4. Federal Furnace Road, Carver (duplicate sample collected here) (FF; FFDUP)
5. Purchase Street, Middleborough (PUR)
6. Main Street at Pleasant Street, Plympton (HAR)
7. Long Neck Road at Every Road, Wareham (control) (PISC)

Figure 2 depicts the general locations of the selected bogs. At the time of sampling, the cranberry crop was not ripe and was not expected to be ready for harvesting for at least another month or more.

Sampling Procedure

Each bog, including the control, was sampled in the same overall manner. Five separate sample jars (subsamples) were collected from each bog from approximately the four corners of the bog and the center. Field sample jars were 500 mL in capacity, amber glass, precleaned and certified clean from the manufacturer. Amber (dark) colored bottles were selected because the target analyte (sumithrin) is known to be sensitive to photodegradation. The subsamples from each bog were composited (mixed) in the analytical laboratory, Golden Pacific Laboratories, LLC (GPL), before analysis resulting in a single representative sample from each bog. Therefore, a total of 2500 mL (1 composite sample) of cranberries was collected from each bog. This same protocol was used for pre- and post-spray sampling, including duplicate and control samples (i.e., a grand total of 16 composite samples for the study, including field duplicates).

Three teams conducted the sampling both pre- and post-spray in order to reach all the required geographical areas in a timely manner. For the pre-spray sampling, each team consisted of one member of the CCCGA and two staff from MDPH/BEH. The post-spray sampling was conducted with one member of the CCCGA and one or two members of MDPH/BEH staff. The cranberries were harvested from the bogs by the members of the CCCGA because of their familiarity with the activity. Cranberries were removed using a traditional cranberry harvesting tool composed of metal and wood in the form of a scoop with teeth (see Figure 3).

The amount of product for typically filling one jar was scooped from the bog by the CCCGA member. The cranberries were then transferred to the glass jar (see Figure 4). Only cranberries were collected in each jar; sticks, vines and other non-cranberry material was excluded to the extent feasible. Each jar was filled to the top, but not packed.

Once they were filled and sealed with the lid, each jar was labeled with the name and code for the bog and the date and time of collection. The same information, along with details about the location of the bog, the locations for the individual samples, and other notes, were collected on a sampling log sheet. Filled jars were placed in a cooler with ice packs.

At one location, Federal Furnace Road in Carver as indicated above, a duplicate sample was collected in the same manner as the original samples. Duplicate samples are used to assess the variability in analytical results that originate in the sampling technique or heterogeneity in the bulk material as present in the field. It is a standard quality control practice to collect and analyze duplicate samples for a percentage of sampling sites.

For the purposes of QA/QC transit control samples (i.e. field blanks consisting of empty, untreated sample containers) were brought along during each sampling round, one in each sample collection cooler (a total of 4 transit controls per round). The control location in Wareham (outside of spray area) was used to prepare laboratory controls and quality control samples.

No specific decontamination procedures were used for the sampling tools; however, the control bog located in Wareham was sampled before the other bogs that team sampled to reduce the potential for cross contamination from the tools used.

Sample Handling and Shipping

Samples were held in the coolers with ice until they were delivered later the same day to the MDPH State Laboratory Institute (SLI) in Jamaica Plain for temporary storage and shipment. At the SLI, the samples were logged in by staff and refrigerated. Samples were kept overnight under refrigeration and then repackaged for shipment to the analytical laboratory, GPL, in Fresno, CA, the following day. Samples sent to GPL were packaged with dry ice and sent via UPS next morning service. Transit control samples were labeled and shipped with the study samples for analysis. The samples were received the next morning as expected for each of the two sampling events. Chain of custody forms were used to transmit the samples to GPL. Once at GPL, the cranberry samples were kept stored under refrigeration until they were used for analysis.

Sample Analysis

Analysis of cranberries was conducted in accordance with EPA, FIFRA, Good Laboratory Practice Standards (GLP); 40 CFR, Part 160 (October, 1989). The analysis of sumithrin on cranberries was previously validated by GPL in study 060242 (2006a, b; MDPH/BEH 2007). The analytical method measured sumithrin using liquid chromatography tandem mass spectrometry (LC-MS/MS). The established limit of quantitation (LOQ) is 10 ppb and the limit of detection (LOD) is 2.0 ppb.

The handling and analysis of samples at GPL was conducted in accordance with the written protocol from the laboratory. All analyses were performed in accordance with all Standard Operating Procedures (SOPs) for the lab and all deviations from SOPs were documented by the laboratory and described in the report they prepared for MDPH/BEH (2006a).

III. RESULTS

Results of all analyses of cranberries for sumithrin revealed no detectable levels of sumithrin in any sample, whether taken prior to the aerial application event or after the event (see Tables 1 and 2, respectively) (Golden Pacific Laboratories, 2010). The

laboratory reported the Limit of Detection (LOD) was 2 parts per billion (ppb). A LOD is defined as the lowest detectable limit on a given instrument for a given analysis. The limit of quantitation (LOQ) for the analysis was 10 ppb. The LOQ is defined as the lowest validated level established during method validation. In addition, the methods developed for the analysis of cranberries for sumithrin residues were successful under the quality assurance and quality control procedures used at the laboratory and were documented in a separate Good Laboratory Practices report to be produced by Golden Pacific Laboratories.

IV. DISCUSSION

Results from the testing of cranberries for sumithrin, an active ingredient of the pesticide used for aerial application in southeastern Massachusetts showed no detectable levels of this compound in any cranberry sample, either pre- or post-application (ND = 0.002 ppm), meaning no exceedances of the federal food tolerance for sumithrin residues (0.01 ppm) on cranberries. The post-application samples were taken approximately 48 – 72 hours after the final application and hence, it is not expected that future applications of this pesticide will result in residues.

V. CONCLUSIONS

Since no measureable residues of sumithrin were detected in any of the cranberry samples, the consumption of cranberries harvested from bogs located in the spray area would not be expected to pose health concerns. MDPH concludes no exposure opportunities of health concern related to consumption of cranberries are present.

VI. RECOMMENDATIONS

The results of the cranberry sampling did not reveal the presence of sumithrin, hence, no specific recommendations or follow-up activities are recommended at this time.

Copies of this report will be provided to the Massachusetts Department of Agricultural Resources, the Cape Cod Cranberry Growers Association, and other interested parties.

VIII. REFERENCES

Golden Pacific Laboratories, LLC. 2006a. Analytical phase report: Determination of residues of sumithrin in cranberry samples, GPL study number 060242. Fresno, CA.

Golden Pacific Laboratories, LLC. 2006b. Study protocol: Determination of residues of sumithrin in cranberry samples, GPL study number 060242. Fresno, CA.

Golden Pacific Laboratories, LLC. 2010. Analytical phase report: Determination of residues of sumithrin in cranberry samples, GPL study number 100358. Fresno, CA.

Massachusetts Department of Public Health, Bureau of Environmental Health (MDPH/BEH). 2007. Health consultation: Cranberry sampling for Anvil 10+10, southeastern Massachusetts. Prepared by MDPH/BEH under a cooperative agreement with the federal Agency for Toxic Substances and Disease Registry (ATSDR), U.S. Department of Health and Human Services (US DHHS), Atlanta, GA: March 9, 2007.

United States Environmental Protection Agency (US EPA). 2008a. Memorandum: d-Phenothrin (Sumithrin®) Acute and Chronic Dietary and Drinking Water Exposure and Risk Assessment for the Reregistration Eligibility Decision (RED) and Petition PP# 7F7251 and Associated Section 3 Registration Action. US EPA Office of Prevention, Pesticides, and Toxic Substances, February 6, 2008.

United States Environmental Protection Agency (US EPA). 2008b. Memorandum: d-Phenothrin (Sumithrin®) Reregistration Eligibility Decision (RED) Document PC Code No. 069005; DP Barcode No. 326933 and Petition PP# 7F7251 and Associated Section 3 Registration Action. US EPA Office of Prevention, Pesticides, and Toxic Substances, February 6, 2008.

United States Environmental Protection Agency (US EPA). 2008c. Reregistration eligibility decision for d-Phenothrin. US EPA Office of Prevention, Pesticides, and Toxic Substances, September 25, 2008.

APPENDIX

Figures and Tables

Figure 1: Geographic extent of August 5 – 7, 2010 aerial application, Bristol and Plymouth Counties, MA

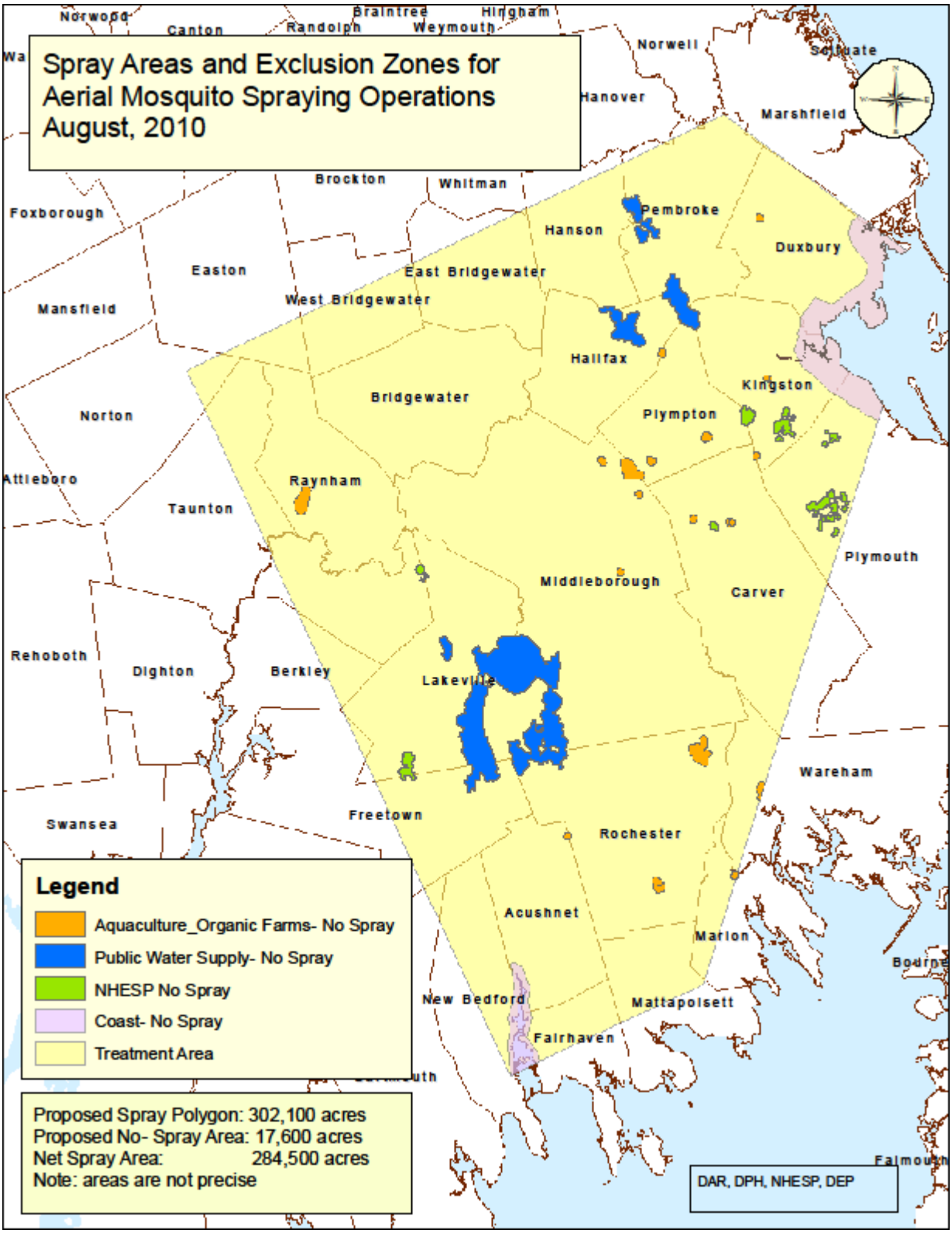

Figure 2: Geographic extent of August 5 – 7, 2010 aerial application with approximate bog sampling locations, Bristol and Plymouth counties, MA

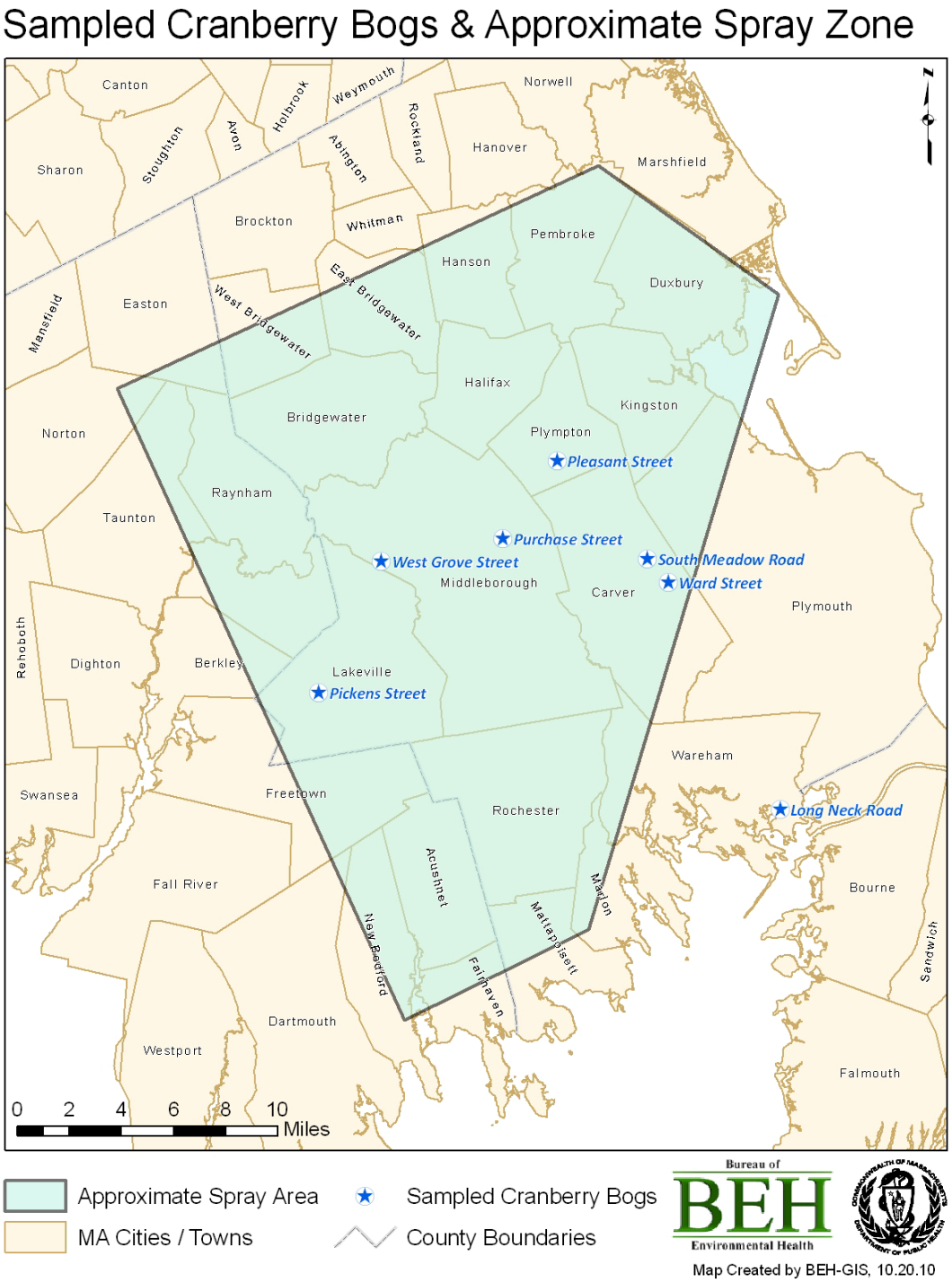

Figure 3: Cranberry Harvesting/Sampling Tool

Figure 4: Procedure for filling sample collection jar

Table 1: Results of pre-spray samples collected on August 4, 2010

Table 1 of 1

Summary of Analytical Results of Sumithrin Residue in Cranberries and Transit Containers

GPL Study # 100358 Sponsor Study # NA

Date Printed: 9/17/2010

Prepared By:

Extraction Set: 358SET01

Analysis Set: 358SET01

Extraction Date: 8/18/2010

Analysis Date: 8/18/2010

Injection Volume: 10 µL

Standard Injections: **Sumithrin**

Standard ID	Standard Amount (ng/ml)	Peak Area	Back Calc of Standard (ng/ml)	RPD
981-9	0.250	2566.4	0.273	8.80
981-8	0.500	5827.8	0.529	5.64
981-7	1.00	11205.1	0.951	5.02
981-6	2.00	22158.9	1.81	9.97
981-5	5.00	59578.6	4.74	5.34
981-4	10.0	132270.3	10.4	3.92

Curve Equation: $y = ax + b$
where y is response in peak area units
and x is concentration in ng/ml (1/x weighting)

$a = 1.28 \times 10^6$

$b = -919$

Coefficient of Determination (r^2): 0.9960

Correlation Coefficient (r): 0.9980

NA = Not applicable

LOQ = Limit of Quantitation

ND = Not Detected

RPD = Relative Percent Difference

where, $RPD = \frac{|\text{Std Back calc} - \text{Std Amount}| \times 2 \times 100}{(\text{Std Back calc} + \text{Std Amount})}$

Sample Information:

Cranberries Lab ID	Sample ID	Sample Amount (g)	Final Volume (ml)	Peak Area	Concentration from Curve (ng/ml)	Sample Concentration[1] (ppb)	Fortification Amount (ppb)	Percent Recovery[2] (%)
358SET01-1	Control (P1SC1 Composite)	10.00	130	0.0	<0.250	ND	NA	NA
358SET01-2	Low Spike (0.01 ppm)	10.01	130	7686.4	0.675	8.77	9.99	87.8
358SET01-3	High Spike (0.1 ppm)	9.98	1300	7930.3	0.694	90.4	100	90.4
358SET01-4	PUR1 Composite	10.03	130	0.0	<0.250	ND	NA	NA
358SET01-5	FF1 Composite	9.99	130	0.0	<0.250	ND	NA	NA
358SET01-6	FFDUP1 Composite	9.99	130	0.0	<0.250	ND	NA	NA
358SET01-7	HAR1 Composite	10.02	130	0.0	<0.250	ND	NA	NA
358SET01-8	WARD1 Composite	10.01	130	0.0	<0.250	ND	NA	NA
358SET01-9	HBB1 Composite	10.01	130	0.0	<0.250	ND	NA	NA
358SET01-10	WG1 Composite	10.01	130	0.0	<0.250	ND	NA	NA

Transit Control Conatainers Lab ID	Sample ID	Sample Amount (container)	Final Volume (ml)	Peak Area	Concentration from Curve (ng/ml)	Sample Concentration[3] (ng/container)
358SET01-11	FB1smTm1	1	130	0.0	<0.250	ND
358SET01-12	FB1WhTm2	1	130	0.0	<0.250	ND
358SET01-13	FB1Blue Tm1	1	130	0.0	<0.250	ND
358SET01-14	FBBlueTm3	1	130	0.0	<0.250	ND

[1] Sample Conc. in ppb = (Conc. from curve in ng/ml x Final Volume in ml) ÷ (Sample Amount (g)).

[2] Percent Recovery (%) = Sample Concentration in ppb ÷ Fortification Amount in ppb x 100.

[3] Sample Conc. in ng/container = Conc. from curve in ng/ml x Final Volume in ml x Sample Amount

Cranberries LOQ = 10 ppb, LOD = 2.0 ppb; Transit Control Containers LOD 32.5 ng/container

Note: Sample Concentration, Percent Recovery and RPD values are calculated by Excel. All other calculations are performed by Analyst v. 1.4.2 These values are rounded to three significant figures and transcribed to the Excel spreadsheet.

Table 2: Results of post-spray samples collected on August 10, 2010

Table 1 of 1
Summary of Analytical Results of Sumithrin Residue in Cranberries and Transit Containers
GPL Study # 100358 Sponsor Study # NA

Date Printed: 9/17/2010
Prepared By:

Extraction Set: 358SET02
Analysis Set: 358SET02
Extraction Date: 8/23/2010
Analysis Date: 8/23/2010
Injection Volume: 10 µL

Standard Injections: Sumithrin

Standard ID	Standard Amount (ng/ml)	Peak Area	Back Calc of Standard (ng/ml)	RPD
981-9	0.250	1875.4	0.242	3.25
981-8	0.500	4437.0	0.523	4.50
981-7	1.00	8884.9	1.01	0.995
981-6	2.00	17468.6	1.96	2.02
981-5	5.00	44861.9	4.97	0.602
981-4	10.0	91163.5	10.1	0.995

Curve Equation: y = ax + b
where y is response in peak area units
and x is concentration in ng/ml (1/x weighting)
a= 9.1×10^{3}
b= -323
Coefficient of Determination (r^2): 0.9998
Correlation Coefficient (r): 0.9999

NA = Not applicable
LOQ = Limit of Quantitation
ND = Not Detected

RPD = Relative Percent Difference
where, RPD = $\frac{|\text{Std Back calc - Std Amount}| \times 2 \times 100}{(\text{Std Back calc + Std Amount})}$

Sample Information:

Lab ID	Sample ID	Sample Amount (g)	Final Volume (ml)	Peak Area	Concentration from Curve (ng/ml)	Sample Concentration[1] (ppm)	Fortification Amount (ppm)	Percent Recovery[2] (%)
358SET02-1	Control (PISC2 Composite)	10.03	130	0.0	<0.250	ND	NA	NA
358SET02-2	Low Spike (0.01 ppm)	9.99	130	5866.7	0.680	8.85	10.0	88.5
358SET02-3	High Spike (0.1 ppm)	10.03	1300	6561.8	0.757	98.1	99.7	98.4
358SET02-4	PUR2 Composite	10.02	130	0.0	<0.250	ND	NA	NA
358SET02-5	FF2 Composite	9.96	130	0.0	<0.250	ND	NA	NA
358SET02-6	FFDUP2 Composite	10.00	130	0.0	<0.250	ND	NA	NA
358SET02-7	HAR2 Composite	10.00	130	0.0	<0.250	ND	NA	NA
358SET02-8	WARD2 Composite	9.97	130	0.0	<0.250	ND	NA	NA
358SET02-9	HBB2 Composite	10.00	130	0.0	<0.250	ND	NA	NA
358SET02-10	WG2 Composite	9.99	130	0.0	<0.250	ND	NA	NA

Transit Control Constainers						
Lab ID	Sample ID	Sample Amount (container)	Final Volume (ml)	Peak Area	Concentration from Curve (ng/ml)	Sample Concentration[3] (ng/container)
358SET02-11	FB2umTm1	1	130	0.0	<0.250	ND
358SET02-12	FB2WhTm2	1	130	0.0	<0.250	ND
358SET02-13	FB2Blue Tm1	1	130	0.0	<0.250	ND
358SET02-14	FB2BlueTm3	1	130	0.0	<0.250	ND

[1] Sample Conc. in ppb = (Conc. from curve in ng/ml x Final Volume in ml) ÷ (Sample Amount (g)).
[2] Percent Recovery (%) = Sample Concentration in ppb ÷ Fortification Amount in ppb x 100.
[3] Sample Conc. in ng/container = Conc. from curve in ng/ml x Final Volume in ml x Sample Amount
Cranberries LOQ = 10 ppb, LOD = 2.0 ppb; Transit Control Containers LOD 32.5 ng/container
Note: Sample Concentration, Percent Recovery and RPD values are calculated by Excel. All other calculations are performed by Analyst v. 1.4.2