EVALUATION OF AIRBORNE HERBICIDE MOVEMENT TO WINE GRAPE VINEYARDS IN THE WALLA WALLA VALLEY OF WASHINGTON STATE

By

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To the Faculty of Washington State University:

The members of the Committee appointed to examine the thesis of Kenneth F. Holshue find it satisfactory and recommend that it be accepted.

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Chair

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Abstract

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The amine salt and ester formulations of 2,4-dichlorophenoxy acetic acid (2,4-D) are dominant pre-emergent broadleaf herbicides for various cereal and minor crop production in the Pacific Northwest. Unfortunately, wine grape vineyards in proximity to production-cereal-grain fields have traditionally experienced vine injury ranging from mild to near-complete yield loss. The assumption that observed injury to wine grape vineyards is caused strictly by local off-target movement of 2,4-D has given way to the idea that this observed injury may in fact be due to off-target movement of 2,4-D from fields miles away from the wine grape vineyard. Previous studies suggest that directional long-range atmospheric transport of phenoxy herbicide formulations can occur, affecting wine grape vineyards at a time when the plants can be most susceptible to injury and yield reduction. To characterize herbicide movements that could adversely affect the Walla Walla Valley wine-grape producing region of Walla Walla County, Washington, and Umatilla County, Oregon, ambient air and both dry and wet deposition samples were collected between April 10, 2003, and June 27, 2003. During this time, wine grapes are most susceptible to injury by the off-target aerial movement of phenoxy herbicides. The majority of the air samples at the six vineyard locations contained 2,4-D. Representative leaves were

observed on three vines at each study site. A mean leaf injury index was modified for rating the severity of phenoxy-type injury on each observed leaf. The data suggests that 2,4-D damage to grape leaves existed within the study area, and that the damage is uniform throughout the study area. Thus, there existed low level 2,4-D concentrations in the ambient air of the study area, which caused low levels of grape leaf damage uniformly across the study area.

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Introduction

Wine grape vineyards have historically been exposed to phenoxy-type herbicides in regions with mixed cereal and minor crop production (Bhatti et al. 1996). The production of a variety of grapes for fine wines has been steadily expanding in the Walla Walla Valley of Washington State over the past few years (Walla Walla Valley Wine Alliance 2003). This, in combination with the already large grain crops in the area, has been problematic for the growers of grapes and grain alike (Bhatti et al. 1998).

Based on studies by Reisinger and Robinson (1976) and Robinson and Fox (1978), regional trans-state movement of airborne herbicide residues from the northeastern Oregon cereal-grain-growing regions to the Columbia and Walla Walla Valley grape-growing regions of Washington is plausible. These past investigations documented volatile 2,4-dichlorophenoxy acetic acid esters in air samples collected at sampling stations in Washington long after ester restrictions were imposed throughout the state. The presence of these volatile esters presumably emanated from cereal-grain-growing regions in Monroe County, Oregon. Although the use of registered volatile esters has been eliminated in Oregon, the registered use of semi-volatility to low-volatility phenoxy-acid esters continued well after the spring cut-off dates for their use in Washington. Prevailing winds during late April and May may still transport these less volatile phenoxy esters to northern Oregon and southeastern Washington wine grape vineyards at a time when they are most susceptible to plant damage and yield reduction.

The objective of this study, which was conducted in the spring of 2003, was to ascertain the adverse impact of regional source contributions of the phenoxy herbicide 2,4-D on the Walla Walla Valley wine-grape producing region located in Walla Walla County, Washington and Umatilla County, Oregon. This objective was examined by evaluating 2,4 D residues in air, in

wet/dry deposition, and by making biological observations during the critical period between grapevine bud burst and full bloom at six vineyards strategically located in the Walla Walla grape-growing appellation. The fundamental question was to determine if there was a clear association between 2,4-D air mass contamination and observed vine symptoms.

Background

Literature Review

Grape production in the Walla Walla Valley began in the mid 1800s (Walla Walla Valley Wine Alliance 2003). The area's climate and soil provide an excellent location for growing grapes that produce some of the nation's finest wines. The Walla Walla Valley earned its reputation for quality wines in 1977 with the establishment of the first modern-day winery (Walla Walla Valley Wine Alliance 2003). By 1984, the area had four wineries and 24 hectares of wine grape vineyards in production and became recognized as a *Unique American Viticultural Area* (Walla Walla Valley Wine Alliance 2003). Over 400 hectares of wine grape vineyards and more than 40 wineries were in the area by 2003 (Walla Walla Valley Wine Alliance 2003).

In terms of both regional quantity and area, the Walla Walla Valley is home to a large number of grain fields. As a result, wine grape vineyards are often found in close proximity to grain fields. Regional grain producers apply a number of herbicides, including herbicides that contain 2,4-dichlorophenoxy acetic acid, commonly referred to as 2,4-D, to control the growth of broadleaf weeds (Bhatti et al. 1996). 2,4-D controls broadleaf or non-grassy weeds while causing virtually little or no harm to grain crops (Bhatti et al. 1996). 2,4-D mimics natural plant hormones called auxins, which control various plant growth and developmental processes (Cox 1999). Plants regulate the auxin hormones as required for optimal growth (Cox 1999). However, 2,4-D is more stable and persistent than auxin hormones, thereby stimulating the synthesis of nucleic acids and proteins resulting in abnormal growth (Cox 1999). In addition, the synthesis of nucleic acids acts to interfere with the plant transport system and, therefore, death of the plant occurs (Cox 1999).

Commercially available in 1946, 2,4-D became widely used to control broadleaf weeds in

grain crops. 2,4-D accounted for half of United States herbicide production in 1960[1]. After more than 50 years of use, 2,4-D is still the third most widely used herbicide in the United States and Canada, and the most widely used worldwide[2]. Grape vines are extremely sensitive to 2,4-D and damage to wine grape vineyards has been reported since its introduction[2].

Transported by wind, 2,4-D droplets may drift and fail to reach the desired target crop plants (Piper 1997). This type of transport vector is usually caused by the physical application of the chemical. In addition, 2,4-D may volatilize to the atmosphere whereby air currents act to convey the herbicide over long distances (Piper 1997). The herbicide is then deposited with settling dust, moisture, or precipitation. Accordingly, the forecast of weather patterns in preparation for the application of 2,4-D to target crops plays a key role in the prevention of injury to wine grape vineyards.

Previous studies by Reisinger and Robinson (1976) indicate that three distinct weather patterns are associated with wine grape vineyard injury caused by herbicide drift: 1) high, 2) moderate, and 3) low herbicide concentration days . They defined high herbicide concentration days as six or more air sampling stations recording greater than, or equal to (≥) 1.0 $\mu g/m^3$ total 2,4-D, moderate herbicide concentration days as four or five stations recording ≥ 1.0$\mu g/m^3$ total 2,4-D, and low herbicide concentration days as three or fewer stations recording ≥ 1.0$\mu g /m^3$ total 2,4-D. The days with the highest concentration of total 2,4-D detected were accompanied by cloudy, pre-frontal weather associated with weak, Pacific occlusions or cold fronts. Moderate concentration days were associated with a strong pressure gradient off the Oregon or southwest Washington coast and companied by moderate to strong winds. Mechanical mixing produced by

[1]Doherty, R. E., 2001. http://www.chemicalhistory.com. Accessed May 16, 2003.
[2]Industry Task Force II on 2,4-D Research Data. 2001. http://www.24d.org/. Accessed April 28, 2003.

low-level winds appeared to be the only significant 2,4-D dispersion mechanism for both the high and moderate concentration patterns. Low concentration days were accompanied by quasi-stationary high-pressure systems from northwest throughout southeast of the affected areas, or thermally induced low-pressure troughs centered east of the Cascades. Because of the larger volume of air into which the 2,4-D can disperse, predominately convective dispersion effects would be expected to produce a much greater dilution than predominantly horizontal dispersion effects. The larger volume of air may act to reduce a potentially hazardous concentration of 2,4-D emitted near ground level to a relatively dilute amount by the time the air mass reaches a distant sensitive grape crop (Reisinger and Robinson 1976).

A ban on the use of all 2,4-D formulations designated as "highly volatile" was enacted throughout Washington on May 1, 1974 (Reisinger and Robinson 1976). Prior to the statewide ban, the majority of air sample stations were located approximately 16 or more kilometers from any potentially highly volatile 2,4-D source areas. Therefore, the fact that the majority of the 2,4-D detected from samplers throughout the spring months of 1973 and 1974 was of the highly volatile type contributed to a long-distance (tens of kilometers) transport theory (Reisinger and Robinson 1976).

The effect of 2,4-D on grape vines has been studied for many years (Robinson and Fox 1978). Typical symptoms of 2,4-D injury to grape vines include epinasty of the shoot and petiole, rugose leaf surface, stunted leaves, cupping or curling of leaves, strapping, vein clearing, and reduced spacing between internodes (Al-Khatib et al. 1993). Visible symptoms can be caused by doses well below the level that actually reduces yields (Bhatti et al.1996). Clore and Bruns (1955) determined that 0.001 µg 2,4-D acid applied to buds 4 to 8-mm in size caused no definite symptoms while 0.01 µg caused typical symptoms and applications of 0.1 and 1.0 µg per

bud produced severe malformation and stunting of concord grape shoot growth. In this study, 60% to 90% of the leaves actually treated with 1.0 μg were killed. They also reported that while 0.01 μg 2,4-D acid caused detectable malformation of the basal leaves, no significant effects on production could be measured.

As previously stated, 2,4-D is used extensively to control weeds in grain crops in south central Washington and northeastern Oregon. It is often applied in the early spring when grape plant growth is most vigorous and, therefore, more sensitive (Al-Khatib et al. 1993). Newly planted grapevines are more sensitive to herbicides than established vines (Al-Khatib et al. 1993). Because of the differing growth stages of grain from one field to another, the application period for herbicides can extend over a long period of time, thereby creating the potential for multiple herbicide exposures (Al-Khatib et al. 1993). In a study conducted by Al-Khatib (1970), 2,4-D was applied to grapevines at a frequency of up to 3 times per week and at rates that could simulate drift. All applications visibly injured grapevines. As the number and rate of applications increased, the symptoms increased and the total leaf area and grape pruning weight decreased. Newly expanding grape leaves expressed symptoms from single exposures to 2,4-D when applied at 1/3, 1/10, 1/30, and 1/100 of the maximum use rate recommended for wheat. Grape vines showed symptoms within 45-60 days of first application when applied three times at 1/900 of the recommended use rate. No symptoms were observed on leaves that were fully developed before application of 2,4-D, even when applied more than once at the highest rate.

Multiple exposures of grape vines to 2,4-D at 1/100 of the maximum use rate for wheat caused injury that persisted throughout the entire growing season and resulted in lower pruned stem weight (Al-Khatib et al. 1993). Rates that slightly injured grapevines did not reduce growth as measured by pruning weight (Al-Khatib et al. 1993). The appearance of the most severe 2,4-D

symptoms on grape vines was correlated with the detection of the maximum atmospheric levels of 2,4-D. The effects of multiple exposures were additive, with respect to herbicide injury, and recovery was significantly hindered. The most severe damage resulted from three applications of 2,4-D at the highest rate. Only a partial recovery of grapevines occurred when three applications were made at 1/100 the use rate. At the highest rate, pruning weight was reduced in all applications. At the lowest rate, two and three applications reduced the pruning weight. Grapevines recovered rapidly from exposures to simulated herbicide drift. However, recovery was significantly hindered by multiple exposures (Al-Khatib et al. 1993).

In general, newly planted grapes were affected more than those established plants (Al-Khatib et al. 1993). Two months after treatment, growth resumed from buds in the lower part of the plants at all rates. Veins were discolored, anatomized, and extended to form finger-like projections, however, the highest rates of 2,4-D killed newly planted grapes.

The herbicide effect on the reproductive parts appeared to be more severe than those effects on the vegetative parts (Al-Khatib et al. 1993). Treated plants had fewer berries than the control plants and the berries appeared smaller than normal.

Experimental Work

Study Area

The sites selected to study encompassed areas throughout the Walla Walla Valley, in southeastern Washington. The sites were adequately spaced so as to distinguish between a regional and a localized event in the case of 2,4-D drift. Five established wine grape vineyards were selected within Walla Walla County, Washington and one in Umatilla County, Oregon. A three-letter abbreviation was established for each wine grape vineyard for sampling identification purposes.

The first site selected for the study was Ash Hollow Vineyard (RNW), which represented the westernmost site of the study. It was surrounded by grain fields. The vineyard is located at approximately 46º03'154" N, 118º43'618" W and at an elevation of 180-m in Walla Walla County, Washington (Figure 1). The second site was Seven Hills Vineyard (SHV), which represented the southernmost site of the study. It is surrounded by grain fields and various orchards. The vineyard is located at approximately 45º56'699" N, 118º27'234" W and at an elevation of 270-m in Umatilla County, Oregon (Figure 1). The third site was Pepper Bridge Vineyard (PBW). It represented a point between the southernmost and easternmost wine grape vineyard locations. The vineyard was located adjacent to grain, alfalfa, and residential areas at approximately 46º01'310" N, 118º22'697" W and at an elevation of 240-m in Walla Walla County, Washington (Figure 1). The fourth site, Les Collines Vineyard (LCW), represented the easternmost boundary of the wine grape vineyards selected for the study. It was adjacent to numerous crops including peas, grain, and asparagus. The vineyard was located at approximately 46º00'309" N, 118º15'949" W at the foot of the Blue Mountains in Walla Walla County, Washington, at an elevation of 384-m (Figure 1). Located approximately 46º03'129" N,

118º27'514" W, immediately south of State Highway 12 and midway between Walla Walla and Lowden in Walla Walla County, Washington, the fifth site was Three Rivers Winery (TRW). It lies between the easternmost and northernmost wine grape vineyard study locations. Grain, asparagus, and onions were the major crops in the immediate area (Figure 1). The sixth site was Woodward Canyon Vineyard (WWC). It was the northernmost boundary for this study. The vineyard was located at approximately 56º05'893" N, 118º35'333" W and at an elevation of 252-m in Walla Walla County, Washington. It is near various grain crops (Figure 1).

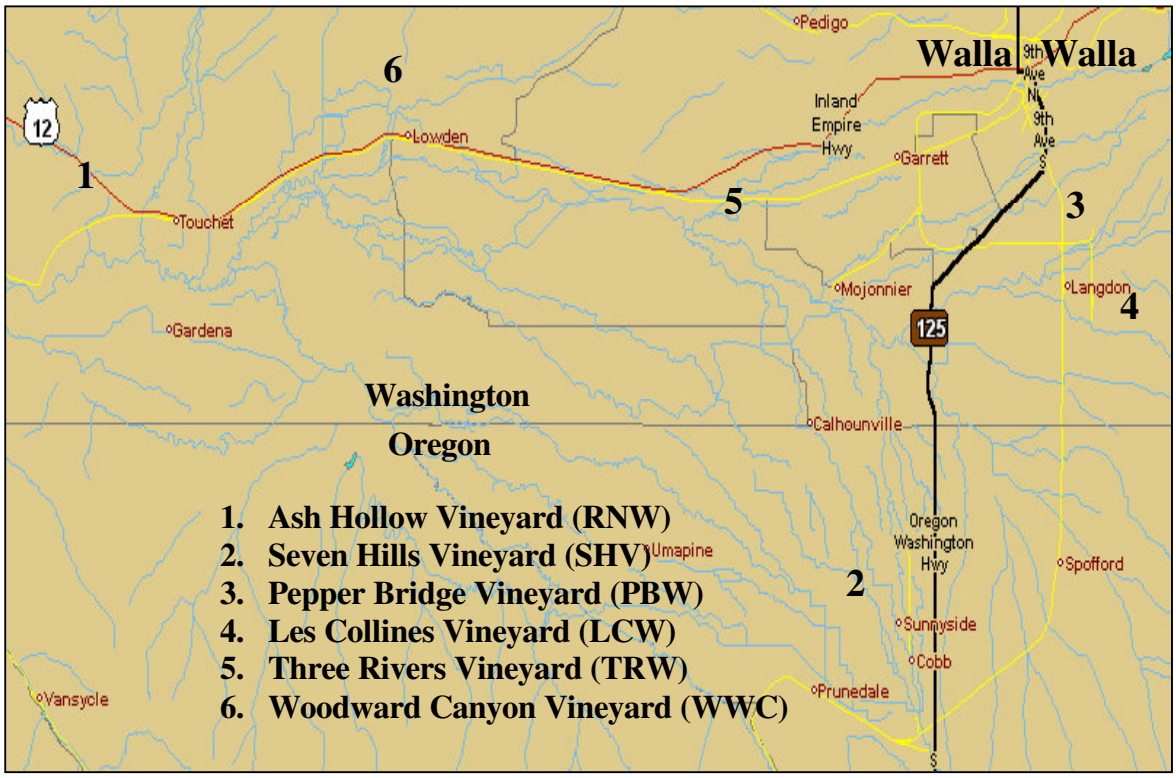

Figure 1. Wine Grape Vineyard Sampling Site Locations.

Sample Methods

Ambient air and wet/dry deposition sampling was conducted for the detection of airborne 2,4-D residues at each of the six wine grape vineyards. Sampling was conducted between April 10, 2003, and June 27, 2003. It should be noted that the sample collection period coincides with

the maturation period of wine grapes (i.e., from bud burst to full bloom) when the plant is most susceptible to herbicide injury.

Air sampling was conducted using six, ThermoAndersen®, two-stage high-volume air samplers (Figure 2). The first, or upper stage of each air sampler consisted of cellulose, ashless, Whatman® No. 41 filter paper, 9-cm diameter, 20 µm, designed to collect particulate residues. The second, or lower stage contained a polyurethane foam plug which is designed to collect small particulates and gaseous pesticide residues. At all test vineyards, air samplers were operated at a frequency of two times per week and duration of approximately 1,440 minutes. The Whatman® No. 41 filter paper and polyurethane foam plug were collected after each air sample duration. The polyurethane foam plug was placed in a glass, laboratory quality, sample container and the Whatman® No. 41 filter paper wrapped in aluminum foil which was utilized for ease of sample collection and to minimize loss of potential chemical particulate. Samples were then placed in an ice chest and transported by automobile to the Food and Environmental Quality Laboratory (FEQL) located on the campus of Washington State University Tri-Cities in Richland, Washington. Upon arrival, samples were removed from the ice chest and placed in an approximately -20 °C freezer until analyzed. Storage-stability studies for the air and deposition samples were evaluated to verify stability and degradation of the 2,4-D acid and ester over the maximum cold storage duration.

Figure 2. Air Sampling Instrumentation.

Wet and dry deposition sampling was conducted using 4-L bottles with 25-cm funnels and aluminum trays elevated with wire stands, respectively (Figure 3). Wet deposition samples were collected at each of the six wine grape vineyard study sites. A single 4-L bottle with a 25-cm funnel sealed to the opening was placed at each site to collect precipitation. The collection bottles were partially submerged in the soil for stability. The wet-deposition collection bottles were checked during each visit to each site. If water was present, it was collected in sample jars, placed in an ice chest, and returned to the FEQL where it was placed in refrigerated storage until analyzed.

Dry deposition samples were collected at each of the six wine grape vineyard study sites. The sample collections consisted of four aluminum trays elevated on wire stands. In one-week intervals, deposition sample pans were exposed to atmospheric conditions to capture either wet or dry deposition of 2,4-D residues. Weekly, the exposed deposition filter papers were replaced with unexposed filter papers and composite samples, consisting of all deposition sample papers

from a single site, were collected. At the time of collection, if the deposition sample pans contained standing water, the water was emptied, not retained, and filter papers collected for analysis. Composite samples were sealed in foil envelopes, placed in an ice chest, and returned to the FEQL, where they were placed in an approximately -20 °C freezer until analyzed.

Figure 3. Wet & Dry Deposition Sampling Instrumentation.

Because of a prolonged delay in receiving 20.3- x 25.4-cm filter paper, the first two sample periods consisted of trays that contained six, 12.5-cm diameter filter papers, cut square to dimensions of approximately 10- x 8.5-cm to closely approximate the 20.3- x 25.4-cm single filter paper that would be used for the remainder of the sample period. Total surface area for the deposition collection was 2,064 cm^2. See Appendix A and Appendix B for detailed field and sampling data.

Chemical Analysis

Methods suitable for the analysis of the free acid of 2,4-D were modified and validated to quantify residues in air samples, deposition filter papers, and wet deposition samples. These

analytical methods were derived from EPA Method 8151A (revised 1996). These working methods and detailed validation results for analysis of dry deposition paper and wet deposition material can be found in Appendix B. The analytical methods used for the determination of 2,4-D utilized a base-solution extraction to hydrolyze the various formulations of 2,4-D to the free acid state. Liquid to liquid partition and derivatization with diazomethane of the free acids were then performed for determination by gas chromatography using electron capture detection. Method recoveries for 2,4-D in ambient air, deposition, and wet samples are provided in Table 1. The detailed analytical methods used in this study can be found in Appendix B. The results of residue analyses from the deposition and air samples are summarized in Appendix B.

Grape Vine Observations

In addition to collecting air, wet, and dry samples, grape vine observations were conducted on a weekly basis. Three representative vines from five of the wine grape vineyards were selected and flagged for weekly observation. A representative vine was one that was fruit bearing and comparable in size to other vines of that variety in the vineyard. No vines were selected from TRW because of carryover symptoms of phenoxy-type herbicide injury from the previous year. A merlot variety of grape was selected at RNW, SHV, PBW, and WWC Vineyards while at LCW, cabernet sauvignon was selected. Leaves on the selected vines were sequentially numbered directly on the leaf with a black permanent marker after the cutin had formed (Appendix C). The selected vines were vertically positioned to keep the tip in an upward position. Visual observations and internode spacing measurements (Appendix D) were recorded in a field book. Photographs were taken of nearly every leaf of the selected vines at each location. The leaf photos and internode measurements were used to aid in comparing field

observation and lab analysis data for any recognizable trends in off-target phenoxy-type herbicide exposure and leaf symptomology.

A concord grape leaf index rating developed by Alex Ogg (Ogg et.al. 1991) was modified and expanded to better characterize severity of off-target phenoxy-type herbicide symptoms (Holshue et. al., 2004). Each leaf was assigned a rating (0 to 5 severity scale) according to this system (Figures 4-9).

Figure 4. Mean Leaf Index Value = 0.

Legend: Mean Leaf Index Value, 0, has no visible symptoms of phenoxy-like herbicide contact with well-defined leaf margins and lobes and no apparent rugose texture.

Figure 5. Mean Leaf Index Value = 1.

Legend: Mean Leaf Index Value, 1, display signs of rugose, or bumpy, leaf surface features and/or shortened lobes and sinus. The leaf grows to normal or near normal size.

Figure 6. Mean Leaf Index Value = 2.

Legend: Mean Leaf Index Value, 2, portrays rugose features as well as marginal disfiguration. The leaf is unable to fully open with the leaf margins curled slightly, upward. The leaf is not significantly smaller than leaves with a Mean Leaf Index Value of 0 or 1.

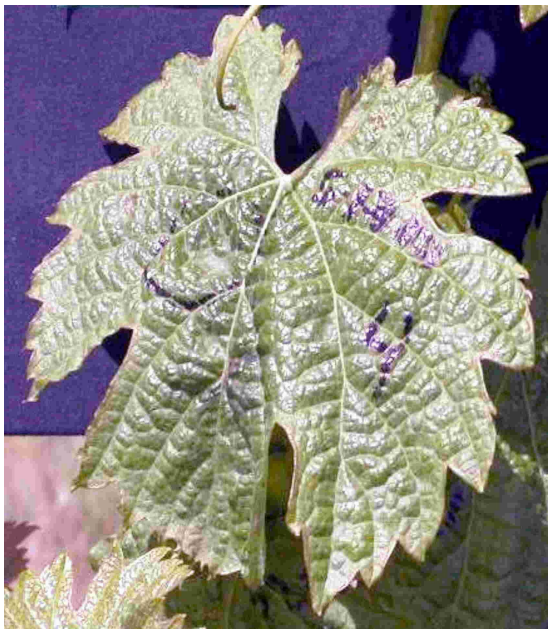

Figure 7. Mean Leaf Index Value = 3.

Legend: Mean Leaf Index Value, 3, shows deformation of leaf margins including diminished or lack of sinus. The leaf is significantly smaller than leaves with a Mean Leaf Index Value of 0, 1 or 2.

Figure 8. Mean Leaf Index Value = 4.

Legend: Mean Leaf Index Value, 4, with a definite deformation of the leaf margins and sinuses, has practically parallel leaf veination and stunted size.

Figure 9. Mean Leaf Index Value = 5.

Legend: Mean Leaf Index Value , demonstrates gross leaf deformation and dwarfism. Leaf veination is parallel and the terminal margins of the leaf resemble the "bristle ends" of a straw broom.

Statistical Analysis

MINITAB® Release 14, Software, Copyright© 2005, Pearson Education, Inc., was the computer software used to perform statistical analysis. Analysis of variance (ANOVA) was used to determine if there was a relationship among the residues detected in the various vineyards; among the biological observations in the various vineyards; between the residues detected and the biological observations at each vineyard; and among biological observations within each vineyard. ANOVA is useful for identifying sources of variability from one or more potential sources. The concept behind ANOVA is to compare the ratio of between group variance to within group variance. If the variance caused by the interaction between the samples of different groups is much larger when compared to the variance that appears among the samples within each group, then it is because the means of the two groups are not the same. The null hypothesis that the average leaf index, internode lengths, and 2,4-D residue values were not different among

vineyards and observation days, was rejected when the p-value for each test was less than 0.05. A small p-value is evidence against the null hypothesis while a large p-value means little or no evidence against the null hypothesis.

The results of the individual types of sample collections, dry deposition, particulate filter, polyurethane foam, and wet deposition were compared. The weekly results of each method of sample collection was compared among the vineyards to determine if there is a significant difference in the amount of residue detected by each sample method.

Then, the total amount of quantifiable residue, meaning the total of dry deposition, particulate filter, polyurethane foam, and wet deposition, was looked at to determine if there is a significant difference between the vineyards on a weekly basis. Details of the statistical analysis can be found in Appendix E.

Results and Discussion

Overview of Biological and Chemical Observations

Biological observations were performed once a week from April 25, 2003 through July 7, 2003. The first observation noted how many leaves were expanded on that day. Leaves that had expanded were sequentially marked with a permanent marker as to their position, or order of unfurling. Field notes documented the number of leaves expanded and any other unusual morphological features. The following weeks of observations continued in the same manner.

At the beginning of the observation period, there were up to three leaves that had already expanded, meaning the leaf had unfurled and cutin had formed. Before the leaf unfurls, phenoxy-type herbicide exposure can cause the leaf to grow abnormally. The severity of leaf abnormality from 2,4-D exposure is relative to the concentration at point of exposure. The leaf index values generally increased with the advance of the growing season even though the concentration of 2,4-D did not share this observation. The increase of leaf symptomology as the growing season progressed may simply have been related to the stress from the 2,4-D exposure, thereby reducing its leaf size and photosynthesis capabilities.

Internode measurements began May 20, 2003 and continued through July 15, 2003. The internodes were measured each time leaf observations were conducted. The internode lengths increased and decreased fairly evenly across all four observed vineyards. This increase and decrease of internode length is a normal expectation as the plant grows rapidly at first and then expends more resources on fruit production and less on vegetative growth. For this reason, and the fact that internode length can be influenced through management practices, internode length did not appear to be a good field indicator of 2,4-D injury.

Air sampling began April 10, 2003 and ended June 26, 2003. Samples were gathered two times per week during this period. The twice-weekly air sample results were combined to form one weekly residue value for each collection method (i.e., the particulate filter paper and the polyurethane foam). The particulate filter samples resulted in a fairly even distribution of positive results in both number and residue quantity, indicating a study-area airmass contamination. RNW results were higher than the other locations early in the sample period, indicating some possible localized events had occurred in that area (Table E-1). The polyurethane foam samples were more random among the vineyards but the weeks in which quantifiable amounts were observed were grouped within each vineyard. (Table E-2). The dry deposition samples were collected on a weekly basis that began April 18, 2003 and ended June 26, 2003. The first week of deposition sample placement resulted in four of the six samples with quantifiable residue. The third week of sample placement was the only other time a deposition sample returned a quantifiable result (Table E-3). The wet deposition samples were collected each visit there was water present in the collection bottle. There were a total of three weeks in which residue amounts were quantifiable, the first of which, the week of May 12, 2003, resulted in more than 411µg of 2,4-D residue. This large amount was attributed to a localized application event as the other samples did not have quantifiable residue. In addition, the vineyard manager reported seeing spray applications during this period. The second week with a positive result occurred the week of June 26, 2003. Again, only the RNW sample returned a quantifiable result, possibly due to a localized event. The week of June 23, 2003 indicated a regional dispersion of residue as two locations returned quantifiable results (Table E-4).

Over the period from April through June 2003, 2,4-D residues at or above the method's level of detection (LOD) of 0.001 $\mu g/m^3$ were observed in 97 of 129 particulate filter samples.

Twenty of those 97 samples were above the method's limit of quantification (LOQ) of 0.004 $\mu g/m^3$. During this same period, 54 of the 129 polyurethane foam (PUF) samples had 2,4-D residues at or above the LOD. Only a single PUF sample (RNW) was above the 0.004 $\mu g/m^3$ LOQ. This occurred April 10, 2003. The greatest concentration (0.0436 $\mu g/m^3$) detected from a particulate filter sample occurred the same day at the same location.

Later in the growing season, in general, the residues detected in the air samples depicted a study-area trend of 2,4-D residue in air mass since multiple sites contained comparable residues on the same days.

Deposition samples were also collected from April through June 2003. Sixty-four deposition samples were analyzed. Forty-eight of the samples contained 2,4-D residues at or above the 0.12 $\eta g/cm^2$ LOD with 32 of those samples containing residues $\geq$ LOQ of 0.48$\eta g/cm^2$. On April 18, 2003, residue levels $\geq$ LOQ were detected at four sample locations. The greatest amount detected in a dry deposition sample was 4.51 $\eta g/cm^2$ at RNW on April 18, 2003.

Wet deposition samples were collected each visit when there was water present in the collection bottle. Twenty samples were collected and analyzed. Of those, seven contained residue $\geq$ the LOD of 2 $\mu g/L$. Five of the samples contained residue levels $\geq$ LOQ of 7 $\mu g/L$. One particular site, RNW, had significant wet deposition 2,4-D residue amounts (2.8 mg/L and 79 $\mu g/L$, respectively) on two consecutive days, May 12, and 13, 2003. The high concentration at RNW was associated with a localized 2,4-D application event.

Table 1. Method Percent Recoveries for 2,4-D in Dry & Wet Deposition, and Air Samples

	Dry Deposition	Wet Deposition	Particulate Filters	Polyurethane Foam
2,4-D	80.9 ± 20.4%	80 ± 6.6%	79.7 ± 13.6%	70.3 ± 16.4%
	n = 11	n = 2	n = 23	n = 23

n = total number of fortified samples evaluated.

Overall, the particulate filter residue accounted for the majority of all measurable 2,4-D residues with the exception of location RNW where the wet deposition accounted for the majority of measurable 2,4-D residues. There was no quantifiable wet or dry deposition for LCW while both SHV and TRW had no quantifiable wet deposition. (Figure 10).

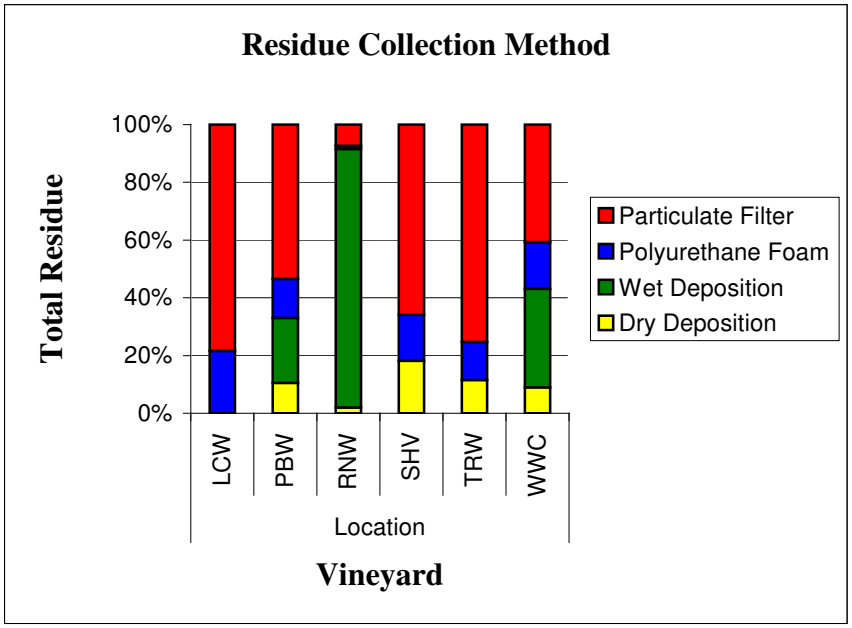

Figure 10. Percent 2,4-D By Collection Method.
Values are in relation to the total amount of quantifiable residue observed at each location.

Wind direction data from the WSU Weather Station, 2 kilometers south of Touchet, Washington, was collected for comparison against residue results and leaf index values for any relationship and possible indication of direction of airmass movement (Tables E-5 and E-6).

Trends in 2,4-D Residues Among Vineyards

To test for weekly differences in total quantifiable residue between vineyards, the null hypothesis was that there would be no significant weekly difference in total quantifiable 2,4-D residue detected among the six vineyards (Figure 11). To test this hypothesis, a regression

analysis of the total quantifiable residue was performed using date versus location. The result yielded p-values of 0.508 for SHV to 0.916 for PBW (Table E-7). Since there is no significant difference, the null hypothesis was accepted.

ANOVA was used to test residue differences between vineyards. With a resulting p-value of 0.316, indicating no significant difference between the vineyards, the null hypothesis is accepted (Table E-8).

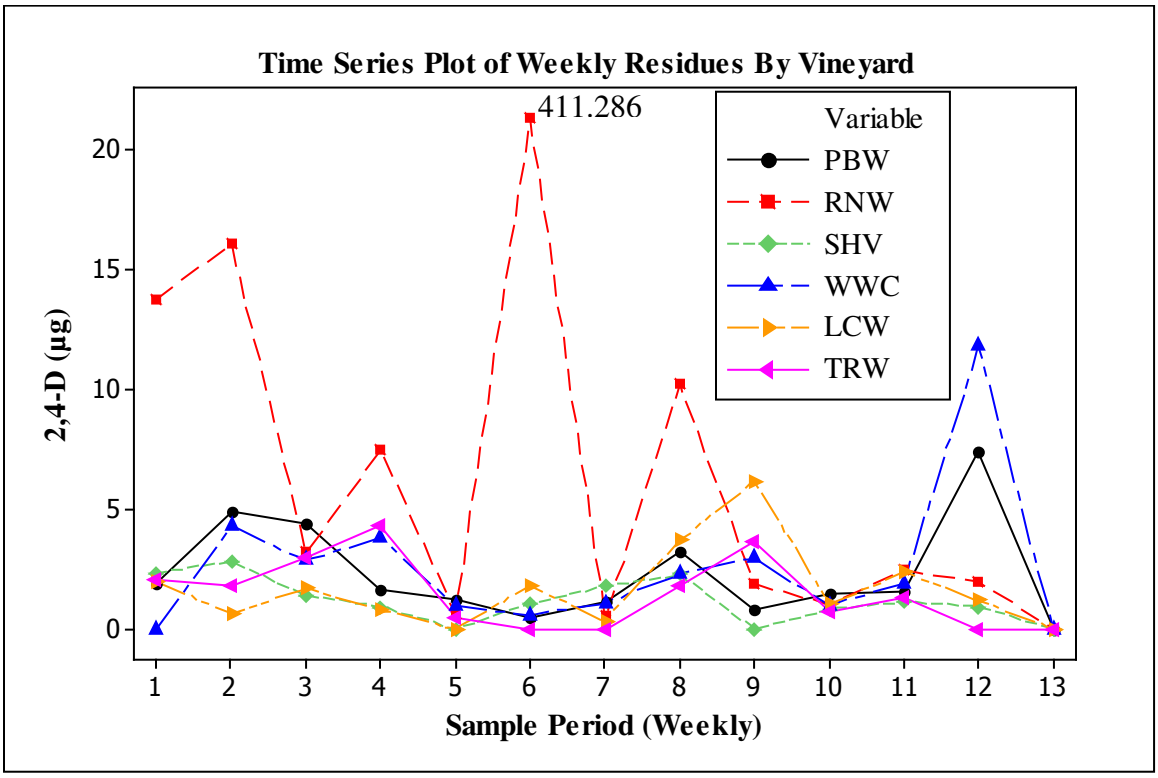

Figure 11. Wine Grape Vineyard 2,4-D Residue (µg) Time Series Plot.
Legend: LCW-Les Collines Vineyard, RNW-Ash Hollow Vineyard, TRW-Three Rivers Vineyard, PBW-Pepper Bridge Vineyard, SHV-Seven Hills Vineyard, WWC-Woodward Canyon Vineyard. Note: RNW at week six was modified to reduce the spread in residue amount for the ease of viewing the graph. The correct value is noted above point RNW week six.

Leaf Observations

Phenoxy-type herbicides cause the grape vines to exhibit distinct injury symptoms as discussed previously. The leaves on each of the three vines at each observation location were sequentially numbered after the leaf had expanded and cutin had formed. Observations were noted as to type and degree of injury and photos were taken of observed leaves. Each observed leaf was assigned a value of injury using the Leaf Index Value scale. The same number leaf on each of the three observed vines at each vineyard were averaged for a single complete sample to represent that vineyard on any observation date (Figure 12).

With a p-value less than 0.05, the null hypothesis that there is no statistically significant difference in the overall Leaf Index Value by week among the four vineyards in which biological observations were conducted is rejected (Table E-9).

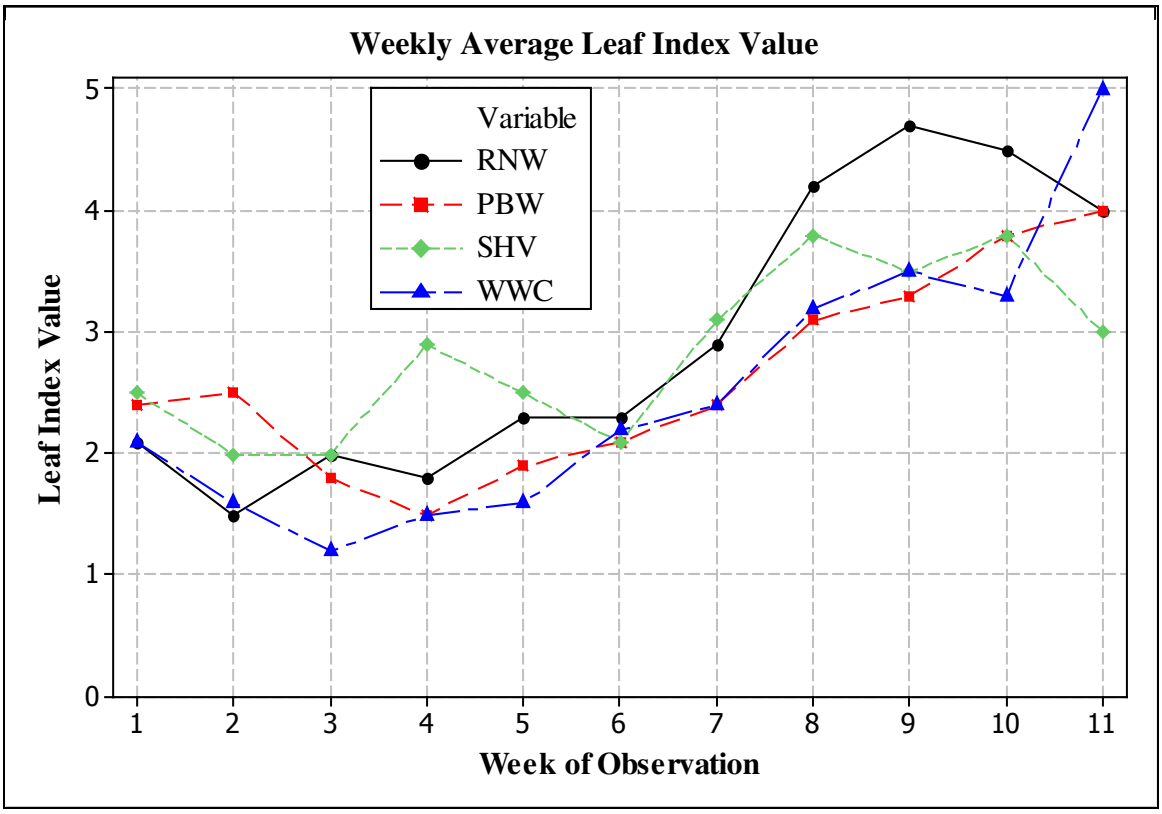

Figure 12. Wine Grape Vineyard Leaf Index Value Time Series Plot.

Legend: RNW-Ash Hollow Vineyard, PBW-Pepper Bridge Vineyard, SHV-Seven Hills Vineyard, WWC-Woodward Canyon Vineyard. Note: The Leaf Index Values followed a similar pattern for most of the observation period.

When comparing the overall average Leaf Index Value between vineyards, an ANOVA p-value of 0.283 is observed (Figure 13, Table E-10). The null hypothesis that there is no difference in leaf index value between vineyards is accepted.

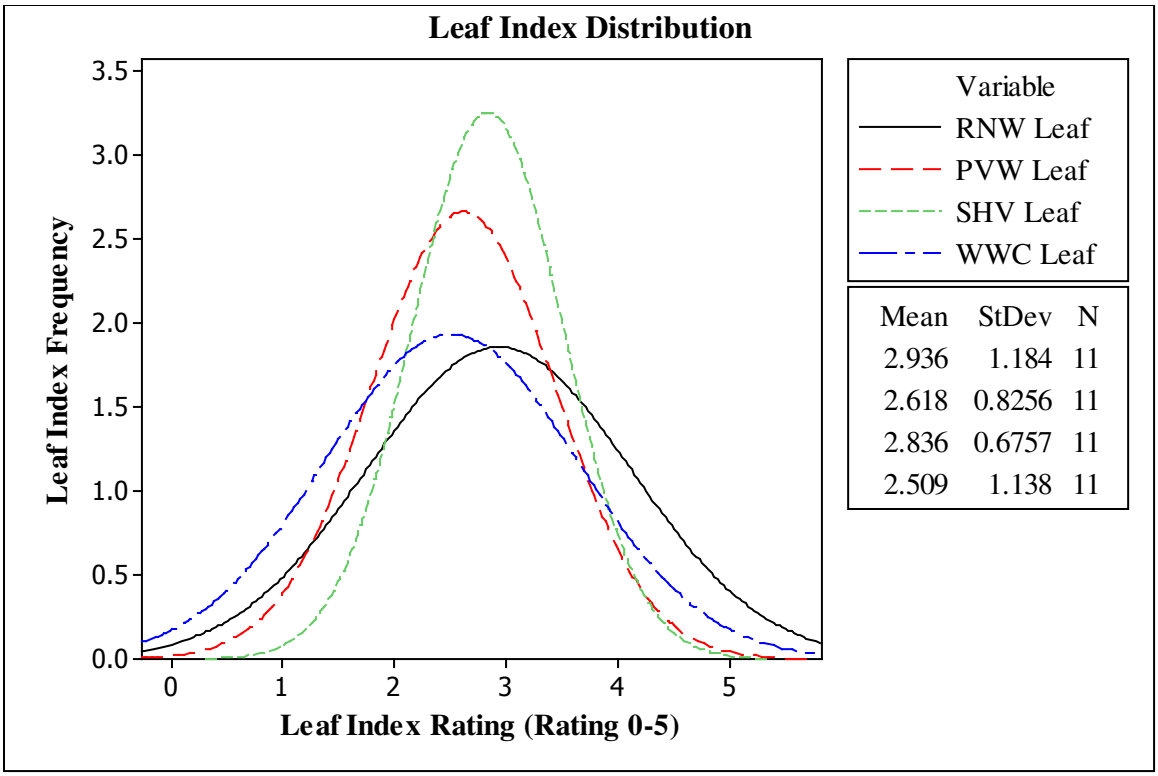

Figure 13. Wine Grape Vineyard Leaf Index Distribution.

Legend: RNW-Ash Hollow Vineyard, PBW-Pepper Bridge Vineyard, SHV-Seven Hills Vineyard, WWC-Woodward Canyon Vineyard. Note: Analysis was also performed to check for leaf variance within each vineyard. There were no significant differences within each of the vineyards.

Regression was performed using weekly vineyard 2,4-D residues against average weekly vineyard leaf index values. There is no indication of a clear relationship between the two variables (Figure 14).

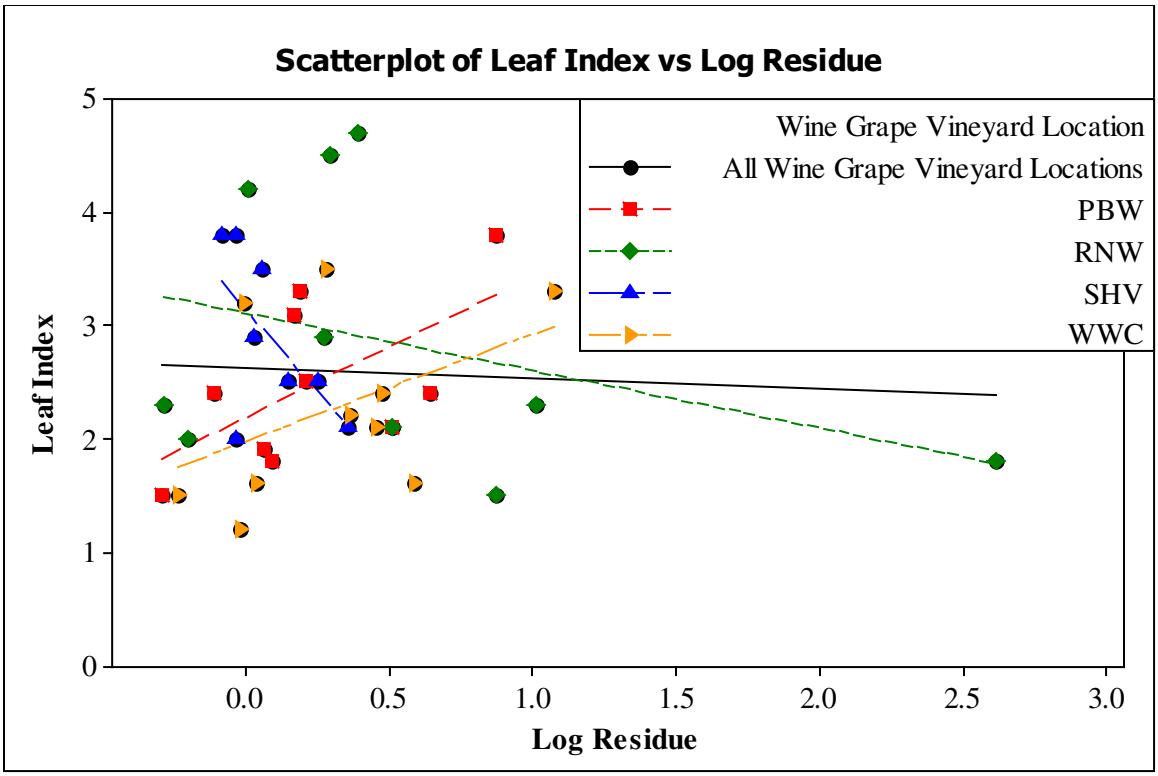

Figure 14. Regression Analysis: Leaf Index Versus Log Residue.

Legend: The regression equation is Leaf Index = 2.63 - 0.094 Log Residue
76 cases used, 44 cases contain missing values

Predictor	Coef	SE Coef	T	P
Constant	2.6285	0.1196	21.97	0.000
Log Residue	-0.0942	0.2018	-0.47	0.642

S = 0.897028 R-Sq = 0.3%

Internode Length

The internode lengths were measured on each of the three vines at RNW, SHV, PBW, and WWC on a weekly basis. The same internode from each vine at each vineyard location was averaged for a single complete internode length sample. There were no significant differences between vineyards by week or distribution of internode lengths (Figures 15 and 16).

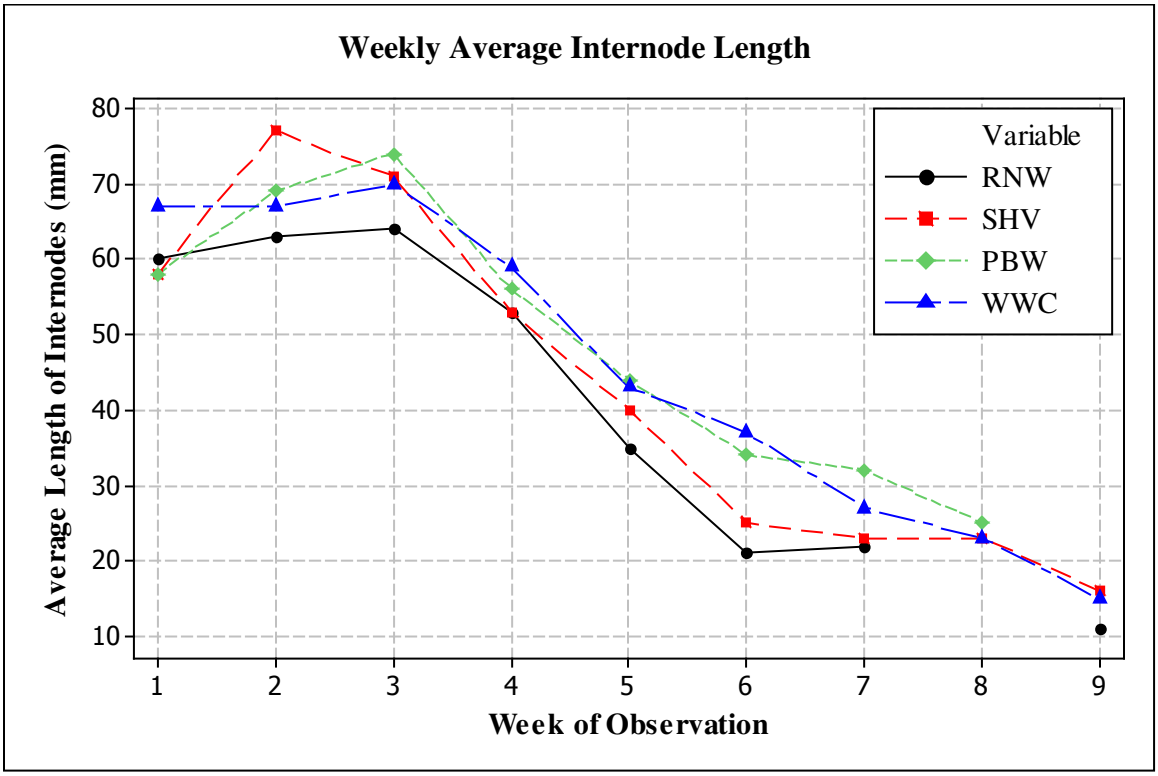

Figure 15. Wine Grape Vineyard Leaf Internode Length.

Legend: RNW-Ash Hollow Vineyard, PBW-Pepper Bridge Vineyard, SHV-Seven Hills Vineyard, WWC-Woodward Canyon Vineyard. Note: The average vineyard internode length showed a consistent pattern among all vineyards.

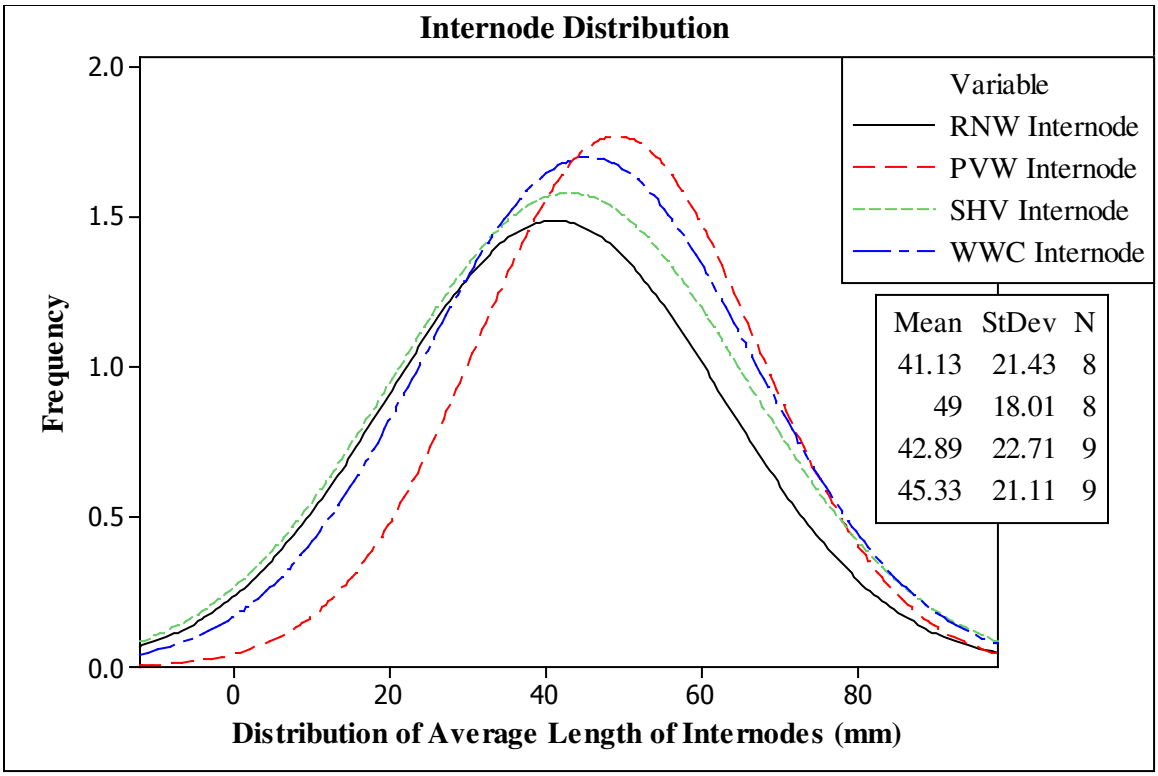

Figure 16. Wine Grape Vineyard Leaf Internode Length Mean Distribution.
Legend: LCW-Les Collines Vineyard, RNW-Ash Hollow Vineyard, TRW-Three Rivers Vineyard, PBW-Pepper Bridge Vineyard, SHV-Seven Hills Vineyard, WWC-Woodward Canyon Vineyard. Note: Histogram illustrates average length of internode and frequency of each length at each vineyard internodes were measured.

Internode lengths were also compared within each vineyard for differences. At SHV, vine number one was less vigorous than the others were and displayed more severe leaf symptomology and shorter internodes. Similarly, at WWC, vine number one appeared to be more vigorous than vines two and three with longer internodes and lower leaf index values. The sample size was too small to conclude anything other than a random observation.

The differences between total residue and leaf index value, and total residue and internode length within each vineyard were tested. There were no significant differences observed. Each p-value was greater than 0.05 and accompanied by a small R^2 value, indicating

the differences in internode length and leaf index value is poorly associated with variations in residue values (Tables E11-E20).

Conclusion

The air and deposition sampling results correlate with the vine observations of mild broadleaf-herbicide injury in 2003. The results of nine air sample dates at the six wine grape vineyard locations usually showed similar residue concentration patterns, thus indicating a possible low-level contamination of the study area airmass. Dry deposition samples were positive for residue from all sites for April 18, 2003. The results of four collection days of wet deposition were positive for 2,4-D residue. The wet deposition sample taken at one location in mid-May showed very high concentrations of 2,4-D. However, this single site observation indicates a localized rather than regional contamination event. Overall, the consistency of low residues detected at all wine grape vineyard sites suggest that the airmass was contaminated 2,4-D which was probably responsible for the low-level plant injury that was generally observed in the wine grape vineyards. At one location, localized spray applications likely contributed to the very high 2,4-D residues found in the rainwater.

Wind data from the Touchet Weather Station show the wind direction during the months of April, May, and June of 2003 were predominantly from the southwest. This is consistent with botanical observations and residue analysis.

While there were several days in which residues were detected, there was no noticeable associated change in leaf symptoms. Likewise, when the mean leaf index ratings and residues at each wine grape vineyard were directly compared, there was no significant relationship between total residue detected and severity of leaf injury.

While not depicting a significant difference between residues and leaf index values between vineyards, the totals of each, along with the wind data, give indication that the airmass contamination could have originated southwest of the study area.

Measures have been taken over the years to reduce the effect of phenoxy-type herbicide injury to off-target crops. The mean leaf index rating is one tool by which managers of wine grape vineyards can better evaluate conditions of the vineyard and apply appropriate measures to minimize vineyard injury caused by 2,4-D drift.

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APPENDICES

Appendix A

Field Sampling Data

Table A-1. Dry Deposition Sample History Ash Hollow Vineyard (RNW)

FEQL Lab Number	Sample Position Date	Sample Collection Date	Lab Receipt Date	Sample Analysis Date
Ash Hollow Vineyard (RNW)				
RNW-D-041803	04/10/03	04/18/03	04/18/03	07/28/03
RNW-D-042403	04/18/03	04/24/03	04/24/03	08/04/03
RNW-D-050103	04/24/03	05/01/03	05/01/03	08/05/03
RNW-D-050803	05/01/03	05/08/03	05/08/03	08/06/03
RNW-D-051503	05/08/03	05/15/03	05/15/03	08/07/03
RNW-D-052203	05/15/03	05/22/03	05/22/03	08/11/03
RNW-D-052903	05/22/03	05/29/03	05/29/03	08/14/03
RNW-D-060503	05/29/03	06/05/03	06/05/03	08/18/03
RNW-D-061203	06/05/03	06/12/03	06/12/03	08/19/03
RNW-D-061903	06/12/03	06/19/03	06/19/03	08/20/03
RNW-D-062603	06/19/03	06/26/03	06/26/03	08/21/03

Table A-1. Dry Deposition Sample History Seven Hills Vineyard (SHV)

FEQL Lab Number	Sample Position Date	Sample Collection Date	Lab Receipt Date	Sample Analysis Date
Seven Hills Vineyard (SHV)				
SHV-D-041803	04/10/03	04/18/03	04/18/03	07/28/03
SHV-D-042403	04/18/03	04/24/03	04/24/03	08/04/03
SHV-D-050103	04/24/03	05/01/03	05/01/03	08/05/03
SHV-D-050803	05/01/03	05/08/03	05/08/03	08/06/03
SHV-D-051503	05/08/03	05/15/03	05/15/03	08/07/03
SHV-D-052203	05/15/03	05/22/03	05/22/03	08/11/03
SHV-D-052903	05/22/03	05/29/03	05/29/03	08/14/03
SHV-D-060503	05/29/03	06/05/03	06/05/03	08/18/03
SHV-D-061203	06/05/03	06/12/03	06/12/03	08/19/03
SHV-D-061903	06/12/03	06/19/03	06/19/03	08/20/03
SHV-D-062603	06/19/03	06/26/03	06/26/03	08/21/03

Table A-1. Dry Deposition Sample History Pepper Bridge Vineyard (PBW)

FEQL Lab Number	Sample Position Date	Sample Collection Date	Lab Receipt Date	Sample Analysis Date
Pepper Bridge Vineyard (PBW)				
PBW-D-041803	04/11/03	04/18/03	04/18/03	07/28/03
PBW-D-042403	04/18/03	04/24/03	04/24/03	08/04/03
PBW-D-050103	04/24/03	05/01/03	05/01/03	08/05/03
PBW-D-050803	05/01/03	05/08/03	05/08/03	08/06/03
PBW-D-051503	05/08/03	05/15/03	05/15/03	08/07/03
PBW-D-052203	05/15/03	05/22/03	05/22/03	08/11/03
PBW-D-052903	05/22/03	05/29/03	05/29/03	08/14/03
PBW-D-060503	05/29/03	06/05/03	06/05/03	08/18/03
PBW-D-061203	06/05/03	06/12/03	06/12/03	08/19/03
PBW-D-061903	06/12/03	06/19/03	06/19/03	08/20/03
PBW-D-062603	06/19/03	06/26/03	06/26/03	08/21/03

Table A-1. Dry Deposition Sample History Les Collines Vineyard (LCW)

FEQL Lab Number	Sample Position Date	Sample Collection Date	Lab Receipt Date	Sample Analysis Date
Les Collines Vineyard (LCW)				
LCW-D-041803	04/11/03	04/18/03	04/18/03	07/28/03
LCW-D-042403	04/18/03	04/24/03	04/24/03	08/04/03
LCW-D-050103	04/24/03	05/01/03	05/01/03	08/05/03
LCW-D-050803	05/01/03	05/08/03	05/08/03	08/06/03
LCW-D-051503	05/08/03	05/15/03	05/15/03	08/07/03
LCW-D-052203	05/15/03	05/22/03	05/22/03	08/11/03
LCW-D-052903	05/22/03	05/29/03	05/29/03	08/14/03
LCW-D-060503	05/29/03	06/05/03	06/05/03	08/18/03
LCW-D-061203	06/05/03	06/12/03	06/12/03	08/19/03
LCW-D-061903	06/12/03	06/19/03	06/19/03	08/20/03
LCW-D-062603	06/19/03	06/26/03	06/26/03	08/21/03

Table A-1. Dry Deposition Sample History Three Rivers Vineyard (TRW)

FEQL Lab Number	Sample Position Date	Sample Collection Date	Lab Receipt Date	Sample Analysis Date
Three Rivers Vineyard (TRW)				
TRW-D-041803	04/11/03	04/18/03	04/18/03	07/28/03
TRW-D-042403	04/18/03	04/24/03	04/24/03	08/04/03
TRW-D-050103	04/24/03	05/01/03	05/01/03	08/05/03
TRW-D-050803	05/01/03	05/08/03	05/08/03	08/06/03
TRW-D-051503	05/08/03	05/15/03	05/15/03	08/07/03
TRW-D-052203	05/15/03	05/22/03	05/22/03	08/11/03
TRW-D-052903	05/22/03	05/29/03	05/29/03	08/14/03
TRW-D-060503	05/29/03	06/05/03	06/05/03	08/18/03
TRW-D-061203	06/05/03	06/12/03	06/12/03	08/19/03
TRW-D-061903	06/12/03	06/19/03	06/19/03	08/20/03
TRW-D-062603	06/19/03	06/26/03	06/26/03	08/21/03

Table A-1. Dry Deposition Sample History Woodward Canyon Vineyard (WWC)

FEQL Lab Number	Sample Position Date	Sample Collection Date	Lab Receipt Date	Sample Analysis Date
Woodward Canyon Vineyard (WWC)				
WWC-D-041803	04/11/03	04/18/03	04/18/03	07/28/03
WWC-D-042403	04/18/03	04/24/03	04/24/03	08/04/03
WWC-D-050103	04/24/03	05/01/03	05/01/03	08/05/03
WWC-D-050803	05/01/03	05/08/03	05/08/03	08/06/03
WWC-D-051503	05/08/03	05/15/03	05/15/03	08/07/03
WWC-D-052203	05/15/03	05/22/03	05/22/03	08/11/03
WWC-D-052903	05/22/03	05/29/03	05/29/03	08/14/03
WWC-D-060503	05/29/03	06/05/03	06/05/03	08/18/03
WWC-D-061203	06/05/03	06/12/03	06/12/03	08/19/03
WWC-D-061903	06/12/03	06/19/03	06/19/03	08/20/03
WWC-D-062603	06/19/03	06/26/03	06/26/03	08/21/03

Table A-2. Deposition Sampling - Number of Positive Results & Maximum Residues

Location	Number of Samples	Number of Positive Results	Maximum Residue Detected
Site 1 (RNW)	11	11	4.51 ng/cm^2
Site 2 (SHV)	10	7	1.71 ng/cm^2
Site 3 (PBW)	10	7	2.87 ng/cm^2
Site 4 (LCW)	10	8	1.11 ng/cm^2
Site 5 (TRW)	11	8	4.30 ng/cm^2
Site 6 (WWC)	11	9	1.45 ng/cm^2
Method LOQ=0.48 ng/cm^2; LOD=0.12 ng/cm^2			

Table A-3. Wet Deposition Sample History Ash Hollow Vineyard (RNW)

FEQL Lab Number	Sample Collection Date	Lab Receipt Date	Sample Analysis Date
Ash Hollow Vineyard (RNW)			
RNW-W-050803	05/08/03	05/08/03	09/30/03
RNW-W-051203	05/12/03	05/12/03	09/30/03
RNW-W-051303	05/13/03	05/13/03	09/30/03
RNW-W-052603	05/26/03	05/26/03	10/01/03

Table A-3. Wet Deposition Sample History Seven Hills Vineyard (SHV)

FEQL Lab Number	Sample Collection Date	Lab Receipt Date	Sample Analysis Date
Seven Hills Vineyard (SHV)			
SHV-W-050803	05/08/03	05/08/03	09/30/03
SHV-W-051203	05/12/03	05/12/03	09/30/03
SHV-W-051303	05/13/03	05/13/03	09/30/03
SHV-W-052603	05/26/03	05/26/03	10/01/03

Table A-3. Wet Deposition Sample History Pepper Bridge Vineyard (PBW)

FEQL Lab Number	Sample Collection Date	Lab Receipt Date	Sample Analysis Date
Pepper Bridge Vineyard (PBW)			
PBW-W-052603	05/26/03	05/26/03	10/01/03
PBW-W-062303	06/23/03	06/23/03	10/01/03

Table A-3. Wet Deposition Sample History Les Collines Vineyard (LCW)

FEQL Lab Number	Sample Collection Date	Lab Receipt Date	Sample Analysis Date
Les Collines Vineyard (LCW)			
LCW-W-050503	05/05/03	05/05/03	09/30/03
LCW-W-050803	05/08/03	05/08/03	09/30/03
LCW-W-051203	05/12/03	05/12/03	09/30/03
LCW-W-051303	05/13/03	05/13/03	09/30/03
LCW-W-052603	05/26/03	05/26/03	10/01/03
LCW-W-062303	06/23/03	06/23/03	10/01/03

Table A-3. Wet Deposition Sample History Three Rivers Vineyard (TRW)

FEQL Lab Number	Sample Collection Date	Lab Receipt Date	Sample Analysis Date
Three Rivers Vineyard (TRW)			
TRW-W-052603	05/26/03	05/26/03	10/01/03
TRW-W-062303	06/23/03	06/23/03	10/01/03

Table A-3. Wet Deposition Sample History Woodward Canyon Vineyard (WWC)

FEQL Lab Number	Sample Collection Date	Lab Receipt Date	Sample Analysis Date
Woodward Canyon Vineyard (WWC)			
WWC-W-052603	05/26/03	05/26/03	10/01/03
WWC-W-062303	06/23/03	06/23/03	10/01/03

Table A-4. Wet Deposition, Number of Positive Results & Maximum Residues

Location	Number of Samples	Number of Positive Results	Maximum Residue Detected
Site 1 (RNW)	4	3	2.8 mg/L
Site 2 (SHV)	4	1	5.9 µg/L
Site 3 (PBW)	2	1	47.3 µg/L
Site 4 (LCW)	6	0	ND
Site 5 (TRW)	2	0	ND
Site 6 (WWC)	2	2	ND
Method LOQ=7 µg/L; LOD= ca. 2 µg/L; ND = concentration less than method LOD			

Table A-5. Air Sample History Ash Hollow Vineyard (RNW)

FEQL Lab Number	Sample Positioned Date	Air Sample Start Time	Sample Collection Date	Air Sample End Time	Lab Receipt Date	Particulate Filter Analysis Date	Polyurethane Foam Analysis Date
Ash Hollow Vineyard (RNW)							
RNW-A041003-F	04/10/03	0925	04/11/03	0846	04/11/03	06/19/03	05/02/03
RNW-A-041403	04/14/03	0935	04/15/03	0940	04/15/03	06/26/03	05/05/03
RNW-A-041703	04/17/03	1120	04/18/03	1200	04/18/03	07/03/03	05/06/03
RNW-A-042103	04/21/03	1000	04/22/03	0915	04/22/03	07/10/03	05/07/03
RNW-A-042403	04/24/03	0950	04/25/03	0920	04/25/03	07/15/03	05/12/03
RNW-A-042803	04/28/03	0945	04/29/03	0945	04/29/03	07/16/03	05/12/03
RNW-A-050103	05/01/03	0905	05/02/03	0815	05/02/03	07/23/03	05/14/03
RNW-A-050503	05/05/03	0900	05/06/03	0950	05/06/03	07/24/03	06/09/03
RNW-A-050803	05/08/03	1045	05/09/03	0930	05/09/03	07/28/03	06/11/03
RNW-A-051203	05/12/03	0930	05/13/03	0815	05/13/03	07/29/03	06/17/03
RNW-A-051503	05/15/03	0810	05/16/03	0930	05/16/03	07/31/03	06/17/03
RNW-A-051903	05/19/03	1013	05/20/03	0820	05/20/03	08/05/03	06/23/03
RNW-A-052203	05/22/03	0850	05/23/03	0930	05/23/03	08/05/03	06/24/03
RNW-A-052603	05/26/03	0840	05/27/03	0910	05/27/03	08/05/03	06/30/03
RNW-A-052903	05/29/03	*	05/30/03	*	05/30/03	08/05/03	07/01/03
RNW-A-060203	06/02/03	*	06/03/03	*	06/03/03	08/15/03	05/19/03
RNW-A-060503	06/05/03	0815	06/06/03	0750	06/06/03	08/16/03	05/19/03
RNW-A-060903	06/09/03	0755	06/10/03	0805	06/10/03	08/18/03	05/21/03
RNW-A-061203	06/12/03	0805	06/13/03	0805	06/13/03	08/19/03	05/27/03
RNW-A-061603	06/16/03	0850	06/17/03	0820	06/17/03	08/25/03	05/28/03
RNW-A-061903	06/19/03	0855	06/20/03	0810	06/20/03	08/26/03	06/02/03
RNW-A-062303	06/23/03	0915	06/24/03	0825	06/24/03	08/27/03	06/03/03
RNW-A-062603	06/26/03	0820	06/27/03	0550	06/27/03	08/25/03	06/09/03
* Indicates incomplete sample data							

Table A-5. Air Sample History Seven Hills Vineyard (SHV)

FEQL Lab Number	Sample Positioned Date	Air Sample Start Time	Sample Collection Date	Air Sample End Time	Lab Receipt Date	Particulate Filter Analysis Date	Polyurethane Foam Analysis Date
Seven Hills Vineyard (SHV)							
SHV-A-041003-F	04/10/03	1025	04/11/03	0950	04/11/03	06/19/03	04/29/03
SHV-A-041403	04/14/03	1015	04/15/03	1030	04/15/03	06/26/03	05/05/03
SHV-A-041703	04/17/03	1210	04/18/03	1250	04/18/03	07/03/03	05/06/03
SHV-A-042103	04/21/03	1045	04/22/03	1005	04/22/03	07/10/03	05/07/03
SHV-A-042403	04/24/03	1100	04/25/03	1115	04/25/03	07/15/03	05/12/03
SHV-A-042803	04/28/03	1040	04/29/03	1125	04/29/03	07/16/03	05/12/03
SHV-A-050103	05/01/03	1010	05/02/03	0850	05/02/03	07/23/03	05/14/03
SHV-A-050503	05/05/03	0940	05/06/03	1100	05/06/03	07/24/03	06/09/03
SHV-A-050803	05/08/03	1140	05/09/03	1010	05/09/03	07/28/03	05/19/03
SHV-A-051203	05/12/03	1225	05/13/03	1440	05/13/03	07/29/03	06/17/03
SHV-A-051503	05/15/03	0910	05/16/03	1015	05/16/03	07/31/03	06/17/03
SHV-A-051903	05/19/03	1055	05/20/03	1011	05/20/03	08/05/03	06/23/03
SHV-A-052203	05/22/03	1000	05/23/03	0910	05/23/03	08/05/03	06/24/03
SHV-A-052603	05/26/03	0925	05/27/03	1040	05/27/03	08/05/03	06/30/03
SHV-A-052903	05/29/03	0940	05/30/03	0830	05/30/03	08/05/03	07/01/03
SHV-A-060203	06/02/03	0840	06/03/03	0950	06/03/03	08/15/03	05/19/03
SHV-A-060503	06/05/03	0920	06/06/03	0830	06/06/03	08/16/03	05/19/03
SHV-A-060903	06/09/03	0840	06/10/03	0930	06/10/03	08/18/03	05/21/03
SHV-A-061203	06/12/03	0910	06/13/03	0900	06/13/03	08/19/03	05/27/03
SHV-A-061603	06/16/03	0935	06/17/03	1030	06/17/03	08/25/03	05/28/03
SHV-A-061903	06/19/03	*	06/20/03	*	06/20/03	08/26/03	06/02/03
SHV-A-062303	06/23/03	1010	06/24/03	0945	06/24/03	08/27/03	06/03/03
SHV-A-062603	06/26/03	0920	06/27/03	0630	06/27/03	08/25/03	06/09/03

* Indicates incomplete sample data

Table A-5. Air Sample History Pepper Bridge Vineyard (PBW)

FEQL Lab Number	Sample Positioned Date	Air Sample Start Time	Sample Collection Date	Air Sample End Time	Lab Receipt Date	Particulate Filter Analysis Date	Polyurethane Foam Analysis Date
Pepper Bridge Vineyard (PBW)							
PBW-A-041403	04/14/03	1045	04/15/03	1110	04/15/03	06/26/03	05/05/03
PBW-A-041703	04/17/03	1250	04/18/03	1425	04/18/03	07/03/03	05/06/03
PBW-A-042103	04/21/03	1110	04/22/03	1040	04/22/03	07/10/03	05/07/03
PBW-A-042403	04/24/03	1210	04/25/03	1235	04/25/03	NA	05/12/03
PBW-A-042803	04/28/03	1120	04/29/03	1220	04/29/03	07/16/03	05/12/03
PBW-A-050103	05/01/03	1105	05/02/03	0915	05/02/03	07/23/03	05/14/03
PBW-A-050503	05/05/03	1005	05/06/03	1150	05/06/03	07/24/03	06/09/03
PBW-A-050803	05/08/03	1245	05/09/03	1030	05/09/03	07/28/03	05/19/03
PBW-A-051203	05/12/03	1110	05/13/03	1345	05/13/03	07/29/03	06/17/03
PBW-A-051503	05/15/03	0950	05/16/03	1045	05/16/03	07/31/03	06/17/03
PBW-A-051903	05/19/03	1130	05/20/03	1150	05/20/03	08/05/03	06/23/03
PBW-A-052203	05/22/03	1055	05/23/03	0935	05/23/03	08/05/03	06/24/03
PBW-A-052603	05/26/03	1000	05/27/03	1210	05/27/03	08/05/03	06/30/03
PBW-A-052903	05/29/03	1020	05/30/03	0850	05/30/03	08/05/03	07/01/03
PBW-A-060203	06/02/03	0915	06/03/03	1105	06/03/03	08/15/03	05/19/03
PBW-A-060503	06/05/03	1000	06/06/03	1000	06/06/03	08/16/03	05/19/03
PBW-A-060903	06/09/03	0910	06/10/03	1130	06/10/03	08/18/03	05/21/03
PBW-A-061203	06/12/03	0955	06/13/03	0925	06/13/03	08/19/03	05/27/03
PBW-A-061603	06/16/03	1005	06/17/03	1210	06/17/03	08/25/03	05/28/03
PBW-A-061903	06/19/03	1255	06/20/03	1210	06/20/03	08/26/03	06/02/03
PBW-A-062303	06/23/03	1100	06/24/03	1115	06/24/03	08/27/03	06/03/03
PBW-A-062603	06/26/03	1005	06/27/03	0710	06/27/03	08/25/03	06/09/03

NA = sample not analyzed

Table A-5. Air Sample History Les Collines Vineyard (LCW)

FEQL Lab Number	Sample Positioned Date	Air Sample Start Time	Sample Collection Date	Air Sample End Time	Lab Receipt Date	Particulate Filter Analysis Date	Polyurethane Foam Analysis Date
Les Collines Vineyard (LCW)							
LCW-A-041003-F	04/10/03	1235	04/11/03	1055	04/11/03	06/19/03	05/02/03
LCW-A-041403	04/14/03	1115	04/15/03	1145	04/15/03	06/26/03	05/05/03
LCW-A-041703	04/17/03	1320	04/18/03	1530	04/18/03	07/03/03	05/06/03
LCW-A-042103	04/21/03	1140	04/22/03	1100	04/22/03	07/10/03	05/07/03
LCW-A-042403	04/24/03	1245	04/25/03	1340	04/25/03	07/15/03	05/12/03
LCW-A-042803	04/28/03	1155	04/29/03	1300	04/29/03	07/16/03	05/12/03
LCW-A-050103	05/01/03	1150	05/02/03	0930	05/02/03	07/23/03	05/14/03
LCW-A-050503	05/05/03	1030	05/06/03	1230	05/06/03	07/24/03	06/09/03
LCW-A-050803	05/08/03	1335	05/09/03	1055	05/09/03	07/28/03	06/11/03
LCW-A-051203	05/12/03	1140	05/13/03	1315	05/13/03	07/29/03	06/17/03
LCW-A-051503	05/15/03	1020	05/16/03	1100	05/16/03	07/31/03	06/17/03
LCW-A-051903	05/19/03	1155	05/20/03	1250	05/20/03	08/05/03	06/23/03
LCW-A-052203	05/22/03	1135	05/23/03	1010	05/23/03	08/05/03	06/24/03
LCW-A-052603	05/26/03	1025	05/27/03	1300	05/27/03	08/05/03	06/30/03
LCW-A-052903	05/29/03	1100	05/30/03	0915	05/30/03	08/05/03	07/01/03
LCW-A-060203	06/02/03	0945	06/03/03	1215	06/03/03	08/15/03	05/19/03
LCW-A-060503	06/05/03	1055	06/06/03	1025	06/06/03	08/16/03	05/19/03
LCW-A-060903	06/09/03	0935	06/10/03	1225	06/10/03	08/18/03	05/21/03
LCW-A-061203	06/12/03	1030	06/13/03	0945	06/13/03	08/19/03	05/27/03
LCW-A-061603	06/16/03	1030	06/17/03	1305	06/17/03	08/25/03	05/28/03
LCW-A-061903	06/19/03	1325	06/20/03	1230	06/20/03	08/26/03	06/02/03
LCW-A-062303	06/23/03	1130	06/24/03	1205	06/24/03	08/27/03	06/03/03
LCW-A-062303	06/26/03	1055	06/27/03	0735	06/27/03	08/25/03	06/09/03

Table A-5. Air Sample History Three Rivers Vineyard (TRW)

FEQL Lab Number	Sample Positioned Date	Air Sample Start Time	Sample Collection Date	Air Sample End Time	Lab Receipt Date	Particulate Filter Analysis Date	Polyurethane Foam Analysis Date
Three Rivers Vineyard (TRW)							
TRW-A-041003-F	04/10/03	1440	04/11/03	*	04/11/03	06/19/03	04/29/03
TRW-A-041403	04/14/03	1210	04/15/03	1305	04/15/03	06/26/03	05/05/03
TRW-A-041703	04/17/03	1430	04/18/03	1630	04/18/03	07/03/03	05/06/03
TRW-A-042103	04/21/03	1330	04/22/03	1155	04/22/03	07/10/03	05/07/03
TRW-A-042403	04/24/03	1345	04/25/03	1500	04/25/03	07/15/03	05/12/03
TRW-A-042803	04/28/03	1305	04/29/03	1405	04/29/03	07/16/03	05/12/03
TRW-A-050103	05/01/03	1240	05/02/03	1025	05/02/03	07/23/03	05/14/03
TRW-A-050503	05/05/03	1230	05/06/03	1335	05/06/03	07/24/03	06/09/03
TRW-A-050803	05/08/03	1450	05/09/03	1155	05/09/03	07/28/03	06/11/03
TRW-A-051203	05/12/03	1035	05/13/03	1156	05/13/03	07/29/03	06/17/03
TRW-A-051503	05/15/03	1140	05/16/03	1140	05/16/03	07/31/03	06/17/03
TRW-A-051903	05/19/03	1400	05/20/03	1320	05/20/03	08/05/03	06/23/03
TRW-A-052203	05/22/03	1350	05/23/03	1110	05/23/03	08/05/03	06/24/03
TRW-A-052603	05/26/03	1120	05/27/03	1420	05/27/03	08/05/03	06/30/03
TRW-A-052903	05/29/03	1235	05/30/03	0955	05/30/03	08/05/03	07/01/03
TRW-A-060203	06/02/03	1050	06/03/03	1325	06/03/03	08/15/03	05/19/03
TRW-A-060503	06/05/03	1255	06/06/03	1110	06/06/03	08/16/03	05/19/03
TRW-A-060903	06/09/03	1045	06/10/03	1335	06/10/03	08/18/03	05/21/03
TRW-A-061203	06/12/03	1135	06/13/03	1020	06/13/03	08/19/03	05/27/03
TRW-A-061603	06/16/03	1150	06/17/03	1405	06/17/03	08/25/03	05/28/03
TRW-A-061903	06/19/03	1405	06/20/03	1310	06/20/03	08/26/03	06/02/03
TRW-A-062303	06/23/03	1200	06/24/03	1315	06/24/03	08/27/03	06/03/03
TRW-A-062603	06/26/03	1145	06/27/03	0810	06/27/03	08/25/03	06/09/03

* Indicates incomplete sample data

Table A-5. Air Sample History Woodward Canyon Vineyard (WWC)

FEQL Lab Number	Sample Positioned Date	Air Sample Start Time	Sample Collection Date	Air Sample End Time	Lab Receipt Date	Particulate Filter Analysis Date	Polyurethane Foam Analysis Date
Woodward Canyon Vineyard (WWC)							
WWC-A-041403	04/14/03	1250	04/15/03	1330	04/15/03	06/26/03	05/05/03
WWC-A-041703	04/17/03	1505	04/18/03	1730	04/18/03	07/03/03	05/06/03
WWC-A-042103	04/21/03	1400	04/22/03	1300	04/22/03	07/10/03	05/07/03
WWC-A-042403	04/24/03	1420	04/25/03	1340	04/25/03	07/15/03	05/12/03
WWC-A-042803	04/28/03	1340	04/29/03	1430	04/29/03	07/16/03	05/12/03
WWC-A-050103	05/01/03	1310	05/02/03	1055	05/02/03	07/23/03	05/14/03
WWC-A-050503	05/05/03	1200	05/06/03	1400	05/06/03	07/24/03	06/09/03
WWC-A-050803	05/08/03	1530	05/09/03	1210	05/09/03	07/28/03	06/11/03
WWC-A-051203	05/12/03	1010	05/13/03	1025	05/13/03	07/29/03	06/17/03
WWC-A-051503	05/15/03	1225	05/16/03	1220	05/16/03	07/31/03	06/17/03
WWC-A-051903	05/19/03	1425	05/20/03	1340	05/20/03	08/05/03	06/23/03
WWC-A-052203	05/22/03	1440	05/23/03	1150	05/23/03	08/05/03	06/24/03
WWC-A-052603	05/26/03	1200	05/27/03	1445	05/27/03	08/05/03	06/30/03
WWC-A-052903	05/29/03	1310	05/30/03	1015	05/30/03	08/05/03	07/01/03
WWC-A-060203	06/02/03	1110	06/03/03	1345	06/03/03	08/15/03	05/19/03
WWC-A-060503	06/05/03	1340	06/06/03	1135	06/06/03	08/16/03	05/19/03
WWC-A-060903	06/09/03	1210	06/10/03	1400	06/10/03	08/18/03	05/21/03
WWC-A-061203	06/12/03	1215	06/13/03	1040	06/13/03	08/19/03	05/27/03
WWC-A-061603	06/16/03	1215	06/17/03	1425	06/17/03	08/25/03	05/28/03
WWC-A-061903	06/19/03	1440	06/20/03	0925	06/20/03	08/26/03	06/02/03
WWC-A-062303	06/23/03	1230	06/24/03	1340	06/24/03	08/27/03	06/03/03
WWC-A-062603	06/26/03	1230	06/27/03	0830	06/27/03	08/25/03	06/09/03

Table A-6. Air Sampling - Number of Positive Results and Maximum Residues

	Particulate Filter			Polyurethane Foam Plug		
Location	Number of Samples	Number of Positive Results	Maximum Residue Detected	Number of Samples	Number of Positive Results	Maximum Residue Detected
Site 1 (RNW)	21	18	0.0436 $\mu g/m^3$	21	8	0.0047 $\mu g/m^3$
Site 2 (SHV)	20	14	0.0085 $\mu g/m^3$	20	5	Trace
Site 3 (PBW)	21	16	0.0087 $\mu g/m^3$	21	8	Trace
Site 4 (LCW)	23	17	0.0104 $\mu g/m^3$	23	10	Trace
Site 5 (TRW)	22	16	0.0071 $\mu g/m^3$	22	9	Trace
Site 6 (WWC)	22	16	0.0075 $\mu g/m^3$	22	14	Trace

Method LOQ=0.004 $\mu g/m^3$; LOD=0.001 $\mu g/m^3$

Trace = non-quantifiable concentration greater than method LOD (>0.001 $\mu g/m^3$), but less than LOQ (<0.004 $\mu g/m^3$)

Table A-5. Air Sample History Woodward Canyon Vineyard (WWC)

FEQL Lab Number	Sample Positioned Date	Air Sample Start Time	Sample Collection Date	Air Sample End Time	Lab Receipt Date	Particulate Filter Analysis Date	Polyurethane Foam Analysis Date
Woodward Canyon Vineyard (WWC)							
WWC-A-041403	04/14/03	1250	04/15/03	1330	04/15/03	06/26/03	05/05/03
WWC-A-041703	04/17/03	1505	04/18/03	1730	04/18/03	07/03/03	05/06/03
WWC-A-042103	04/21/03	1400	04/22/03	1300	04/22/03	07/10/03	05/07/03
WWC-A-042403	04/24/03	1420	04/25/03	1340	04/25/03	07/15/03	05/12/03
WWC-A-042803	04/28/03	1340	04/29/03	1430	04/29/03	07/16/03	05/12/03

Appendix B

Analytical Summary

A. Scope

The analytical methods used in this study were derived from EPA Method 8151A (revised 1996) *"Chlorinated Herbicides by GC Using Methylation or Pentafluorobenzylation Derivatization."* The modifications to the above method for the specific requirements of analyzing 2,4-D residue in air and deposition samples are stated in the working methods.

The herbicides monitored for the 2003 study are the various formulations of 2,4-D.

B. Principles

The analytical method for the measurement of chlorinated herbicides involved extraction of the sampling media with base solution, hydrolysis, a liquid-liquid partition into methyl tert-butyl ether, and derivatization with diazomethane. Finally, a solvent exchange was performed prior to analysis by Gas Chromatography using electron capture detection (ECD).

C. Equipment

The following equipment and/or its equivalent were used in this study:

Sartorius Micro M5P analytical balance

Sartorius LC3200D top-loading balance

Standard laboratory glassware and equipment

Ultrasonic bath (VWRbrand)

Varian Star Chromatography Workstation

Varian Star 3400cx Gas Chromatograph

Varian 8200cx Auto Sampler

Zymark Turbo Vap II solvent evaporator

D. Reagents

The following reagents and/or equivalents were used in this study. All solvents were pesticide-analysis grade or better.

Acetone

Acetonitrile

Analytical Standards, Chem Service, Inc.

Diazomethane (prepared w/ 1-methyl-3-nitro-1-nitrosoguanidine, 5 N NaOH, and ethyl ether)

Ethyl acetate

Filter paper (Whatman No. 41)

Glass Wool, acidified

Methanol

Methyl t-butyl ether

Polyurethane foam plugs

Potassium hydroxide solution, 0.05 and/or 0.1 N

Sodium sulfate, pesticide grade (anhydrous, acidified)

Water, deionized and/or HPLC grade

E. Standards

Derivatized standards for the determination of total 2,4-D residues were prepared concurrently with derivatization of the field samples. For example, a matrix solution was fortified with 4 µg 2,4-D acid, derivatized and then brought to 2 mL for a 2 µg/mL derivatized standard solution. Dilutions of this matrix standard were then made to create linearity standards, typically 0.1 µg/mL, 0.5 µg/mL, and 1.0 µg/mL. The following test substances, standards, and standard dilutions were used throughout this study:

Test substance

Compound	Substance No.	Purity
2,4-D isooctyl ester	125800	99% mix of isomers
2,4-D	126000	98%

Stock Solution

Compound	Substance No.	Solvent	Conc.
2,4-D isooctyl ester	125830	methanol	1 mg/mL
2,4-D	126040	methanol	1 mg/mL

Dilution of Stock Solution

Compound	Substance No.	Solvent	Conc.
2,4-D isooctyl ester	125831	methanol	0.1 mg/mL
2,4-D	126041	methanol	0.1 mg/mL

Fortification Solutions

Compound	Substance No.	Solvent	Conc.
2,4-D isooctyl ester	125831	methanol	0.1 mg/mL
2,4-D	126041	methanol	0.1 mg/mL

The test substances were stored upon receipt in a ca. –20°C freezer according to standard operational practices for the handling of test substances: FEQL SOP 305, Storage Areas for Test Substances and Systems. All standard solutions were stored in a freezer at temperature below -15°C (Prancer).

F. Deposition Samples Analytical Method

Sample Preparation

To obtain representative deposition samples, four sampler trays were placed at each field site. Initially, 24, 12.5-cm diameter Whatman 41 filter papers were cut to fit the four pans for a total 2062 cm^2 surface area. Later in the study, a less-cumbersome 20.3 cm x 25.4 cm Whatman 41 filter paper sheet was used to fill each tray for the same overall surface area. The filters were combined to form a single composite sample at each site and sealed in a foil envelope on the day of collection. Each week, the six composite samples were dated on the day of collection and taken to the FEQL. All composite deposition samples were kept frozen at approximately -20 ˚C until matrix extraction. The first two sets analyzed used the full composite sample but due to excessive contaminants in the large sample size, GC analysis was not outstanding. Therefore, only one-fourth of the composite sample was extracted and analyzed for the remaining samples.

Sample Fortification

For validating the analytical method and for quality control sample fortifications Whatman 41, 12.5-cm diameter filter papers were fortified with the test substance. The 12.5 cm filter papers were used for the first two sets of deposition sample analysis. The remaining sample fortifications were conducted using Whatman 41, 20.3 cm x 25.4 cm filter papers. Fortifications

were made using a prepared 0.1 mg/mL solution of 2,4-D isooctyl ester (Ref. No. 125831) in methanol. All fortifications were administered directly onto the filter paper using microliter syringes prior to the initial extraction.

Procedure

The working method, "Method for the determination of residues of total 2,4-D on deposition paper samples by gas chromatography using electron capture detection" and the amendment to the working method (Amendment 2, see Appendix D) describe the extraction and analysis of 2,4-D from deposition samples.

Analytical Limits

The method sensitivities were determined by fortifying and recovering the isooctyl ester formulation of 2,4-D from untreated filter papers. The fortifications were made prior to the addition of base in the initial extraction. The method was validated with 2 µg and 5 µg 2,4-D isooctyl ester on deposition filter papers (i.e., equivalent to 0.967 ng/cm^2 and 2.42 ng/cm^2, respectively). The method limit of quantitation (LOQ) for the chlorinated herbicide was established at 1 µg or 0.48 ng/cm^2 of deposition surface area. The method limit of detection (LOD) was estimated to be 0.25 µg or 0.12 ng/cm^2. Table B-1 lists validation recovery results for the method. During the course of analysis, 2,4-D recovery results ranged from 64% to 124%, with an average recovery of 80.9% $\pm$ 20.4% (n =11).

Wet Deposition Samples Analytical Method

1. Sample Preparation

Wet deposition is considered any herbicide drift deposited by rain or irrigation water. Large bottles were sunk into the ground with 10-inch funnels secured to the opening to collect any wet deposition. Wet deposition collection jars were checked during each visit to the sites (four times per week); samples were taken on a random basis based on the presence of water in the jar. All wet deposition samples were kept refrigerated until matrix extraction.

2. Sample Fortification

For validating the analytical method and for quality control sample fortifications deionized water was fortified with the test substance. Fortifications were made using a prepared 0.1mg/mL solution of 2,4-D acid (Ref. No. 126041) in methanol. All fortifications were administered directly into the water using microliter syringes prior to the initial extraction.

3. Procedure

The working method, "Method for the determination of residues of total 2,4-D in rain water deposition by gas chromatography using electron capture detection" describes the extraction and analysis of 2,4-D from wet deposition samples.

4. Analytical Limits

The method sensitivity was determined by fortifying and recovering 2,4-D from 150 mL of laboratory water. The fortifications were made prior to the addition of base in the initial extraction. The method was validated at the 1-µg level of 2,4-D acid (i.e., equivalent to 7 µg/L of water collected. The method limit of quantitation (LOQ) for the chlorinated herbicide was established at 7 µg/L wet deposition. The method limit of detection (LOD) was estimated to be

ca. 2 µg/L. Table B-2 lists validation recovery results for the method. During the course of analysis, 2,4-D recovery results ranged from 75% to 85%, with an average recovery of 80% ± 6.6% (n =2).

G. Air Sample Particulate Filter Analytical Method

1. Sample Preparation

The first stage particulate filter was removed from the high-volume air samplers and sealed in a foil envelope on the day of sampling. These samples were then transferred to the FEQL. All samples were maintained at approximately -20°C until matrix extraction.

2. Sample Fortification

Whatman 41 filter papers were used for validating the analytical method and for quality control sample fortifications. The same manufacturing lot of papers was used for all method validation, field samples, fortification, and control samples. All fortifications were made directly onto the filter paper using microliter syringes prior to the initial extraction. Initially the method was validated for the analysis of 2,4-D acid, it was later validated for the isooctyl ester formulation of 2,4-D. Prepared 0.1-mg/mL solutions of 2,4-D (Ref. No. 126041) in methanol, and 2,4-D isooctyl ester (Ref. No. 125831) in methanol were used for fortifications.

3. Procedure

The working method, "Method for the determination of residues of total 2,4-D in air sample particulate filter by gas chromatography using electron capture detection" and the

amendment to the working method (Amendment 2, see Appendix D) describe the determination of total 2,4-D from particulate filters.

4. Analytical Limits

The method sensitivity was determined by fortifying and recovering 2,4-D or 2,4-D isooctyl ester from untreated filter papers. The fortifications were made prior to the initial extraction. The method was validated at 0.5 µg, 2-µg, and 5 µg 2,4-D acid and 2 µg 2,4-D isooctyl ester on particulate filter papers. Table B-3 summarizes validation recovery results for the method.

The limit of quantitation (LOQ) for the chlorinated herbicide in air samples was estimated to be 0.004 µg/m^3 (roughly equivalent to 0.5 µg total accumulation in air samples). The method limit of detection (LOD) was estimated to be 0.001 µg/m^3. During sample analysis, the average fortification recovery result was 79.7% $\pm$ 13.6 % (n=28).

H. Air Sample Polyurethane Foam Analytical Method

1. Sample Preparation

The second stage polyurethane foam plug (PUF) was removed from the air sampling canisters and sealed in a glass jar on the day of sampling. These samples were transferred to the FEQL. All samples were maintained at approximately -20^{o}C until matrix extraction.

2. Sample Fortification

New or freshly cleaned polyurethane foam plugs were used for validating the analytical method and for quality control sample fortifications. All fortifications were made using

microliter syringes prior to the initial extraction. Fortifications were made using prepared 0.1 mg/mL solutions of 2,4-D isooctyl ester (Ref. No. 125831).

3. Procedure

"Method for the determination of residues of total in air samples of polyurethane foam by gas chromatography using electron capture detection" (Appendix D) is the working method for the determination of total 2,4-D from polyurethane foam.

4. Analytical Limits

The PUF extraction method sensitivities were determined by fortifying and recovering 2,4-D isooctyl esters from untreated polyurethane foam. The fortifications were made prior to the addition of solvent in the initial extraction. The polyurethane foam working method was validated at 2 µg, 10 µg, and 20 µg 2,4-D isooctyl esters. Table B-4 lists the validation recovery results for the PUF extraction method. Average recovery during sample analysis was 70% ± 16% (n=22) for 2,4-D isooctyl esters.

The limit of quantitation (LOQ) for total 2,4-D in air samples was estimated to be 0.004 $\mu g/m^3$. The method limit of detection (LOD) was estimated to be 0.001 $\mu g/m^3$.

I. Instrumentation

Total 2,4-D residues were determined using a Varian Star 3400CX Gas Chromatograph with Electron Capture Detection (ECD) and a Varian Star 8200CX Auto Liquid Sampler (ALS). Typical operating conditions are described below:

GC/ECD CONDITIONS:

Column: Fused silica EC-5 bonded phase, 30 m x 0.25mm I.D. x 0.25 µm film thickness (Alltech Inc.).

Carrier gas: Ultrapure helium; Column flow rate: 3 ml/min.

Make-up Gas: Argon/Methane

Temperatures: Injector port: Temperature program from 80 °C to 250 °C at 250 °C per minute; hold at final temperature for seven minutes.

Column: Temperature program from 100 °C to 280 °C at 15 °C per minute; hold at final temperature for six minutes.

Detector: 320°C

2,4-D Retention Time: Approximately 7.4 min.

Injection volume: 1 µL

Quantitation

The quantitation of residues was performed by electronic peak area measurement and comparison to the linear regression from a minimum of four external standards in the concentration range of the matrix-sample residues. For quality control during the GC operation, all residue samples were bracketed with external calibration standards. For each analytical set, all linearity and calibration standards were included in the calculation of the linear regression curve using a spreadsheet program (Microsoft Excel®). The estimated concentration of residue in the sample extract was corrected for dilution by using a dilution factor. The residue values (in µg) were calculated according to the following equations.

Eq 1 Total Residue (µg) = (x µg/mL detected concentration) (Final volume of extract)

For example, deposition sample set dated 091803 included the preparation of deposition sample PBW-D-61203. One-fourth of the composite sample (one deposition paper) was processed for analysis to a final volume of 2 mL. The 2,4-D linear regression line of best fit calculated from the combined linearity and calibration standards (n =7, R^2 = 0.997) of this set was:

Y (area counts) = 470592X (detected concentration in µg/mL) + 30298

The 2,4-D-peak area count for this residue sample was 144135. Therefore, the concentration (in µg/mL) was:

$$X = \frac{(144135-30298)}{470592} = 0.24 \text{ µg/mL}$$

The total residue is then figured according to Eq. 1:

0.24 µg/mL x 2 mL = 0.48 µg Total 2,4-D

To assess overall analysis precision and percent recovery on a per-set basis, a control sample was fortified with a known amount of 2,4-D or 2,4-D isooctyl ester prior to extraction. For each analytical set, percent recovery for the fortified sample was calculated using peak areas according to the Equation 2.

$$\text{Eq.2: \% Recovery} = \frac{(\text{Fortified Peak} - \text{Control Peak})\text{Calculated Residue}}{\text{Fortification Amount}} \times 100$$

Example: For particulate filter sample set dated 082703, a particulate filter was fortified with 2-µg 2,4-D isooctyl ester. This fortification is equivalent to 1.33 µg 2,4-D in the acid form. The sample extract was prepared to a final volume of 2 mL for residue determination.

The linear regression line of best fit for 2,4-D calculated from the combined linearity and calibration standards (n=8, R^2=0.993) of this set was:

Y (area counts) = 477827X + 58790

The 2,4-D peak area count for this fortified sample was 350856. The peak area count for its corresponding control at the same dilution was 15848 area counts. The fortified sample concentration was:

$$(350856\text{-}15848) = 477827X + 58790$$

$$X = \frac{335008 - 58790}{477827} = 0.578\ \mu g/mL\ 2,4\text{-D}$$

The total residue is then calculated according to Eq. 1:

$$0.578\ \mu g/mL \times 2\ mL = 1.16\ \mu g\ 2,4\text{-D}$$

Calculated similarly, the control residue is

From Eq. 2, the percent recovery for this fortified sample was:

$$\text{Percent Recovery} = \frac{1.16\ \mu g}{1.33\ \mu g} \times 100 = 87\%$$

Confirmatory Techniques

Analytical standards, derivatized with the samples, were used to detect the presence 2,4-D residues in air and deposition samples by retention time. In the event that GC did not confirm the presence of a suspected pesticide residue, values were reported as “None Detected” (ND).

Time Required For Analysis

The time required for an experienced person to work up a set of samples (four to six samples) for analysis was approximately 6 hours. The time required for the GC analysis of a single sample was approximately 19 minutes. The duration of the GC analysis of a sample set depended upon the number of samples in a set and was automated using the auto sampler

associated with the instrument. Practical places to stop the sample work up are: 1) after the base extraction step, or 2) after the liquid/liquid partition step.

Information/Raw Data

Storage and Shipping

The deposition and air samples were transferred on the day of collection to the Food & Environmental Quality Laboratory (FEQL), Washington State University, 2710 University Drive, Richland, WA where they were logged and placed in frozen (-20^{o}C) storage.

Analytical Method Validation

Each method was independently validated to recover 2,4-D or 2,4-D isooctyl ester from the matrix. The isooctyl ester represents a typical ester formulation of 2,4-D. While the intent of the analytical methods is to determine total 2,4-D, it is recognized that the isooctyl ester of 2,4-D is the limiting species for analysis. That is, it is the most commonly used by area growers and it may be the most slowly hydrolyzed species of interest. Therefore, while the methods were initially validated for 2,4-D acid, validation and fortification recovery samples with the ester indicated that the methods were suitable for these species as well. Therefore, the methods were considered validated for measurement of total 2,4-D. Also included in this validation were appropriate controls. Tables B-1, B-2, B-3, and B-4 detail the validation results for each of the methods discussed.

Storage Stability

Six-month storage stability of 2,4-D acid on Whatman 41 filter was previously established for the FEQL study, "Year 2001 Impact of Airborne Herbicide Residues on Wine Grape Production." The 2,4-D compound was recovered at 98.7% after 182 days in frozen storage. Refer to the above project report for more information.

To determine the stability of other 2,4-D formulations on the filter paper media, FEQL fortified 12 Whatman No. 41 filter papers (lot #B1038944) with 25 µL of a 0.1-mg/mL standard solution of 2,4-D isooctyl ester (Ref. no. 125831) on August 4, 2003. This level of fortification results in 2.5-µg of 2,4-D isooctyl ester, equivalent to 1.66 µg 2,4-D acid, on each filter paper. The filter papers were packaged in aluminum foil envelopes and placed in a freezer at temperature ca. –20 °C (Dasher). The first set of three samples was analyzed immediately on 08/04/03, the second set of three samples was analyzed on 9/15/03, and the third set of three samples was analyzed on 10/27/03, after 84 days, to encompass the maximum time samples spent in frozen storage. The storage stability of the residues on these filter papers serves as stability information for both the first-stage particulate air filter and the deposition filter papers. Table B-5 lists the filter paper storage stability results.

To determine the storage stability of 2,4-D formulations on the polyurethane foam plug matrix, FEQL fortified 12 PUF plugs with 25 µL of a 0.1-mg/mL standard solution of 2,4-D isooctyl ester (Ref. no. 125831) on June 16, 2003. This level of fortification results in 2.5-µg of 2,4-D isooctyl ester or 1.66 µg of 2,4-D acid. The PUF plugs were packaged in aluminum foil and placed in a freezer at temperature ca. –20 °C (Dasher). The first set of three samples was analyzed immediately on 06/16/03, the second set of three samples was analyzed on 6/30/03, and

the third set of three samples was analyzed on 07/21/03, after 35 days, representing the maximum time samples spent in frozen storage. Table B-6 provides the PUF media storage stability results.

Residue Analyses

To determine chlorinated herbicide residue concentrations for each of the sample matrices, samples were extracted, partitioned and derivatized in accordance with the above-referenced analytical methods. Deposition sample residue results are listed in Table B-8. Wet deposition results are provided in Table B-9. The results for both first-stage particulate filter and polyurethane foam air samples are provided in Table B-10.

Results

A. Analytical Method Validation

The analytical methods for the measurement of formulations of the selective herbicide 2,4-D were validated in triplicate at 2 µg and 5 µg for deposition samples; 1 µg for wet deposition; 0.5 µg, 2 µg, and 5 µg for particulate filters; and, 2 µg, 10 µg, and 20 µg for polyurethane foam plugs. The method limit of quantitation (LOQ) was estimated to be 0.48 ng/cm^2 on deposition samples; 7 µg/L in wet deposition samples; and, 0.004 $µg/m^3$ in air sample matrices. The individual method validation recovery information can be found in Tables B-1, B-2, B-3, and B-4.

Representative chromatograms of standards, untreated matrix samples (controls), and fortification/recovery samples are presented in Appendix C. The residue methods for dry deposition, wet deposition, polyurethane foam, and particulate filter papers were shown to be reliable.

B. Residue Analyses

Method validation and recovery data are summarized in Table B-7. Calculated residue values from the composite deposition samples and wet deposition samples are presented in Tables B-8 and B-9, respectively. Residue results from the high volume air samplers are presented in Table B-10.

Average recovery of laboratory fortifications of 2,4-D analyzed during sample analysis of deposition papers was 80.9% $\pm$ 20.4% (n=11).

Average recovery of laboratory fortifications of 2,4-D analyzed during wet deposition sample analysis was 80.0% $\pm$ 6.6% (n=2).

The average recovery of fortified samples analyzed during particulate filter sample analysis was 91.8% $\pm$ 10.2% (n=28).

Finally, the average recovery for laboratory fortifications of polyurethane foam run during sample analysis was 68.9% $\pm$ 11.1% (n=22).

Representative chromatograms are provided in Appendix C.

C. Modifications and Potential Problems

Due to the nature of the sampling, in most cases analysis could not be repeated when a low fortification recovery occurred. Outside of possible extraction efficiency problems, the poor performance for some of the recovery fortifications cannot be explained since the analysts who performed each of the tasks did so in constructible, routine, and reproducible manners. When recovery issues were present, work on residue samples was stopped in order to identify and resolve the problem before re-initiating sample analysis. Any 2,4-D formulations potentially

present on the samples was converted to the acid form by base hydrolysis followed by isolation, and derivatization to form a methyl ester (see Appendix D).

For GC evaluation of the extracts, it was necessary to maintain a clean, well-silanized insert in the injection port to prevent peak splitting or peak tailing. Peak splitting can occur if the temperature programmable injection port is not properly set up for rapid volatilization of the sample. Additionally, the column hold-time was extended to eliminate late-eluting peaks, which could interfere in the chromatographic window. High-quality reagents that are free of interferences should be used to avoid chromatography problems with co-eluting peaks.

Conclusions

Methods suitable for the analysis of formulations of 2,4-D were developed and validated in order to measure residues in air samples and deposition samples. All reagents and instruments used during the course of this study were commercially available and typical of what would be present in most analytical laboratories.

References

Chlorinated herbicides by GC using methylation or pentafluorobenzylation derivatization, EPA Method 8151A, Rev.1, Dec. 1996.

Table B-1. Dry Deposition Samples Method Validation Results

Sample Identification Number	2,4-D Isooctyl Ester Fortification Level (µg)	Percent Recovery
072103-DEP-F1	2	99.4
072103-DEP-F2	2	103.4
072103-DEP-F3	2	77.9
Average: 93.6, Standard Deviation: 13.7.		
072403-FS-1	5	98.6
072403-FS-2	5	86.1
072803-FS-1	5	78
072803-FS-2	5	125.3
072803-FS-3	5	113.2
Average: 100.2, Standard Deviation: 19.3. Overall Average: 97.7, Overall Standard Deviation: 16.7.		

Table B-2. Wet Deposition Samples Method Validation Results

Sample Identification Number	2,4-D Isooctyl Ester Fortification Level (µg)	Percent Recovery
092403-W-FS-1	1	99.2
092403-W-FS-2	1	94.2
092403-W-FS-3	1	110.4
Average: 101.3, Standard Deviation: 8.3.		

Table B-3. Particulate Filter Method Validation

Sample Identification Number	2,4,D Acid Fortification (µg)	Percent Recovery
031003-FS4	0.5	94.9
031003-FS5	0.5	98.8
031003-FS6	0.5	100.5
Average: 98.1, Standard Deviation: 2.9.		
031003-FS1	2	97.2
031003-FS2	2	99.7
031003-FS3	2	104.9
Average: 100.6, Standard Deviation: 3.9.		
040703-PF-FS1	5	91.1
040703-PF-FS2	5	97.6
040703-PF-FS3	5	73.6
Average: 87.4, Standard Deviation: 12.4. Overall Average: 95.4, Overall Standard Deviation: 9.0.		

Table B-4. Particulate Filter Method Validation

Sample Identification Number	2,4,D Isooctyl Ester Fortification (µg)	Percent Recovery
091103-PF-FS-1	2	83.2
091103-PF-FS-2	2	84.8
091103-PF-FS-3	2	75.5
Average: 81.2, Standard Deviation: 5.0.		

Table B-5. Polyurethane Foam Method Validation Results

Sample Identification Number	2,4,D Isooctyl Ester Fortification (µg)	Percent Recovery
042903-LP-FS1	2	81.3
042903-LP-FS2	2	80.0
042903-LP-FS3	2	78.5
Average: 79.9, Standard Deviation: 1.4.		
042303-LP-FS3	10	51.5
042303-LP-FS4	10	73.4
042303-LP-FS5	10	62.6
050203-LP-FS4	10	63.6
Average: 62.8, Standard Deviation: 9.0.		
050203-LP-FS2	20	74.5
050203-LP-FS3	20	55.0
Average: 64.8, Standard Deviation: 13.8.		
Overall Average: 68.9, Overall Standard Deviation: 11.1.		

Table B-6. Filter Paper Storage Stability Results

Laboratory Sample Identification Number	Days of Storage	2,4-D Ester Fortification Level (µg)	Equivalent 2,4-D Fortification (µg)	2,4-D Recovered (µg)	Percent Recovery
080403-SS-FS1	0	2.5	1.66	1.34	80.8
080403-SS-FS2	0	2.5	1.66	1.24	74.9
080403-SS-FS3	0	2.5	1.66	1.31	79.3
080403-SS-FS4	42	2.5	1.66	1.32	79.7
080403-SS-FS5	42	2.5	1.66	1.38	83.5
080403-SS-FS6	42	2.5	1.66	1.32	79.4
080403-SS-FS7	84	2.5	1.66	1.81	109.3
080403-SS-FS8	84	2.5	1.66	1.71	102.8
080403-SS-FS9	84	2.5	1.66	1.71	103.2
Date Fortified: 08/04/03.					

Table B-7. Polyurethane Foam Storage Stability Results

Laboratory Sample Identification Number	Days of Storage	2,4-D Ester Fortification Level (µg)	Equivalent 2,4-D Fortification (µg)	2,4-D Recovered (µg)	Percent Recovery
060103-LP-FS1-SS	0	2.5	1.66	1.72	103.9
060103-LP-FS2-SS	0	2.5	1.66	1.54	92.7
060103-LP-FS3-SS	0	2.5	1.66	1.85	111.3
060103-LP-FS4-SS	14	2.5	1.66	1.70	102.6
060103-LP-FS5-SS	14	2.5	1.66	1.93	116.7
060103-LP-FS6-SS	14	2.5	1.66	1.96	118.0
060103-LP-FS7-SS	35	2.5	1.66	1.46	88.0
060103-LP-FS8-SS	35	2.5	1.66	1.65	99.7
060103-LP-FS9-SS	35	2.5	1.66	1.83	110.4
Date Fortified: 06/16/03.					

Table B-8. Storage Stability, Percent Recovery Results

	Recovery Range	Average	Standard Deviation
Deposition Samples			
Method Validation	77.9 – 125.3	97.7	16.7 (n=8)
Sample Set Recovery	64.2 – 123.8	80.9	20.4 (n=11)
Wet Deposition Samples			
Method Validation	94.2 – 110.4	101.3	8.3 (n=3)
Sample Set Recovery	75 - 85	80.0	6.6 (n=2)
Particulate Filter			
Method Validation	73.6 – 104.9	91.8	10.2 (n=12)
Sample Set Recovery	43.7 – 104.5	79.7	13.6 (n=28)
Polyurethane Foam			
Method Validation	51.5 – 81.3	68.9	11.1 (n=9)
Sample Set Recovery	36 - 107	70.1	16.4 (n=22)
N = Number of Samples.			

Table B-9. Deposition Sample Residue Results

FEQL Lab Designation			Quantity of Deposition Filters	Deposition Area Analyzed (cm^2)	2,4-D (ng/cm^2)
Ash Hollow Vineyard (RNW)					
RNW -	DEP -	4/18/2003	24	2062	4.51
RNW -	DEP -	4/24/2003	24	2062	0.70
RNW -	DEP -	5/1/2003	4	516	2.29
RNW -	DEP -	5/8/2003	4	516	0.97
RNW -	DEP -	5/15/2003	4	516	1.20
RNW -	DEP -	5/22/2003	4	516	0.70
RNW -	DEP -	5/29/2003	4	516	1.59
RNW -	DEP -	6/5/2003	4	516	(0.45)
RNW -	DEP -	6/12/2003	4	516	(0.41)
RNW -	DEP -	6/19/2003	4	516	(0.14)
RNW -	DEP -	6/26/2003	4	516	1.36
Seven Hills Vineyard (SHV)					
SHV -	DEP -	4/18/2003	24	2062	1.36
SHV -	DEP -	4/24/2003	24	2062	(0.18)
SHV -	DEP -	5/1/2003	1	516	(0.37)
SHV -	DEP -	5/8/2003	1	516	ND
SHV -	DEP -	5/15/2003	1	516	1.71
SHV -	DEP -	5/22/2003	1	516	NA
SHV -	DEP -	5/29/2003	1	516	1.55
SHV -	DEP -	6/5/2003	1	516	(0.45)
SHV -	DEP -	6/12/2003	1	516	0.85
SHV -	DEP -	6/19/2003	1	516	ND
SHV -	DEP -	6/26/2003		516	ND
Pepper Bridge Vineyard (PBW)					
PBW -	DEP -	4/18/2003	23	1976	1.61
PBW -	DEP -	4/24/2003	24	2062	(0.20)
PBW -	DEP -	5/1/2003	4	516	0.62
PBW -	DEP -	5/8/2003	4	516	ND
PBW -	DEP -	5/15/2003	4	516	(0.21)
PBW -	DEP -	5/22/2003	4	516	NA
PBW -	DEP -	5/29/2003	4	516	0.85
PBW -	DEP -	6/5/2003	4	516	2.87
PBW -	DEP -	6/12/2003	4	516	0.93
PBW -	DEP -	6/19/2003	4	516	ND
PBW -	DEP -	6/26/2003	4	516	ND
NA = Not Analyzed, ND = Not Detected, Residue < Level Of Detection, LOD, Numbers in parenthesis are < Level Of Quantitation, LOQ, but > LOD.					

Table B-10. Deposition Sample Residue Results

FEQL Lab Designation			Quantity of Deposition Filters	Deposition Area Analyzed (cm^2)	2,4-D (ng/cm^2)
Les Collines Vineyard (LCW)					
LCW -	DEP -	4/18/2003	24	2062	0.89
LCW -	DEP -	4/24/2003	24	2062	(0.18)
LCW -	DEP -	5/1/2003	4	516	(0.21)
LCW -	DEP -	5/8/2003	4	516	ND
LCW -	DEP -	5/15/2003	4	516	(0.25)
LCW -	DEP -	5/22/2003	4	516	(0.17)
LCW -	DEP -	5/29/2003	4	516	0.48
LCW -	DEP -	6/5/2003	4	516	1.01
LCW -	DEP -	6/12/2003	4	516	1.11
LCW -	DEP -	6/19/2003	4	516	ND
LCW -	DEP -	6/26/2003	No Sample		
Three Rivers Vineyard (TRW)					
TRW -	DEP -	4/18/2003	24	2062	0.87
TRW -	DEP -	4/24/2003	24	2062	ND
TRW -	DEP -	5/1/2003	1	516	4.31
TRW -	DEP -	5/8/2003	1	516	0.60
TRW -	DEP -	5/15/2003	1	516	(0.27)
TRW -	DEP -	5/22/2003	1	516	0.68
TRW -	DEP -	5/29/2003	1	516	(0.43)
TRW -	DEP -	6/5/2003	1	516	0.70
TRW -	DEP -	6/12/2003	1	516	(0.37)
TRW -	DEP -	6/19/2003	1	516	ND
TRW -	DEP -	6/26/2003	1	516	ND
Woodward Canyon Vineyard (WWC)					
WWC -	DEP -	4/18/2003	24	2062	1.45
WWC -	DEP -	4/24/2003	24	2062	(0.16)
WWC -	DEP -	5/1/2003	1	516	0.72
WWC -	DEP -	5/8/2003	1	516	0.72
WWC -	DEP -	5/15/2003	1	516	(0.14)
WWC -	DEP -	5/22/2003	1	516	0.62
WWC -	DEP -	5/29/2003	1	516	0.76
WWC -	DEP -	6/5/2003	1	516	0.50
WWC -	DEP -	6/12/2003	1	516	(0.23)
WWC -	DEP -	6/19/2003	1	516	ND
WWC -	DEP -	6/26/2003	1	516	ND

NA = Not Analyzed, ND = Not Detected, Residue < Level Of Detection, LOD, Numbers in parenthesis are < Level Of Quantitation, LOQ, but > LOD.

Table B-11. Wet Deposition Residue Results

Sample Identification Number	Rainwater volume (mL)	Wet Deposition Residue (µg/L)
Ash Hollow Vineyard (RNW)		
RNW-W-50803	26	ND
RNW-W-51203	125	2,800
RNW-W-51303	132	79.0
RNW-W-52603	24	71.3
Seven Hills Vineyard (SHV)		
SHV-W-50803	66	ND
SHV-W-51203	138	(5.9)
SHV-W-51303	52	ND
SHV-W-52603	148	ND
Pepper Bridge Vineyard (PBW)		
PBW-W-52603	133	ND
PBW-W-062303	108	47.3
Les Collines Vineyard (LCW)		
LCW-W-50503	125	ND
LCW-W-50803	8	ND
LCW-W-51203	138	ND
LCW-W-51303	136	ND
LCW-W-52603	128	ND
LCW-W-062303	110	ND
Three Rivers Vineyard (TRW)		
TRW-W-52603	138	ND
TRW-W-062303	26	ND
Woodward Canyon Vineyard (WWC)		
WWC-W-52603	78	(5.1)
WWC-W-062303	5	80.0
ND = Not Detected, Residue < Level Of Detection, LOD, Numbers in parenthesis are < Level Of Quantitation, LOQ, but > LOD.		

Table B-11. Air Sampler Residue Results

Sample Identification Number			Particulate Filter (ug/m^3)	Polyurethane Foam (ug/m^3)
Ash Hollow Vineyard				
RNW -	A -	04-10-03	0.0436	0.0047
RNW -	A -	04-14-03	0.0141	(0.0013)
RNW -	A -	04-17-03	0.0080	ND
RNW -	A -	04-21-03	0.0066	(0.0014)
RNW -	A -	04-24-03	(0.0030)	ND
RNW -	A -	04-28-03	0.0061	(0.0014)
RNW -	A -	05-01-03	0.0141	(0.0022)
RNW -	A -	05-05-03	ND	ND
RNW -	A -	05-08-03	(0.0023)	ND
RNW -	A -	05-12-03	(0.0015)	ND
RNW -	A -	05-15-03	(0.0014)	ND
RNW -	A -	05-19-03	(0.0017)	ND
RNW -	A -	05-22-03	(0.0017)	ND
RNW -	A -	05-26-03	ND	ND
RNW -	A -	05-29-03	NA	NA
RNW -	A -	06-02-03	NA	NA
RNW -	A -	06-05-03	0.0065	ND
RNW -	A -	06-09-03	(0.0034)	ND
RNW -	A -	06-12-03	ND	ND
RNW -	A -	06-16-03	(0.0031)	ND
RNW -	A -	06-19-03	(0.0035)	(0.0025)
RNW -	A -	06-23-03	(0.0013)	(0.0024)
RNW -	A -	06-26-03	(0.0022)	(0.0023)

Concentration calculations are based on air (m^3) sampled that period. The average volume of air sampled at this site was 297.57 m3

NA=Sample not analyzed. ND = Not Detected, Residue < Level Of Detection, LOD, Numbers in parenthesis are < Level Of Quantitation, LOQ, but > LOD.

Table B-12. Air Sampler Residue Results

Sample Identification Number			Particulate Filter (ug/m^3)	Polyurethane Foam (ug/m^3)
Seven Hills Vineyard				
SHV -	A -	04-10-03	0.0085	ND
SHV -	A -	04-14-03	(0.0013)	ND
SHV -	A -	04-17-03	(0.0013)	ND
SHV -	A -	04-21-03	0.0051	(0.0010)
SHV -	A -	04-24-03	ND	ND
SHV -	A -	04-28-03	(0.0032)	ND
SHV -	A -	05-01-03	(0.0010)	ND
SHV -	A -	05-05-03	ND	ND
SHV -	A -	05-08-03	(0.0024)	ND
SHV -	A -	05-12-03	ND	(0.0013)
SHV -	A -	05-15-03	ND	ND
SHV -	A -	05-19-03	(0.0029)	ND
SHV -	A -	05-22-03	(0.0021)	(0.0021)
SHV -	A -	05-26-03	ND	ND
SHV -	A -	05-29-03	0.0076	(0.0024)
SHV -	A -	06-02-03	(0.0014)	ND
SHV -	A -	06-05-03	NA	NA
SHV -	A -	06-09-03	NA	NA
SHV -	A -	06-12-03	ND	ND
SHV -	A -	06-16-03	(0.0038)	ND
SHV -	A -	06-19-03	NA	NA
SHV -	A -	06-23-03	(0.0013)	(0.0030)
SHV -	A -	06-26-03	(0.0012)	ND

Concentration calculations are based on air (m^3) sampled that period. The average volume of air sampled at this site was 280.82 m3.
NA = Sample not analyzed. ND = Not Detected, Residue < Level Of Detection, LOD, Numbers in parenthesis are < Level Of Quantitation, LOQ, but > LOD.

Table B-13. Air Sampler Residue Results

Sample Identification Number			Particulate Filter (ug/m^3)	Polyurethane Foam (ug/m^3)
Pepper Bridge Vineyard				
PBW -	A -	04-10-03	NA	NA
PBW -	A -	04-14-03	(0.0025)	ND
PBW -	A -	04-17-03	(0.0028)	ND
PBW -	A -	04-21-03	0.0073	(0.0029)
PBW -	A -	04-24-03	(0.0038)	ND
PBW -	A -	04-28-03	(0.0015)	(0.0013)
PBW -	A -	05-01-03	(0.0024)	ND
PBW -	A -	05-05-03	ND	ND
PBW -	A -	05-08-03	(0.0029)	(0.0017)
PBW -	A -	05-12-03	(0.0014)	ND
PBW -	A -	05-15-03	ND	ND
PBW -	A -	05-19-03	(0.0015)	ND
PBW -	A -	05-22-03	(0.0025)	(0.0018)
PBW -	A -	05-26-03	(0.0011)	ND
PBW -	A -	05-29-03	0.0087	(0.0027)
PBW -	A -	06-02-03	(0.0024)	ND
PBW -	A -	06-05-03	NA	NA
PBW -	A -	06-09-03	(0.0036)	(0.0012)
PBW -	A -	06-12-03	ND	ND
PBW -	A -	06-16-03	0.0050	ND
PBW -	A -	06-19-03	ND	ND
PBW -	A -	06-23-03	(0.0013)	(0.0011)
PBW -	A -	06-26-03	ND	(0.0026)

Concentration calculations are based on air (m^3) sampled that period. The average volume of air sampled at this site was 299.17 m3.
NA = Sample not analyzed. ND = Not Detected, Residue < Level Of Detection, LOD, Numbers in parenthesis are < Level Of Quantitation, LOQ, but > LOD.

Table B-14. Air Sampler Residue Results

Sample Identification Number			Particulate Filter (ug/m^3)	Polyurethane Foam (ug/m^3)
Les Collines Vineyard				
LCW -	A -	04-10-03	0.0061	(0.0017)
LCW -	A -	04-14-03	(0.0016)	ND
LCW -	A -	04-17-03	(0.0020)	ND
LCW -	A -	04-21-03	0.0059	ND
LCW -	A -	04-24-03	ND	ND
LCW -	A -	04-28-03	(0.0024)	ND
LCW -	A -	05-01-03	ND	ND
LCW -	A -	05-05-03	ND	ND
LCW -	A -	05-08-03	(0.0012)	(0.0011)
LCW -	A -	05-12-03	ND	(0.0013)
LCW -	A -	05-15-03	0.0044	ND
LCW -	A -	05-19-03	(0.0014)	ND
LCW -	A -	05-22-03	(0.0013)	(0.0012)
LCW -	A -	05-26-03	ND	ND
LCW -	A -	05-29-03	0.0104	(0.0029)
LCW -	A -	06-02-03	0.0054	(0.0022)
LCW -	A -	06-05-03	0.0100	(0.0028)
LCW -	A -	06-09-03	(0.0033)	ND
LCW -	A -	06-12-03	ND	ND
LCW -	A -	06-16-03	(0.0039)	(0.0016)
LCW -	A -	06-19-03	(0.0021)	(0.0010)
LCW -	A -	06-23-03	(0.0019)	(0.0020)
LCW -	A -	06-26-03	(0.0016)	ND

Concentration calculations are based on air (m^3) sampled that period. The average volume of air sampled at this site was 298.53 m3. ND = Not Detected, Residue < Level Of Detection, LOD, Numbers in parenthesis are < Level Of Quantitation, LOQ, but > LOD.

Table B-15. Air Sampler Residue Results

Sample Identification Number			Particulate Filter (ug/m^3)	Polyurethane Foam (ug/m^3)
Three Rivers Vineyard				
TRW -	A -	04-10-03	NA	NA
TRW -	A -	04-14-03	0.0040	ND
TRW -	A -	04-17-03	(0.0023)	ND
TRW -	A -	04-21-03	0.0054	(0.0011)
TRW -	A -	04-24-03	(0.0030)	(0.0015)
TRW -	A -	04-28-03	(0.0028)	(0.0013)
TRW -	A -	05-01-03	(0.0027)	ND
TRW -	A -	05-05-03	ND	ND
TRW -	A -	05-08-03	(0.0019)	(0.0011)
TRW -	A -	05-12-03	ND	ND
TRW -	A -	05-15-03	ND	ND
TRW -	A -	05-19-03	(0.0011)	ND
TRW -	A -	05-22-03	(0.0017)	ND
TRW -	A -	05-26-03	ND	ND
TRW -	A -	05-29-03	0.0072	(0.0010)
TRW -	A -	06-02-03	(0.0019)	(0.0014)
TRW -	A -	06-05-03	0.0071	(0.0026)
TRW -	A -	06-09-03	(0.0022)	ND
TRW -	A -	06-12-03	ND	ND
TRW -	A -	06-16-03	(0.0030)	(0.0016)
TRW -	A -	06-19-03	ND	(0.0010)
TRW -	A -	06-23-03	(0.0011)	ND
TRW -	A -	06-26-03	(0.0010)	ND

Concentration calculations are based on air (m^3) sampled that period. The average volume of air sampled at this site was 293.10 m3.
NA = Sample not analyzed. ND = Not Detected, Residue < Level Of Detection, LOD, Numbers in parenthesis are < Level Of Quantitation, LOQ, but > LOD.

Table B-16. Air Sampler Residue Results

Sample Identification Number			Particulate Filter (ug/m^3)	Polyurethane Foam (ug/m^3)
Woodward Canyon Vineyard				
WWC -	A -	04-21-03	0.0046	(0.0024)
WWC -	A -	04-24-03	(0.0028)	(0.0010)
WWC -	A -	04-28-03	(0.0038)	(0.0020)
WWC -	A -	05-01-03	0.0058	(0.0015)
WWC -	A -	05-05-03	ND	(0.0012)
WWC -	A -	05-08-03	(0.0023)	ND
WWC -	A -	05-12-03	(0.0011)	(0.0018)
WWC -	A -	05-15-03	ND	ND
WWC -	A -	05-19-03	(0.0021)	(0.0011)
WWC -	A -	05-22-03	ND	(0.0019)
WWC -	A -	05-26-03	ND	ND
WWC -	A -	05-29-03	0.0076	(0.0015)
WWC -	A -	06-02-03	ND	(0.0025)
WWC -	A -	06-05-03	0.0074	(0.0016)
WWC -	A -	06-09-03	(0.0034)	(0.0011)
WWC -	A -	06-12-03	ND	ND
WWC -	A -	06-16-03	(0.0028)	(0.0011)
WWC -	A -	06-19-03	(0.0029)	ND
WWC -	A -	06-23-03	(0.0016)	ND
WWC -	A -	06-26-03	(0.0011)	(0.0014)

Concentration calculations are based on air (m^3) sampled that period. The average volume of air sampled at this site was 279.71 m3.
NA = Sample not analyzed. ND = Not Detected, Residue < Level Of Detection, LOD, Numbers in parenthesis are < Level Of Quantitation, LOQ, but > LOD.
Began sampling at WWC April 14, 2003

Appendix C

Mean Leaf Index Values

Each leaf photo and field notes were examined to assign a Mean Leaf Index Value of zero to five, using 0.5 increments (Tables C-1 through C5).

Table C-1. Ash Hollow Vineyard Mean Leaf Index Value

Leaf Number	Vine Number		
	One	Two	Three
1	2.5	2.5	*
2	2.5	2	2
3	2	2	2
4	2	2	2
5	2	2	2
6	1.5	2.5	2
7	1.5	2	2
8	2	2	1.5
9	2.5	2	2.5
10	2.5	2.5	2
11	2.5	*	2
12	2.5	3	2
13	2.5	3	3
14	2.5	4	3
15	2.5	4	4
16	3	4.5	4.5
17	3.5	4.5	5
18	3.5	5	5
19	4	5	5
20	4	5	5
21	4	5	5
22	4	4	
23	4	4	
24		4	

* Indicates no data for that leaf

Table C-2. Seven Hills Vineyard Mean Leaf Index Value

Leaf Number	Vine Number		
	One	Two	Three
1	3	2	2.5
2	2.5	2	2
3	2.5	2	2
4	3.5	1.5	3
5	3.5	2	3
6	2	2	2
7	*	2.5	2
8	*	3	3.5
9	3.5	1	2
10	3.5	1.5	2
11	4	2.5	1
12	4.5	2.5	1
13	4.5	2.5	1
14	4.5	2.5	2
15	5	2.5	2
16		3	3
17		3.5	3
18		*	3.5
19		3	4
20		4	4
21		3	4
22		3	
23		3	
24			

* Indicates no data for that leaf

Table C-3. Pepper Bridge Vineyard Mean Leaf Index Value

Leaf Number	Vine Number		
	One	Two	Three
1	2.5	2	2
2	2.5	2	2
3	3	3	2
4	3	3	1
5	3	3	*
6	1.5	1.5	2
7	1.5	2	2.5
8	2	2	2.5
9	2	2.5	3
10	2	2	2
11	1.5	2.5	2
12	2	2.5	2.5
13	3	2.5	2.5
14	3	3	3
15	3	2	2.5
16	3	3.5	
17	4	4	
18	4	4	
19	4	4	
20	3	3.5	
21	4		
22	4		
23	4		
24			

* Indicates no data for that leaf

Table C-4. Les Collines Vineyard Mean Leaf Index Value

Leaf Number	Vine Number		
	One	Two	Three
1	2	2	2
2	2	2	2
3	2	2	2
4	2	2	1.5
5	1.5	2	1.5
6	1.5	3	2
7	2.5	1.5	2
8	*	1.5	*
9	1.5	1	1
10	1	1	2.5
11	1	*	1.5
12	1.5	2	2
13	1	1.5	1
14	1	1.5	1
15	1	1.5	1
16	0	1	1
17	*	1	1
18	*	0	0
19	2	0	0
20	0	0	
21		0	
22		0	
23		0	
24		0	

* Indicates no data for that leaf

Table C-5. Woodward Canyon Vineyard Mean Leaf Index Value

Leaf Number	Vine Number		
	One	Two	Three
1	*	2	2
2	*	2	2
3	2	2	2
4	2	2	2
5	1.5	3	2
6	2	1.5	1.5
7	1.5	1	1
8	1.5	1.5	1.5
9	1	1.5	1.5
10	1.5	2	2
11	2	2.5	2
12	2	3	2
13	1	3	2.5
14	1	3	2.5
15	1	3.5	3
16	1	3.5	4
17	1	4.5	4
18	1	4.5	4
19	1	4.5	4
20	1.5	4.5	4
21	2	4	5
22	2	4	4.5
23		4	4.5
24		3.5	4

* Indicates no data for that leaf

Appendix D

Internode Measurements

Table D-1. Ash Hollow Internode Lengths

Internode Number	Vine Number		
	One	Two	Three
3	25	35	31
4	64	60	48
5	71	62	77
6	74	61	80
7	79	75	62
8	57	60	80
9	50	53	72
10	76	54	66
11	58	56	79
12	64	56	70
13	87	70	58
14	66	53	64
15	50	46	46
16	60	54	41
17	47	34	41
18	32	32	38
19	36	32	36
20	24	19	15
21	19	14	17
22	17	13	10
23	11	9	
No. of Internodes	21	21	20
Max Length (mm)	87	75	80
Min Length (mm)	11	9	10
Average	50.8	45.1	51.6

Table D-2. Seven Hills Vineyard
Internode Lengths

Internode Number	Vine Number		
	One	Two	Three
3	43	35	35
4	63	72	57
5	58	82	68
6	46	73	60
7	54	72	67
8	43	66	48
9	37	105	58
10	42	95	88
11	36	121	83
12	52	114	80
13	38	88	81
14	37	90	68
15	37	67	41
16	18	50	49
17		38	39
18		30	27
19		25	23
20		25	13
21		21	5
22		21	5
23		19	5
24		16	
25		12	
26		14	
27			
No. of Internodes	14	24	21
Max Length (mm)	63	121	88
Min Length (mm)	18	12	5
Average	43.1	56.3	47.6

Table D-3. Pepper Bridge Vineyard
Internode Lengths

Internode Number	Vine Number		
	One	Two	Three
3	25	26	51
4	35	63	89
5	56	68	78
6	57	71	61
7	44	79	101
8	63	58	76
9	48	102	70
10	46	87	92
11	64	83	61
12	59	91	40
13	54	71	36
14	69	58	24
15	52	60	19
16	46	51	17
17	55	35	
18	46	49	
19	33	43	
20	42	33	
21	35	29	
22	29		
23	22		
24			
25			
26			
27			
No. of Internodes	21	19	14
Max Length (mm)	69	102	101
Min Length (mm)	22	26	17
Average	46.7	60.9	58.2

Table D-4. Les Collines Vineyard
Internode Lengths

Internode Number	Vine Number		
	One	Two	Three
3	22	18	39
4	33	32	61
5	42	42	59
6	35	55	61
7	30	48	72
8	51	54	53
9	40	60	72
10	57	48	82
11	58	55	72
12	59	69	72
13	50	58	107
14	64	52	74
15	54	79	77
16	55	63	90
17	57	57	70
18	43	69	68
19	49	55	87
20	48	58	
21	35	62	
22	40	47	
23		52	
24		53	
25		40	
26		33	
27		37	
No. of Internodes	20	25	17
Max Length (mm)	64	79	107
Min Length (mm)	22	18	39
Average	46.1	51.8	71.5

Table D-5. Woodward Canyon Vineyard Internode Lengths

Internode Number	Vine Number		
	One	Two	Three
3	91	62	38
4	72	76	53
5	136	75	58
6	104	72	79
7	80	62	56
8	72	63	41
9	93	64	49
10	74	57	47
11	91	83	49
12	108	62	66
13	90	70	50
14	84	60	50
15	88	50	56
16	61	55	42
17	54	45	31
18	54	45	37
19	39	45	23
20	34	35	19
21	31	29	27
22		26	15
23			
24			
25			
26			
27			
No. of Internodes	19	20	20
Max Length (mm)	136	83	79
Min Length (mm)	31	26	15
Average	76.6	56.8	44.3

Appendix E

Statistical Analysis Tables

Table E-1. Particulate Filter Paper Results (µg)

Date	LCW	PBW	RNW	SHV	TRW	WWC
April 7, 2003	1.54	1.85	12.41	2.34	2.09	*
April 14, 2003	0.65	1.68	6.41	<LOQ	1.84	1.29
April 21, 2003	1.69	3.5	2.81	1.4	2.53	2.16
April 28, 2003	0.79	1.2	6.31	0.93	1.68	2.79
May 5, 2003	<LOQ	0.78	0.63	<LOQ	0.51	0.56
May 12, 2003	1.36	0.51	<LOQ	0.63	<LOQ	<LOQ
May 19, 2003	<LOQ	0.66	0.52	1.21	<LOQ	0.59
May 26, 2003	2.88	2.47	<LOQ	1.73	1.82	1.92
June 2, 2003	4.64	0.77	1.88	<LOQ	2.47	1.78
June 9, 2003	1.03	1.1	1.01	0.82	0.7	0.99
June 16, 2003	1.82	1.55	1.8	1.14	0.86	1.56
June 23, 2003	0.58	<LOQ	0.61	<LOQ	<LOQ	<LOQ

<LOQ = analytical results that were below level of quantification.
* Indicates no data for that week

Table E-2. Polyurethane Foam Filter Results (µg)

Date	LCW	PBW	RNW	SHV	TRW	WWC
April 7, 2003	0.43	*	1.35	<LOQ	*	*
April 14, 2003	<LOQ	<LOQ	0.36	<LOQ	<LOQ	<LOQ
April 21, 2003	<LOQ	0.87	0.41	<LOQ	0.48	0.69
April 28, 2003	<LOQ	0.43	1.14	<LOQ	0.44	1.04
May 5, 2003	<LOQ	0.45	<LOQ	<LOQ	<LOQ	0.39
May 12, 2003	0.43	<LOQ	<LOQ	0.44	<LOQ	0.58
May 19, 2003	0.33	0.49	<LOQ	0.56	<LOQ	0.49
May 26, 2003	0.81	0.77	<LOQ	0.55	<LOQ	0.38
June 2, 2003	1.53	<LOQ	<LOQ	<LOQ	1.15	1.18
June 9, 2003	<LOQ	0.38	<LOQ	<LOQ	<LOQ	<LOQ
June 16, 2003	0.53	<LOQ	0.65	<LOQ	0.47	0.34
June 23, 2003	0.61	0.66	1.34	0.93	<LOQ	0.34

<LOQ = analytical results that were below level of quantification.
* Indicates no data for that week

Table E-3. Dry Deposition Results (µg)

Date	LCW	PBW	RNW	SHV	TRW	WWC
April 7, 2003	*	*	*	*	*	*
April 14, 2003	<LOQ	3.18	9.30	2.81	<LOQ	3.00
April 21, 2003	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
April 28, 2003	<LOQ	<LOQ	<LOQ	<LOQ	2.22	<LOQ
May 5, 2003	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
May 12, 2003	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
May 19, 2003	<LOQ	*	<LOQ	*	<LOQ	<LOQ
May 26, 2003	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
June 2, 2003	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
June 9, 2003	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
June 16, 2003	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
June 23, 2003	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
June 26, 2003	*	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

<LOQ = analytical results that were below level of quantification.
* Indicates no data for that week

Table E-4. Wet Deposition Results (µg)

Date	LCW	PBW	RNW	SHV	TRW	WWC
April 7, 2003	*	*	*	*	*	*
April 14, 2003	*	*	*	*	*	*
April 21, 2003	*	*	*	*	*	*
April 28, 2003	*	*	*	*	*	*
May 5, 2003	<LOQ	*	<LOQ	<LOQ	*	*
May 12, 2003	<LOQ	*	411.29	<LOQ	*	*
May 19, 2003	*	*	*	*	*	*
May 26, 2003	<LOQ	*	10.19	<LOQ	<LOQ	<LOQ
June 2, 2003	*	*	*	*	*	*
June 9, 2003	*	*	*	*	*	*
June 16, 2003	*	*	*	*	*	*
June 23, 2003	<LOQ	6.76	*	*	<LOQ	11.43

<LOQ = analytical results that were below level of quantification.
* Indicates no data for that week

Table E-5. Daily Average Wind Direction April, May & June 2003

Date	Wind Direction	Date	Wind Direction	Date	Wind Direction
April 1, 2003	209	May 1, 2003	241.6	June 1, 2003	228.7
April 2, 2003	189.5	May 2, 2003	213.5	June 2, 2003	262.1
April 3, 2003	208.9	May 3, 2003	202.1	June 3, 2003	279.3
April 4, 2003	201.3	May 4, 2003	216.7	June 4, 2003	200.2
April 5, 2003	218.4	May 5, 2003	217.3	June 5, 2003	261.4
April 6, 2003	220.4	May 6, 2003	251.3	June 6, 2003	293.2
April 7, 2003	149.3	May 7, 2003	239.4	June 7, 2003	355.9
April 8, 2003	134.6	May 8, 2003	286.2	June 8, 2003	212.3
April 9, 2003	195.8	May 9, 2003	227.6	June 9, 2003	204.2
April 10, 2003	228.8	May 10, 2003	211.9	June 10, 2003	208.1
April 11, 2003	130.4	May 11, 2003	207.4	June 11, 2003	213.3
April 12, 2003	37.8	May 12, 2003	223.3	June 12, 2003	226.6
April 13, 2003	157.3	May 13, 2003	92.7	June 13, 2003	236.5
April 14, 2003	219.2	May 14, 2003	222.3	June 14, 2003	228.7
April 15, 2003	213.7	May 15, 2003	223.9	June 15, 2003	291.4
April 16, 2003	208	May 16, 2003	218	June 16, 2003	255.2
April 17, 2003	212.9	May 17, 2003	214	June 17, 2003	242.2
April 18, 2003	209	May 18, 2003	204.7	June 18, 2003	213
April 19, 2003	295	May 19, 2003	7.3	June 19, 2003	206.3
April 20, 2003	262.4	May 20, 2003	284.9	June 20, 2003	211.4
April 21, 2003	218.5	May 21, 2003	229.2	June 21, 2003	212.5
April 22, 2003	196.8	May 22, 2003	291.6	June 22, 2003	204.1
April 23, 2003	202.3	May 23, 2003	258.7	June 23, 2003	211.9
April 24, 2003	202.6	May 24, 2003	233	June 24, 2003	256
April 25, 2003	25.1	May 25, 2003	220.3	June 25, 2003	214.5
April 26, 2003	217.5	May 26, 2003	195.7	June 26, 2003	312.3
April 27, 2003	38.7	May 27, 2003	45.7	June 27, 2003	330.9
April 28, 2003	210.9	May 28, 2003	238.7	June 28, 2003	278.8
April 29, 2003	322.5	May 29, 2003	256.9	June 29, 2003	260.8
April 30, 2003	244.7	May 30, 2003	206.8	June 30, 2003	239.2
		May 31, 2003	214.5		

Table E-6. Weekly Average Wind Direction

Week	2003		
	April	May	June
1	208	218	229
2	148	234	266
3	231	200	230
4	157	218	221
5	259	193	266
6			239

Table E-7. Regression Analysis: Date versus PBW, RNW, SHV, WWC, LCW, TRW Residues

Predictor	Coef	SE Coef_1	T	P
Constant	37772.2	154	245.3	0
PBW	-10.7	97.53	-0.11	0.916
RNW	-0.3	0.699	-0.4	0.703
SHV	81.8	116.3	0.7	0.508
WWC	-11.4	59.19	-0.19	0.854
LCW	14.3	48.98	0.29	0.78
TRW	-9	59.05	-0.15	0.884

The regression equation is Date = 37772 - 10.7 PBW - 0.279 RNW + 82 SHV - 11.4 WWC + 14.3 LCW - 9.0 TRW S = 243.107. R-Sq = 19.6%

Table E-8. ANOVA: PBW, RNW, SHV, WWC, LCW, TRW Residues

Source	DF	SS	MS	F	P
Factor	5	12793	2559	1.2	0.316
Error	72	153004	2125		
Total	77	165797			
Level	N	Mean	StDev		
PBW	13	2.31	2.1		
RNW	13	36.19	112.83		
SHV	13	1.19	0.92		
WWC	13	2.58	3.09		
LCW	13	1.67	1.7		
TRW	13	1.48	1.47		
S = 46.10 R-Sq = 7.72% Pooled StDev = 46.10					

Table E-9. Regression Analysis: Week versus Leaf Index

Predictor	Coef	SE Coef	T	P
Constant	37716	6.3	5993.53	0
Leaf Index	18.749	2.181	8.6	0
The regression equation is Week = 37716 + 18.7 Leaf Index. 44 cases used, 16 cases contain missing values. S = 13.7275 R-Sq = 63.8%				

Table E-10. ANOVA Leaf Index Value Comparison Between RNW, PBW, SHV, and WWC

Source	DF	SS	MS	F	P
Factor	3	2.88	0.96	1.29	0.283
Error	90	67.006	0.745		
Total	93	69.886			
Level	N	Mean	StDev		
RNW	24	3.0042	1.072		
PBW	23	2.8696	0.7951		
SHV	23	2.8609	0.5719		
WWC	24	2.5333	0.9201		
S = 0.8629 R-Sq = 4.12% Pooled StDev = 0.8629					

Table E-11. Regression Analysis: RNW Residue versus RNW Leaf

Predictor	Coef	SE Coef	T	P
Constant	139.9	110.8	1.26	0.243
RNW	-33.86	36.37	-0.93	0.379
The regression equation is RNWR = 140 - 33.9 RNWL S = 130.038 R-Sq = 9.8%				

Figure E-12. Regression Analysis: PBW Residue versus PBW Leaf Index Value

Predictor	Coef	SE Coef	T	P
Constant	-2.067	2.145	-0.96	0.364
PBW	1.7748	0.8335	2.13	0.066
The regression equation is PBWR = - 2.07 + 1.77 PBWL				
10 cases used, 5 cases contain missing values				
S = 0.732278 R-Sq = 3.5%				

Figure E-13. Regression Analysis: SHV Residue versus SHV Leaf Index Value

Predictor	Coef	SECoef	T	P
Constant	1.558	0.9969	1.56	0.157
SHVL	-0.1858	0.3438	-0.54	0.604
The regression equation is SHVR = 1.56 - 0.186 SHVL				
10 cases used, 5 cases contain missing values				
S = 0.732278 R-Sq = 3.5%				

Figure E-14. Regression Analysis: WWC Residue versus WWC Leaf Index Value

Predictor	Coef	SECoef	T	P
Constant	-1.013	3.027	-0.33	0.747
WWCL	1.741	1.266	1.38	0.206
The regression equation is WWCR = - 1.01 + 1.74 WWCL				
10 cases used, 5 cases contain missing values				
S = 3.13240 R-Sq = 19.1%				

Figure E-15. Regression Analysis of RNW Residue versus RNW Internode Length

Predictor	Coef	SECoef	T	P
Constant	0.249	5.11	0.05	0.963
RNWI	0.05576	0.09852	0.57	0.602
The regression equation is RNWR = 0.25 + 0.0558 RNWI				
6 cases used, 9 cases contain missing values				
S = 3.86285 R-Sq = 7.4%				

Figure E-16. Regression Analysis PBW Residue versus PBW Internode

Predictor	Coef	SECoef	T	P
Constant	8.606	3.681	2.34	0.08
PBWI	-0.10753	0.06402	-1.68	0.168
The regression equation is PBWR = 8.61 - 0.108 PBWI				
6 cases used, 9 cases contain missing values				
S = 2.14727 R-Sq = 41.4%				

Figure E-17. Regression Analysis of SHV Residue versus SHV Internode

Predictor	Coef	SECoef	T	P
Constant	0.702	1.139	0.62	0.571
SHVI	0.00842	0.02004	0.42	0.696
The regression equation is SHVR = 0.70 + 0.0084 SHVI				
6 cases used, 9 cases contain missing values				
S = 0.867192 R-Sq = 4.2%				

Figure E-18. Regression Analysis of WWC Residue versus WWC Internode Length

Predictor	Coef	SECoef	T	P
Constant	14.784	6.456	2.29	0.084
WWCI	-0.1974	0.1102	-1.79	0.148
The regression equation is WWCR = 14.8 - 0.197 WWCI				
6 cases used, 9 cases contain missing values				
S = 3.43117 R-Sq = 44.5%				

Appendix F

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