Appendix B:

Air Sampling Report

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Organophosphorus Pesticide Air Monitoring Project

Air Sampling Report
30 June 2009

1.0 Introduction

This air monitoring report covers the air sampling components of the project including site selection, air sample collection, sampling equipment calibration, and air concentration calculations. Details of the field procedures are contained in the project Standard Operating Procedures attached in Appendix L of this report.

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SOP7 Rotameter Calibration in Laboratory
SOP8 Chain of Custody

*Note: The DryCal name has been replaced with Defender 520. Both the DryCal and the Defender 520 refer to the calibrator used in the study.

2.0 Site Selection

The site selection process first identified two regions. Within each region we contacted potential cooperators as described below. A key aspect to obtaining cooperation from each site was to assure the grower or occupants that participation in the study was confidential, and we should not identify the cooperator or disclose the site location. For every site in the study, study team members conducted a pre-selection visit to determine site suitability and verify that the site met study requirements and was comfortable with the placement of equipment on the property.

2.1 Regions

The site selection process started with identifying two tree fruit regions of Washington State where OP pesticide applications typically occur: the North Central District (Region 1) and the Yakima Valley (Region 2). The chlorpyrifos and azinphos-methyl use-density maps for the North Central District and the Yakima Valley were developed by our research team using data from the WA Department of Agriculture, the National Agricultural Statistical Service, and the U.S. Census. A description of the method used to develop the maps is also included as part of the August 1, 2008 report. Prior to selecting specific sites we

spoke with Agricultural Extension Service scientists and specialists, crop advisors (field men), and growers. We compared their reports of 2008 practices, and pesticide usage to data from the maps. We also used the 2008 information to select appropriate areas within a region from which we recruited specific sites.

2.2 Perimeters sites

The perimeter sampling sites were selected in cooperation with the grower community. The following criteria were used to select these sites.

- Well-defined orchard block that can be treated in one day by a single applicator
- Research staff access to the site 24 hours per day for the 4 day study period
- Application with power blast application equipment
- No drift retardant used during applications
- Secure; based on discussions with the owner
- Use of generators 24 hours per day acceptable to property owners and neighbors
- Treated block at least 100 meters from other orchards that will be treated with chlorpyrifos (Phase 1) or azinphosmethyl (Phase 2) during the study period
- Access to information on the amount of pesticide used during the application

One perimeter site was selected for each region. The same Yakima Valley site was used for both Phase 1 and Phase 2. The grower provided information regarding the application rate, the duration of application, the total amount of active ingredient applied, and other information relevant to an emission rate estimate.

2.3 Receptor sites

Potential sampling sites were identified in cooperation with farm workers, residential and school community members, and community organizations. We selected three sites in each region that had the potential to receive relatively high OP pesticide exposures during power blast application on tree fruit. When possible, we selected sites in proximity to multiple orchards. While we were not able to pre-determine if nearby orchards were being treated with conventional pesticides, staff observed posted signs such as those for re-entry and those posted along road right-of-ways indicating organic orchards. The following were the receptor site requirements.

- Within 100 meters of orchards to be treated with chlorpyrifos (Lorsban®), azinphosmethyl (Guthion®), or phosmet (Imidan®) during the study period
- Secure; fenced or locked or not readily accessible to the public
- Access for staff 7 days per week for 28 days
- Outdoor AC 110 power outlet, if possible
- Low foot traffic

- Not a pet or play area
- No vehicle traffic
- Visitor-friendly pets only
- Sampler located 1-2 meters from the ground
- Sampler distance from buildings, walls, or solid fences at least one-half the height of the structure (for buildings use the roof peak as the structure height)

Three sites in each region were selected for the receptor sampling. Each sample location was documented with GPS coordinates using an Enertech Global Positioning System Recording Meter (Campbell, CA). The quality control air samples were co-located at one of the three receptor sites in each region.

Note: *Replacement sites were recruited as needed following the same protocol as for the original site selection. During Phase 1 one site in Yakima Valley was replaced before sampling started. Before Phase 2 begun, two sites in Yakima Valley were replaced.*

2.4 Ambient community sites

The ambient community sites were situated in a community nearby the receptors sites. The ambient community site criteria were as follows:

- At least 500 meters from orchards to be treated with chlorpyrifos (Lorsban®), azinphosmethyl (Guthion®), or phosmet (Imidan®) during the study period
- Secure; fenced or locked or not readily accessible to the public
- Access for staff 7 days per week for 28 days
- Outdoor AC 110 power outlet, if possible

One ambient community site was selected for each of the two regions.

3.0 Air Sample Collection

Sampling and analysis for volatized OP pesticides were conducted following the NIOSH Analytical Method 5600 *Organophosphorus Pesticides* (NIOSH 1994) and the sampling approach of the California Air Resources Board (CARB) as summarized by Baker et al. (Baker 1996). Modifications to these methods were made to accommodate the requirements of this study and are included in the methods description below.

In accordance with the NIOSH method, we used OVS XAD®-2 sorbent tubes. These sampling tubes consisted of a 13-mm quartz particulate matter filter, followed by a front and a back up section of XAD®-2 sorbent. Sample flow rates were adjusted to approximately 2.0 liters per minute (lpm) for the receptor and ambient samples 6.0 lpm for the perimeter samples. Two samples, one primary and the other a backup sample, were collected in tandem for each sample period at each site and location. (Back up samples are held in reserve and only analyzed if the primary sample is compromised.)

3.1 Sampling apparatus

The sampling train for all sample pairs was attached to a 2 meter 'T'-shaped mast with a cover for rain protection. (See Figure 1.) Each side of the 'T' held one XAD®-2 parallel to the ground. Flow rates for each sample were monitored and adjusted with dedicated rotameters that were calibrated before and after the study period using a Defender 520 Airflow Meter (BIOS International Corporation, model no DCLT-12K, Butler, NJ). The Defender 520 was calibrated to a bubble flow meter (primary standard) prior to the rotameter calibration. (See SOP 1: Sample Apparatus Set-Up, SOP 6: Defender 520 Calibration in Laboratory, and SOP 7: Rotameter Calibration in Laboratory in Appendix B.)

Perimeter samples were collected using SKC Hi-Lite 30 air sampling pumps (cat no 228-031, SKC Inc, Eighty Four, PA). One pump was used for each sample location, with the air flow from the pump split between the two rotameters.

Each near-field receptor and community ambient air sample was collected with a separate SKC Universal Sample Pump (cat no 224-PCXRB, SKC Inc, Eighty Four, PA). Because of the long sample periods (24 hours), the pumps were equipped with a Battery Eliminator (cat no 223-325, SKC Inc, Eighty Four, PA) to enable the use of marine deep cycle batteries or a 110 AC for power. These power sources were used because the pump battery was limited to an 8 hr run time before needing to be recharged.

Figure 1. Air sampling apparatus.
Picture is facing away from the perimeter study block.

3.2 Perimeter site layout and sampling plan

The sample collection procedures are detailed in SOP 3: Perimeter Air Sample Collection and SOP 3A: Perimeter Air Sample Collection-Addendum, located in Appendix L. The addendum includes modifications for Phase 2. SOP 5: Labeling, covers the unique sample identifiers for each sample.

3.2.1 Site layout. For each site, the eight perimeter sampling locations (stations) were set at the same distance from the orchard edge (defined by the outer tree trunks) and were approximately equidistant from each other. Additional factors that influenced the final location placement were as follows:

- One station at approximately each corner of the treated area (up to four)
- Locations not to block orchard access roads that circumvent orchard blocks
- Locations not to interfere with other orchard activities and equipment (e.g. irrigation, other types of applications, thinning, pruning)

Each sample location was documented with GPS coordinates using an Enertech Global Positioning System Recording Meter (Campbell, CA).

3.2.2 Sampling plan. We conducted near-field perimeter sampling following the approach used by the California Air Resources Board (L. Baker, personal communication). The methods were modified to accommodate conditions specific to this project. A four-day sampling schedule was used for each region: pre-spray day; spray day; post-spray day 1; and post-spray day 2. The details of the sampling plan used for bother perimeter sites during Phase 1 and the one site during Phase 2 are included in the Final Report.

Note: *Changes in the proposed sampling plan were made to accommodate orchard application schedules and to increase sample volumes. Changes included: Spray-day, changed from three 8 hr sample periods to two 6 hr sample periods and one 12 hr sample period. Post-spray 1: changed from three 8 hr sample periods to two 12 hr sample periods.*

3.2.3 Field quality control samples*.* Quality control (QC) samples for each sample period in Phase 1 and Phase 2 consisted of two field blanks and two trip spikes. For Phase 1, chlorpyrifos spike loads were 50 ng/tube for the low concentration and 250 ng /tube for the high concentration. For Phase 2 each spike tube was loaded with 50 ng of azinphosmethyl, phosmet, and malathion, and 20 ng of azinphosmethyl-oxon.

3.2.4 Global Positioning System (GPS). During the spray event the tractor path was documented with an Enertech Global Positioning System Recording Meter (Campbell, CA) that recorded the GPS coordinates every 3 seconds. The unit was mounted on the tractor and the distance from the spray nozzles was recorded.

3.3 Near-field receptor and ambient community air samples sampling plan

One set of two side-by-side air samples were collected during each sample period for all receptor and ambient community sites. One set of quality control air samples was collected each sample period at one of receptor sites. The sample period was 24-hr. In Phase 1, sampling took place in March and April and sample periods were scheduled daily for 28 days. In Phase 2, the sampling periods were once every three days over a 70 day period during May, June, and July. Additional information on the sampling plan is included in the Final Report.

Sample collection procedures are described in SOP 4: Receptor & Ambient Air Sample Collection and SOP 4A: Receptor & Ambient Air Sample Collection – Addendum, located in Appendix C. The addendum includes modifications for Phase 2. SOP 5: Labeling covers the unique sample identifiers for each sample.

Note*: During Phase 1, the sampling schedule was extended beyond 28 days due to replacement of one site (Yakima Valley) and the delay of the spray period due to cold weather (North Central District).*

3.3.1 Field quality control samples. For each region, two quality control air samples were co-located at one of the receptor sites. The field quality control samples for each 24 hr sample period consisted of one field blank and one trip spike. The spike load for Phase 1 spike was 12.5 ng/tube of chlorpyrifos. The spike load in Phase 2 was 50 ng each of azinphosmethyl, azinphosmethyl-oxon, phosmet, and malathion/tube.

3.3.2 ***Global Positioning System (GPS).*** Each site position was documented with an Enertech Global Positioning System Recording Meter (Campbell, CA.)

3.4 Sample storage and transport.

After each sample period, the tubes were recapped, placed in individual resealable bags, and stored on ice for transportation to the PNASH field office freezer (-10 C). Samples were then transported on dry ice to the Fenske laboratory freezers (-20 C), where they were stored until they were submitted to the laboratory for analysis.

3.5 Chain of custody

After sample collection and each time custody of sample was transferred, the recipient verified receipt for each sample by matching the identification number on the tube with the number listed on the Chain of Custody data sheets. Also documented were the date, time, temperature, and sample storage method. Each recipient signed for the receipt of the samples. Chain of Custody procedures are detailed in SOP 8: Chain of Custody, located in Appendix C.

4.0 Air Sample Analysis

Samples are being analyzed at the University of Washington's Environmental Health Laboratory and Trace Organics Analytical Center, an AIHA-certified laboratory.

5.0 Calibration

In the field, rotameters were used to measure pump flow rates. The Defender 520 was used to calibrate the rotameters before and after they were deployed in the field. Prior to using the Defender 520, it was calibrated to a primary standard, the bubble flow meter. This two step process allowed for accurate and faster calibration of the rotameters. All field flow were adjusted for both Defender 520 (adj1), and the individual rotameter's calibration (adj2).

5.1 Calibration of the Defender 520

The Defender 520 was calibrated to a bubble flow meter as the primary standard using a five-point calibration curve that encompasses the flow rates in liters per minute (lpm). The equation for the calibration line is used to calculate the actual flow rate of the calibrator. The calibration curve is a straight line where:

Eq 1. $y = mx + b$

y = flowrate (lpm) as read on the Defender
x = flowrate (lpm) on the bubble flow meter (1^o standard)
m = slope of the line
b = y-intercept

The following equation was used to adjust the defender flow rate to the adjusted or 'true' flow rate:

Eq 2. $$FR_{true}\ (lpm) = \frac{FR_{defender}\ (lpm) - b}{m}$$

5.2 Calibration of the Rotameters

The same steps were then taken to calibrate each rotameter to the Defender 520. A calibration curve was developed for the rotameters and the values from the line's equation were used to calculate the flowrate of the Defender 520:

Eq 3. $$FR_{defender} = \frac{FR_{rotameter}\ (lpm) - b}{m}$$

The rotameters were calibrated before and after placement in the field, average of the pre and post calibration was used for the adjusting field flow rates.

5.3 Adjustment of a sample flow rate.

The following is an example of a adjusting the flow rate from the field. For example, receptor sample 3025 was connected to rotameter Y-3 and had a field flow rate (rotameter reading) of 2.0 lpm. The calibration equation for the rotameter was:

$$y = 0.9809X + 0.207$$

As calibrated to the Defender 520, the flow rate was

$$FR_{defender} = \frac{FR_{rotameter}\ (lpm) - 0.207}{0.9809}$$
$$= \frac{2.0\ lpm - 0.207}{0.9809}$$

= 1.8 lpm

Then this flow rate is adjusted to the 'true' flowrate or that of the primary standard. The calibration equation for the Defender was

$$y = 1.0332\ X + (-0.0626)$$

As calibrated to the primary standard the flow rate was

$$FR_{primarystandard} = \frac{FR_{defender}\ (lpm) + 0.0626}{1.0332}$$

$$= \frac{1.8\ lpm + 0.0626}{1.0332}$$

$$= 1.8\ lpm$$

6.0 Air Concentration Calculations

6.1 Total sample times

The duration of a receptor sampling period ($Trec_{sampleperiod}$) in minutes (min) is the stop date and time minus the start date and time.

Eq 4. $Trec_{sampleperiod}$ (min) = Stop date/time – start date/time

For example, receptor sample 3025 had a start time of 14:26 on March 12 and end time of 14:26 on March 13.

$Trec_{sample\ period}$ (min) = (March 13, 14:26) – (March 12, 14:26)
= 1440 min

During each perimeter sampling period, mid period flow rate checks were conducted, the flow rates recorded and adjusted if needed. The duration of each sub-sample period ($tper_n$) was calculated separately and these were summed to determine the total sampling time for each sample period.

Eq 5. $tper_n$ (min) = (beginning date/time for mid $period_n$) – (end date/time for the mid $period_n$)

The total time for a perimeter sampling period ($Tper_{sampleperiod}$) is

Eq 6. $Tper_{sample\ period}$ (min) = $\sum tper_n$

For example the perimeter sample, 6568 had two flow rate checks which divided the sample period into three mid periods.

$Time_{start}$=April 4, 8:51
$Time_1$= April 4 9:33
$Time_2$= April 4 13:52
$Time_{stop}$= April 4 19:11

$tper_1$ (min) = (April 4, 9:33) – (April 4, 8:51) = 42 min
$tper_2$ (min) = (April 4, 13:52) – (April 4, 9:33) = 259 min
$tper_3$ (min) = (April 4, 19:11) – (April 4, 13:52) = 319 min

$Tper_{sample\ period}$ (min) = t1 + t2 + t3
= 42 min + 259 min + 319 min
= 620 min

Sometimes during a perimeter sampling period it was necessary to turn the pumps off to refuel the generators. Therefore the total sample time is the time that the pumps were actually turned on and running. It is not the time between the start time and stop time for the sample period.

6.2 Sample flow rate

The sample flow rates in liters per minute (lpm) for each sampling period is the average of the stop and start flow rate for that sampling period. All flow rates were adjusted for both the calibration of the rotameter and the Defender 520 calibrator.

Eq 7. $FRrec_{sample\ period}$ (lpm) = $\frac{[\text{start flow rate (lpm)} + \text{stop flow rate (lpm)}]}{2}$

The example for the receptor sample 3025 both a start and a stop flow rate of 1.83 lpm

$$FRrec = \frac{(1.83\ lpm + 1.83\ lpm)}{2}$$
$$= 1.83\ lpm$$

For the perimeter samples the flow rates for each mid sampling period were calculated.

Eq 8. $frper_n$ (lpm) = $\frac{[\text{mid period}_n\ \text{start flow rate (lpm)} + \text{mid period}_n\ \text{end flow rate (lpm)}]}{2}$

Perimeter sample 6568 had a start and end adjusted flowrate readings for each of its time periods (3 time periods total). If the flow rate did not need adjusting, the end flow rate for a mid period was the same as the start for the following mid period.

Mid period 1

Start flow rate = 5.905 lpm
End flow rate = 5.53 lpm

$$frper_1 = \frac{(5.90\ lpm + 5.53\ lpm)}{2}$$
$$= 5.72\ lpm$$

Mid period 2

Start flow rate = 5.53 lpm
End flow rate = 5.72 lpm

$$frper_2 = \frac{(5.53\ L/min + 5.72\ lpm)}{2}$$

= 5.63 lpm

Mid period 3

Start flow rate = 5.72 lpm
End flow rate = 5.72 lpm

$$fper_3 = \frac{(5.72 \text{ L/min} + 5.72 \text{ lpm})}{2}$$

= 5.63 lpm

See section 4.3 below for the calculation of the perimeter sample time-weighted average flow rate.

6.3 Sample volume

Sample volume for each receptor sample period (Vrec) was calculated by multiplying the flow rate ($FRrec_{sampleperiod}$) by the sample time ($Trec_{sampleperiod}$). This product is then divided by 1000 l to convert the volume to meters cubed (m^3), as follows

Eq 9. $Vrec_{sample\ period}$ (l) = [$FRrec_{sample\ period}$ (lpm) x $Trec_{sample\ period}$ (min)] x $\frac{1\ m^3}{1000\ l}$

As in the receptor sample example 3025:

$$Vrec_{sampleperiod} = 1.8 \text{ lpm} \times 1440 \text{ min} \times \frac{1\ m^3}{1000\ l}$$

$$= 2.6\ m^3$$

The sample volume for each perimeter mid sample period was calculated as follows.

Eq 10. $vper_n\ (m^3) = vper_n$ (lpm) x $tper_n$ (min) x $\frac{1\ m^3}{1000\ l}$

This is the perimeter example, sample number 6568:

Mid period 1 = 5.71 L/min, 42 min

$$vper_1\ (m^3) = \frac{(5.71 \text{ L/min} * 42 \text{ min} * 1\ m^3)}{1000L} = 0.240\ m^3$$

Mid period 2 = 5.63 L/min, 259 min

$$vper_2\ (m^3) = \frac{(5.63 \text{ L/min} * 259 \text{ min} * 1\ m^3)}{1000L} = 1.457\ m^3$$

Mid period 3 = 5.72 L/min, 319 min

$$vper_3\ (m^3) = \frac{(5.72\ L/min * 319\ min * 1\ m^3)}{1000L} = 1.82\ m^3$$

The total volume for each perimeter sample is the sum of the mid period sample volumes

Eq 11. $Vper\ (m^3) = \sum vper_n$

$$Vper = 0.240\ m^3 + 1.46\ m^3 + 1.82\ m^3 = 3.52\ m^3$$

The time-weighted average flow rate for the perimeter samples was calculated by dividing the total volume for the sample period (Vper) by the total time (Tper). The equation also converts the volume to liters from meter cubed (m^3) by multiplying by 1000/1 m^3.

Eq 12. $$FRper_{sample\ period}\ (lpm) = \frac{Vper_{sample\ period}\ (m3)}{Tper_{sampleperiod}\ (min)} \times \frac{1000\ l}{m^3}$$

For the perimeter sample 6568 the average time-weighted flow rate is

$$FRper_{sampleperiod} = \frac{3.52\ m^3}{620\ min} \times \frac{1000\ l}{1\ m^3}$$
$$= 5.67\ lpm$$

6.4 Sample mass

The EH laboratory provides results for sample mass for both the front and the back section of each tube in nanograms (ng).

According to NIOSH Method 5600 Organophosphorus Compounds, if the back section is greater than one-tenth the front section, then there is potential sample loss.

If the sample mass was reported as less than the limit of detection (LOD), then one-half the LOD was used as the sample mass for computational purposes. The data tables (Appendix C) indicate the limited samples to which this applies and the LOD values for the samples. The mass for each sample is calculated as

Eq 13. Sample mass (ng) = mass front section (ng) + mass back section (ng)

For the receptor sample 3025, the laboratory analytical results were

chlorpyrifos (CPF):
front section= 35 ng
back section= 1 ng

chlorpyrifos-oxon (CPF-oxon):
front section= 5 ng
back section= <1 ng

CPF mass (ng) = 35 ng + 1 ng
= 36 ng

CPF-oxon mass = 5 ng + 0 ng
= 5 ng

(The back section is not added to the front section because it is reported as < 1 or the limit of detection.)

For perimeter sample 6568, the laboratory analytical results were

chlorpyrifos (CPF):
front section= 143 ng
back section = 1 ng
chlorpyrifos-oxon (CPF-oxon):
front section = 30 ng
back section = < 1

CPF mass (ng) = 143 ng + 1 ng
= 144 ng
CPF-oxon mass = 30 ng + 0 ng
= 30 ng

(The back section is not added to the front section because it is reported as < 1 or the limit of detection.)

6.5 Oxon molar equivalent to the parent compound

To sum the parent compound and oxon, the oxon was converted to the parent compound as molar equivalents and added it to the parent compound mass

Eq 14. Total oxon mass as parent molar equivalent (ng)
$$= (\text{Oxon mass (ng)} \times \frac{\text{parent molecular weight}}{\text{oxon molecular weight}}) + (\text{Parent compound mass (ng)})$$

Total mass for the receptor sample, 3025, is

$$\text{CPF Total (ng)} = (5 \text{ ng} \times \frac{350.5879}{334.5219}) + 36 \text{ ng}$$
$$= 41.2 \text{ ng}$$

Total mass for the perimeter sample, 6568, is

$$\text{CPF Total (ng)} = (30 \text{ ng} \times \frac{350.5879}{334.5219}) + 144 \text{ ng}$$
$$= 175 \text{ ng}$$

6.6 Sample air concentration

Sample concentration is calculated as follows.

Eq 15. Concentration (ng/m^3) = $\frac{\text{mass (ng)}}{V\ (m^3)}$

Concentration calculations for the receptor sample 3025 are:

Vrec = 2.6 m^3
CPF mass = 36 ng
CPF concentration (ng/m^3) = $\frac{36\ ng}{2.6\ m^3}$
= 13.8 ng/ m^3

CPF-oxon mass = 5 ng
CPF-oxon concentration (ng/m^3) = $\frac{5\ ng}{2.6\ m^3}$
= 1.9 ng/ m^3

CPF Total mass = 41 ng
CPF-total concentration (ng/m^3) = $\frac{41\ ng}{2.6\ m^3}$
= 15.4 ng/ m^3

Concentration calculations for the perimeter sample 6568 are:

Vrec = 3.5 m^3
CPF mass = 144 ng
CPF concentration (ng/m^3) = $\frac{144\ ng}{3.5\ m^3}$
= 41.1 ng/ m^3
CPF-oxon mass = 30 ng
CPF-oxon concentration (ng/m^3) = $\frac{30\ ng}{3.5\ m^3}$
= 8.6 ng/ m^3

CPF Total mass = 175 ng
CPF-total concentration (ng/m^3) = $\frac{175\ ng}{3.5\ m^3}$
= 50.0 ng/ m^3

7.0 Reference

NIOSH. Organophosphorous Pesticides 5600. In NIOSH Manual of Analytical Methods. Fourth Edition. August 1994.

Table B1. Sample Collection and Analysis
Phase 1

	TRP-Revised sample plan[a]	Primary samples collected[b]	Back-up samples collected[c]	Samples analyzed[d]	% of sample plan[e]
PHASE 1					
Region 1 – North Central District					
Receptor-Ambient[f]					
Receptor 1	14	30	30	15	107
Receptor 2	14	30	30	15	107
Receptor 3	14	30	30	15	107
Co-located QC	14	30	25	15	107
Ambient	14	30	29	15	107
Spikes[g]		30		8	
Blanks[g]		30		8	
Perimeter[h]					
Pre-Spray	5	5	5	5	100
Spray Day	27	27	27	27	100
Post-spray 1	18	18	18	18	100
Post-spray 2	9	9	9	9	100
Spikes		14		6	
Blanks		14		6	
Region 2 – Yakima Valley					
Receptor-Ambient					
Receptor 1	14	21	21	11[i]	79
Receptor 2	14	30	29	15	107
Receptor 3	14	26	26	12[j]	86
Co-located QC	14	30	28	15	107
Ambient	14	36	33	17	121
Spikes		37		8	
Blanks		35		8	
Perimeter					
Pre-Spray	5	5	5	5	100
Spray Day	27	27	27	26[k]	96
Post-spray 1	18	18	18	18	100
Post-spray 2	9	9	9	9	100
Spikes		14		6	
Blanks		14		6	

Table B2. Sample Collection and Analysis
Phase 2

	TRP-Revised sample plan[a]	Primary samples collected[b]	Back-up samples collected[c]	Samples analyzed[d]	% of sample plan[e]
PHASE 2					
Region 2 – Yakima Valley					
Receptor-Ambient					
Receptor 1	20	23	23	23	100
Receptor 2	20	23	18	23	100
Receptor 3	20	22	22	22[l]	96
Co-located QC	20	22	13	22[l]	96
Ambient	20	23	23	23	100
Spikes		23		12	
Blanks		23		12	
Perimeter					
Pre-Spray	5	5	5	5	100
Spray Day	27	17	17	17[m]	63
Post-spray 1	18	18	18	18	100
Post-spray 2	9	9	9	9	100
Spikes		12		4	
Blanks		12		4	

a – TRP-recommended plan called for sampling every other day at receptor/ambient sites over a 28-day period for a total of 14 samples per site; in Phase 2 receptor-ambient site sampling occurred every third day due to the extended sampling period.

b – UW collected samples every day at the receptor/ambient sites, since staff were at the site every day under the every-other-day scenario; these samples could be analyzed if additional funds were identified.

c – UW collected a duplicate or back-up sample at each receptor/ambient site and at each perimeter site location; these samples allowed replacement if a primary sample were lost; these samples can also be used for inter-laboratory comparisons.

d – UW analyzed a sample from every other day for the receptor/ambient sites, and a sample from each sampling location at the perimeter sites; this conforms to the TRP-recommended sampling plan; in Phase 2 all primary samples for the receptor/ambient sites were analyzed. NOTE: each sample tube contained two sections, so two separate analyses were performed for each sample.

e – Percent is number of samples to be analyzed (column 5) divided by number of samples recommended by the Technical Review Panel (column 2), times 100.

f – Receptor sites were less than 100 meters from orchards likely to be treated with OP pesticides; ambient sites were greater than 500 meters from orchards likely to be treated with OP pesticides.

g – Spiked and blank samples were collected every day; samples analyzed represented 10% (each) of total samples to be submitted; e.g., for Phase 1, Region 1, Receptor/Ambient sampling, 75 air samples were analyzed, along with 8 spikes (10%) and 8 blanks (10%); if results from these spikes and blanks did not conform to QC expectations, then additional spikes and blanks could be analyzed.

h – Perimeter sites were orchard blocks that were to be treated with either chlorpyrifos (early spring) or azinphos-methyl (late spring); samples were collected at 4 locations (plus one co-located QC sample) on the pre-spray day, and at 8 locations (plus one co-located QC sample) on the spray day, and for two days post-spray.

i -- Sampling occurred on 21 rather than 28 days for this site. As a result, we analyzed only 11 samples (sample from every other day). Sampling at this site was limited because of battery problems and lack of access to the site on two weekends. No sample was collected on March 7 due to battery failure. We did not have access to this site on the weekend (March 8-9). No sample was collected on March 10 due to battery failure. Thus, the first samples were collected at this site on March 11. No samples were collected on March 13-14 due to battery failure. We did not have access to this site for a second weekend (March 15-16). No sample was collected on March 17 due to battery failure. Samples were collected each day thereafter until March 28, when another battery failure occurred. Sampling then continued through April 7. The sample begun on April 4 extended for 48 hours due to other demands on research staff, so no sample was collected on April 5.

j -- Permission was obtained to sample at the initial Receptor 3 site, but was put on hold one day prior to the beginning of sampling, and was subsequently withdrawn. We therefore had to identify a new Receptor 3 site. We were not able to begin sampling at this new site until March 15. Due to the delay in the start of sampling, we extended sampling at this site through April 11, whereas our other receptor sites ended sampling on April 7. One sample was missed on March 18 due to battery failure. The sample begun on April 4 extended for 48 hours due to other demands on research staff, so no sample was collected on April 5.

k – Region 2, Perimeter, spray day lunch, location 5: both primary and backup samples were submitted for GC-MS analysis, so there was no sample available for the LC-MS analysis.

l – One sample was not collected at the Receptor 3 site and the co-located QC site due to power source failure.

m – Spraying was delayed until late afternoon on the Spray Day, so only two sampling periods occurred on that day; one pump failure occurred.

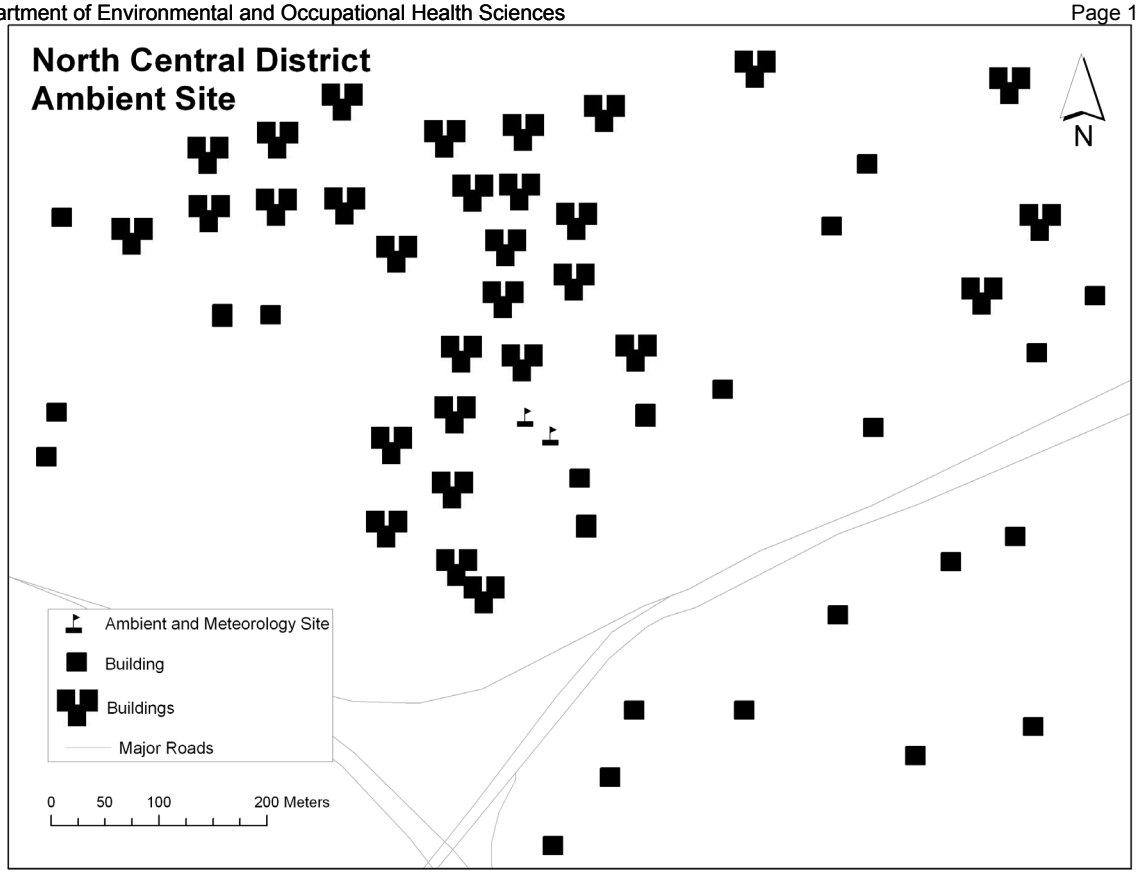


Figure B1.1 Ambient, Receptor, Ambient, & Quality Control Sites Maps: North Central District Ambient Site

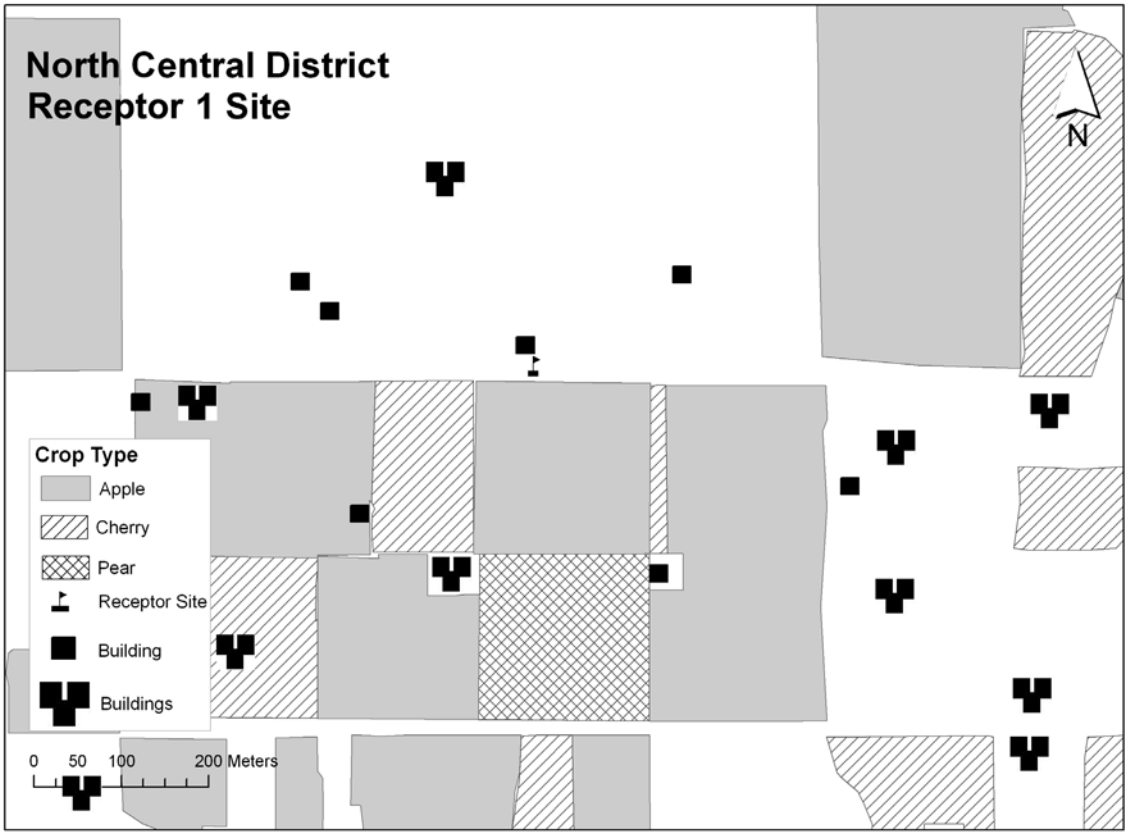


Figure B1.2 Receptor, Ambient, & Quality Control Site Maps: North Central District, Receptor 1 Site

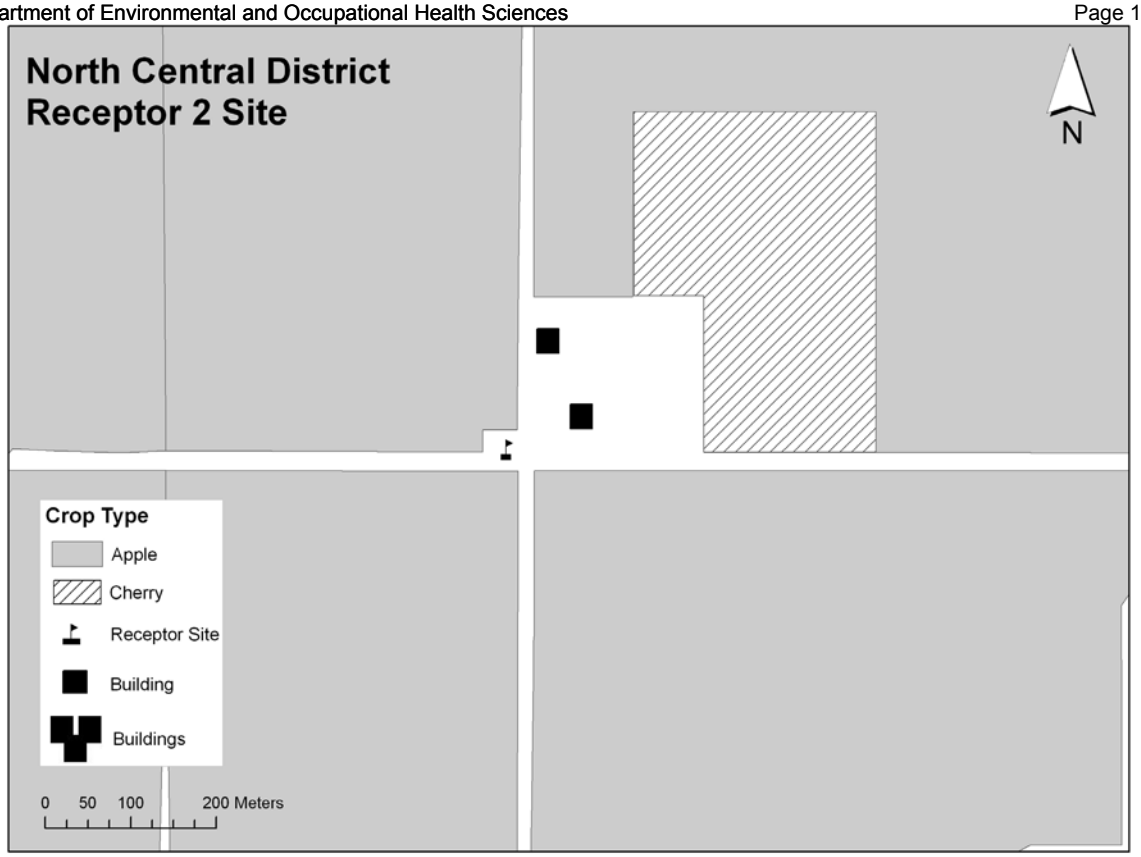


Figure B1.3 Receptor, Ambient, & Quality Control Site Maps: North Central District, Receptor 2 Site

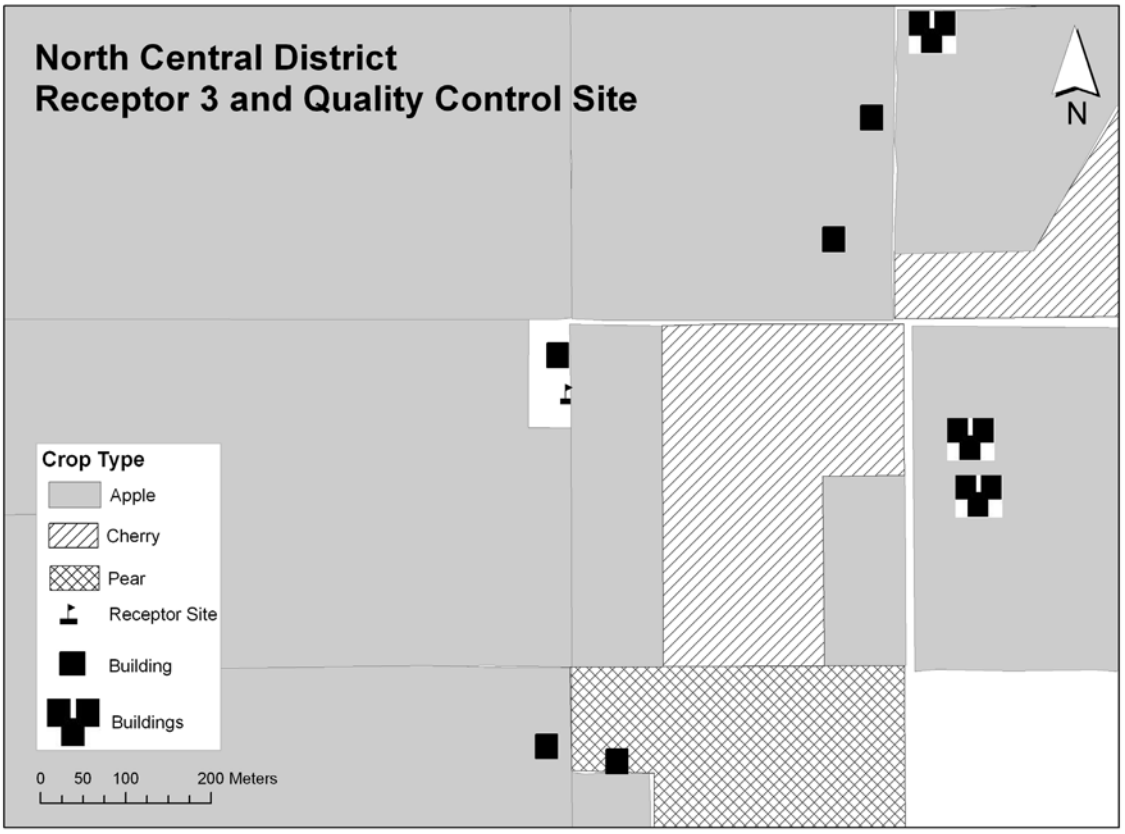


Figure B1.4 Receptor, Ambient, & Quality Control Site Maps: North Central District, Receptor 3 Site & Quality Control Site

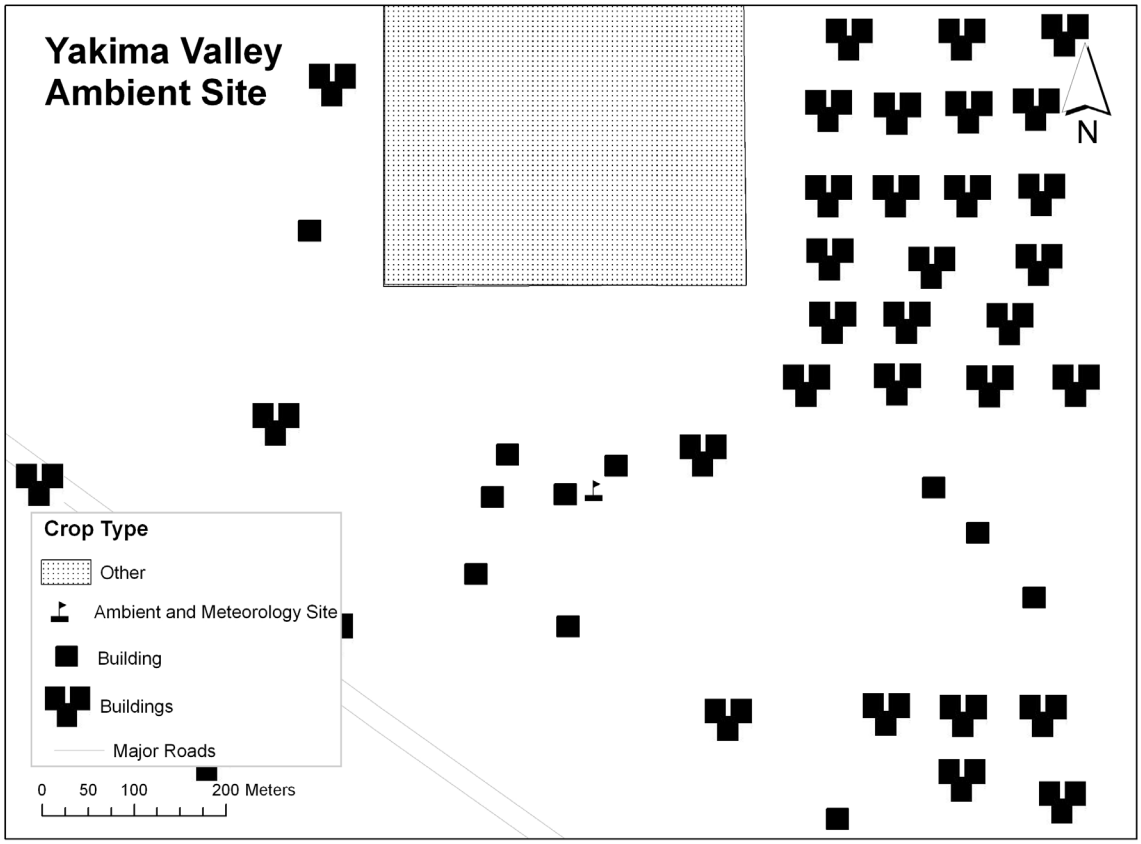


Figure B2.1 Receptor, Ambient, & Quality Control Site Maps: Yakima Valley, Ambient Site

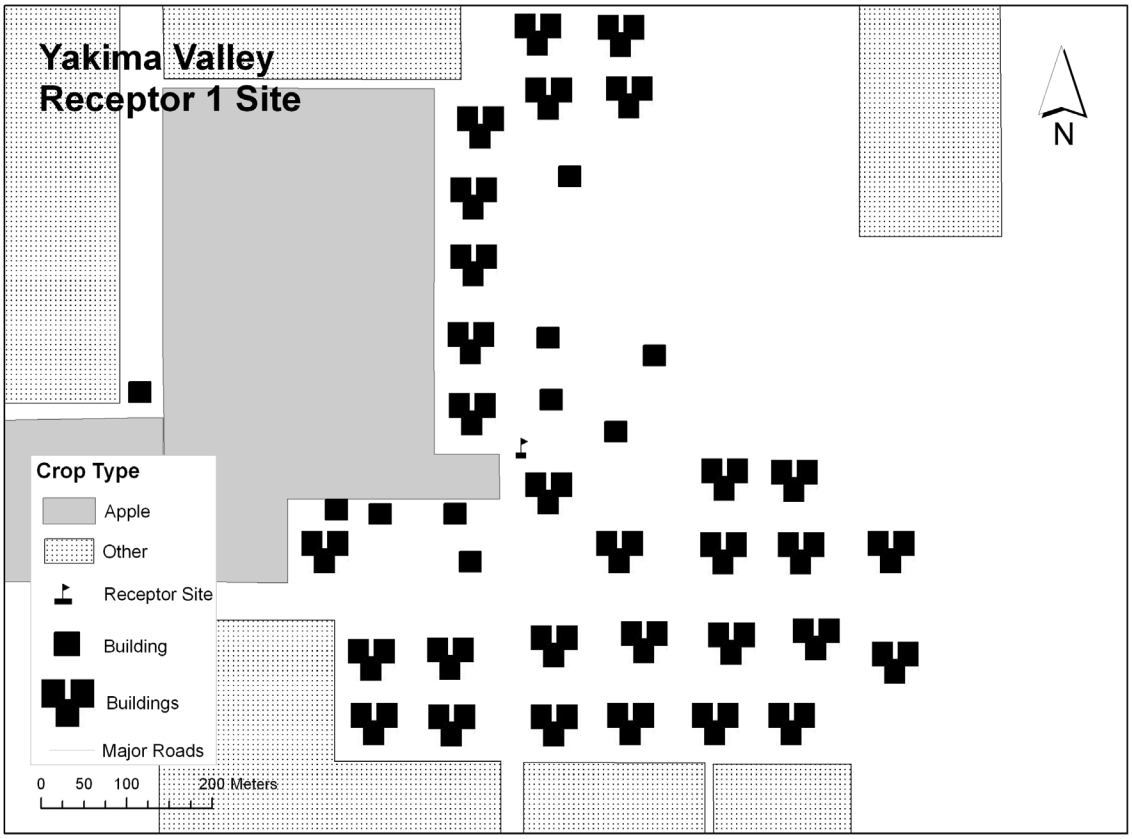


Figure B2.2 Receptor, Ambient, & Quality Control Site Maps: Yakima Valley, Receptor 1 Site (Phase 1 only)

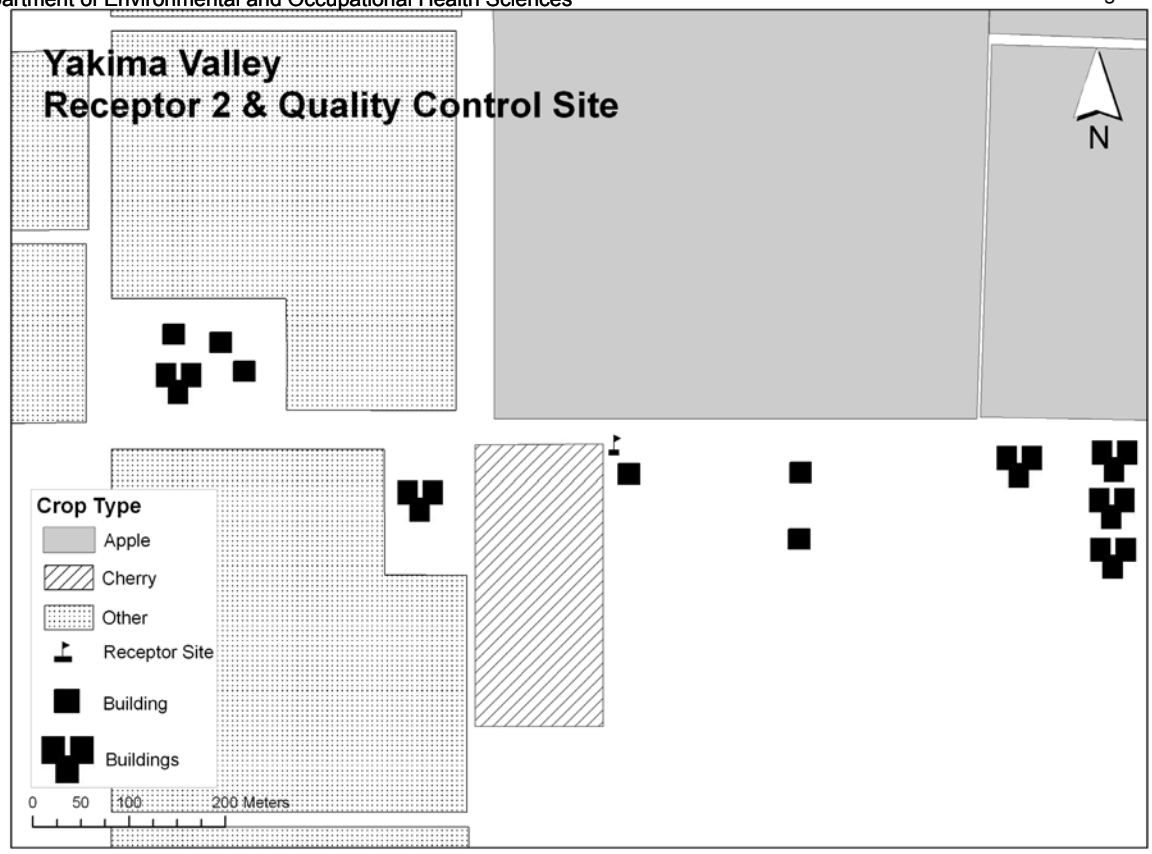


Figure B2.3 Receptor, Ambient, & Quality Control Site Maps: Yakima Valley, Receptor 2 Site and Quality Control Site

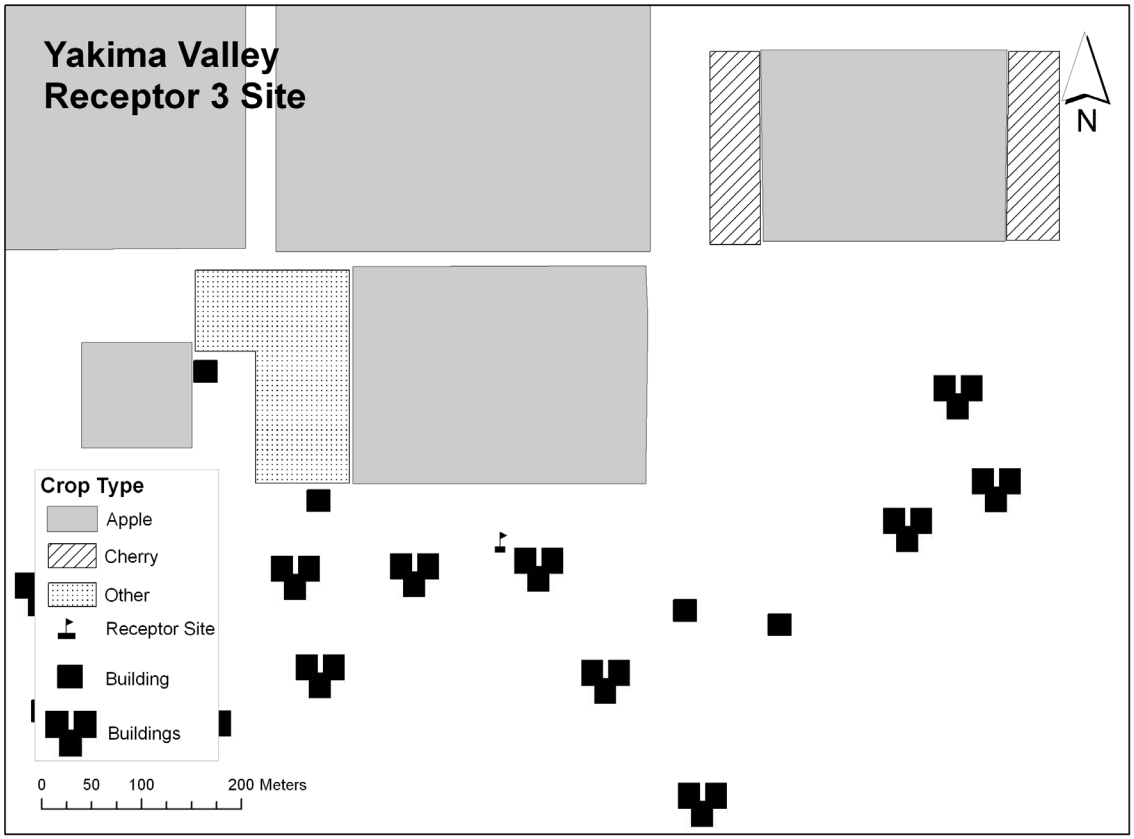


Figure B2.4 Receptor, Ambient, & Quality Control Site Maps: Yakima Valley, Receptor 3 Site (Phase 1 only)

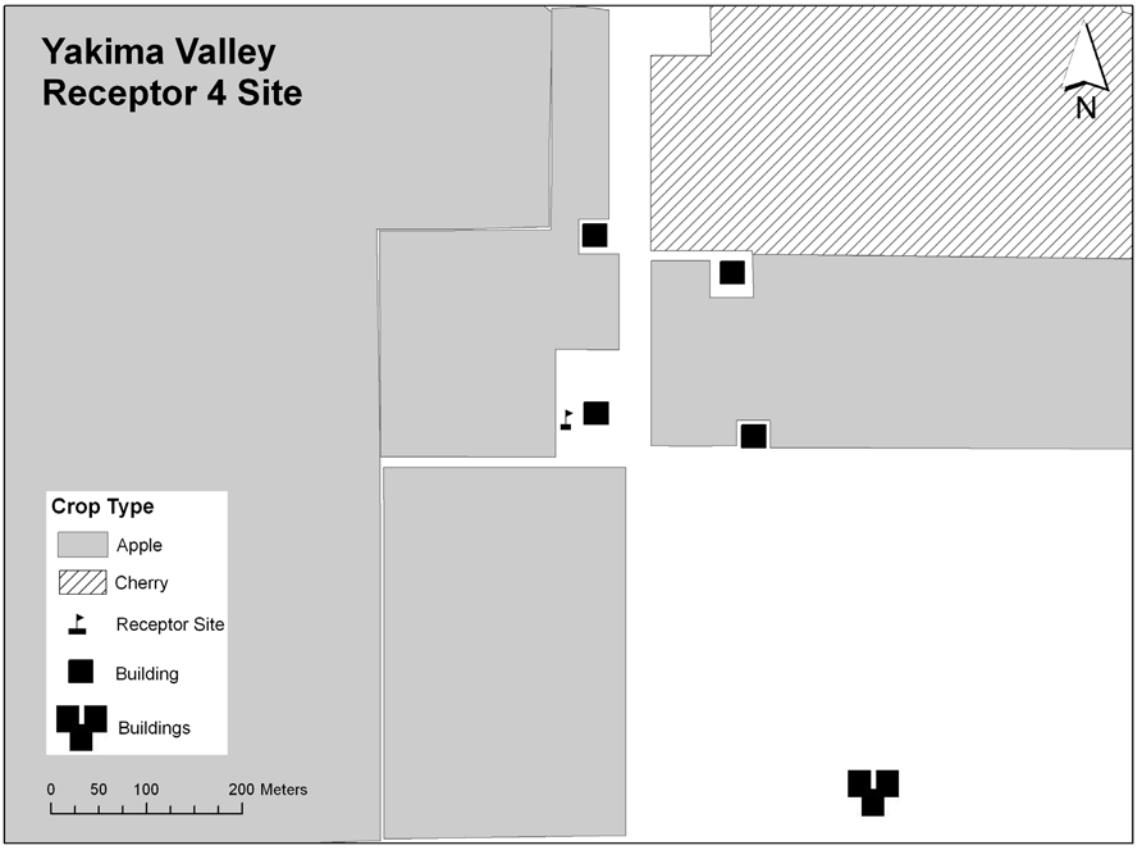


Figure B2.5 Receptor, Ambient, & Quality Control Site Maps: Yakima Valley, Receptor 4 Site (Phase 2 only)

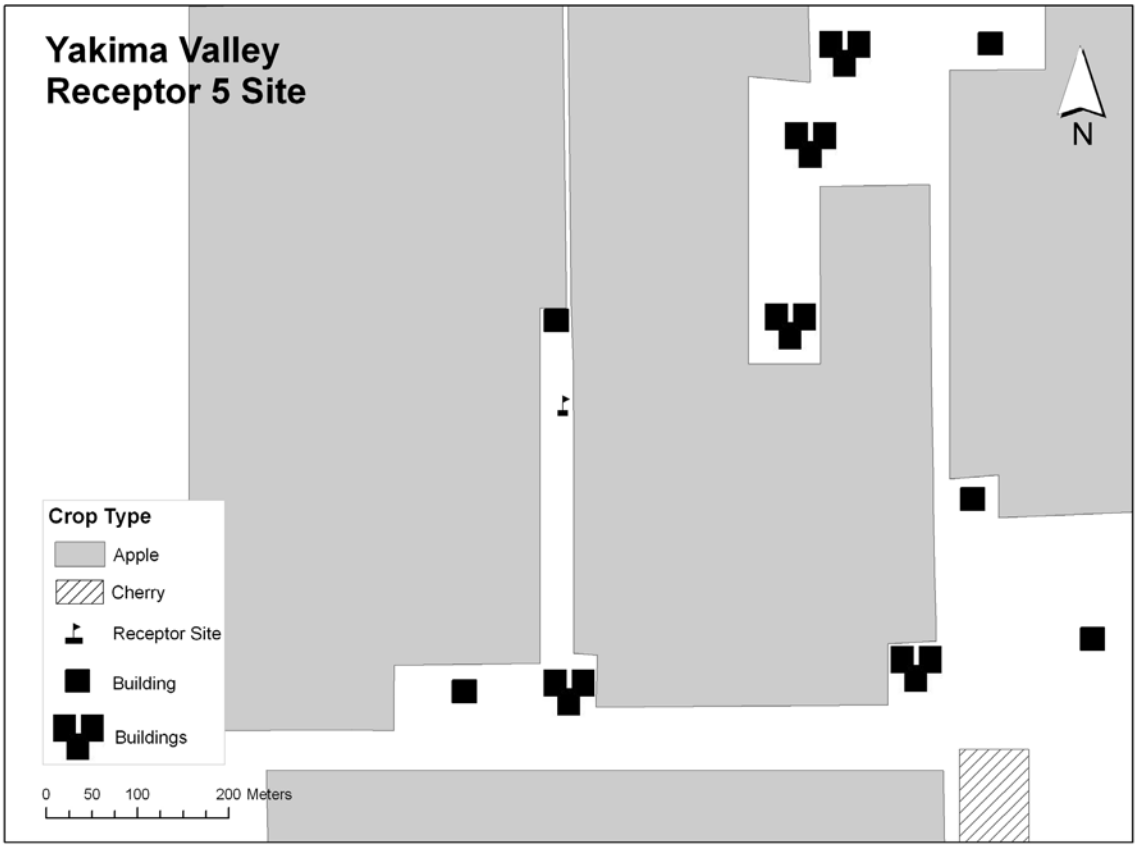


Figure B2.6 Receptor, Ambient, & Quality Control Site Maps: Yakima Valley, Receptor 5 Site (Phase 2 only)

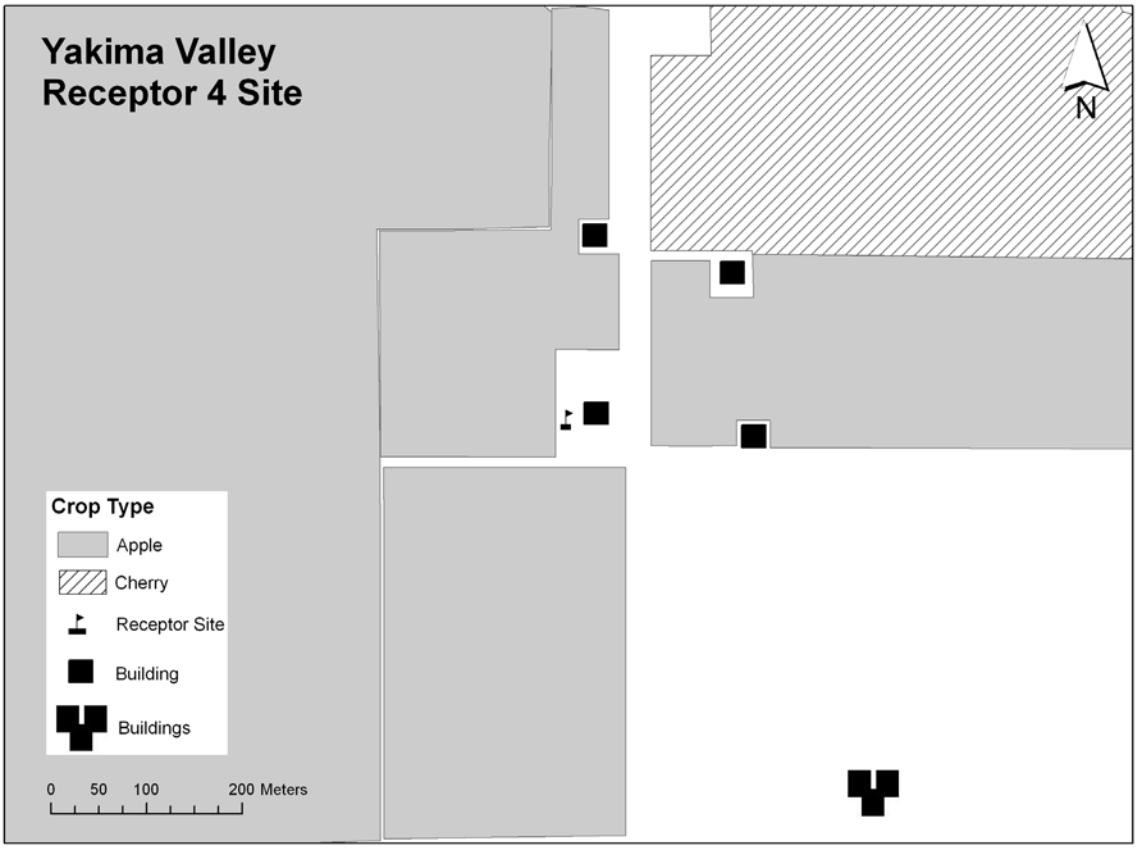


Figure B2.5 Receptor, Ambient, & Quality Control Site Maps: Yakima Valley, Receptor 4 Site (Phase 2 only)

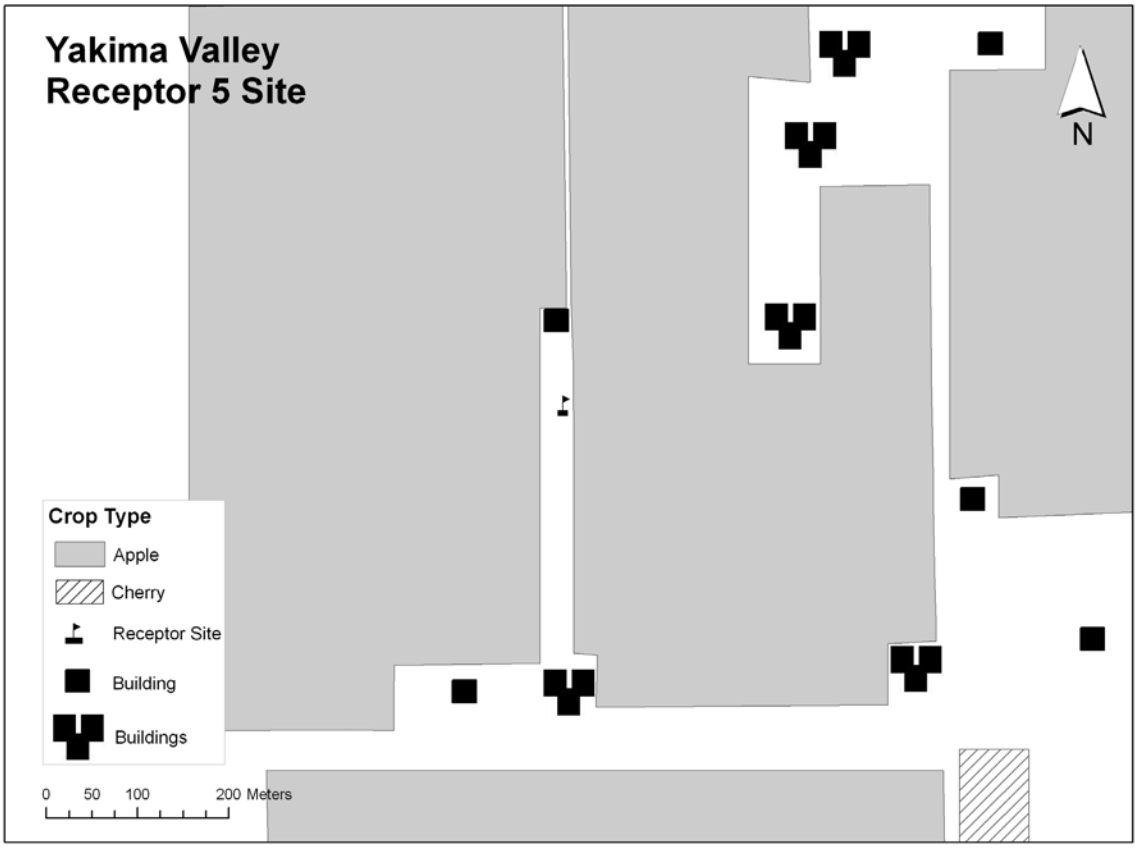


Figure B2.6 Receptor, Ambient, & Quality Control Site Maps: Yakima Valley, Receptor 5 Site (Phase 2 only)

Figure B3: Perimeter Site Layout
North Central District

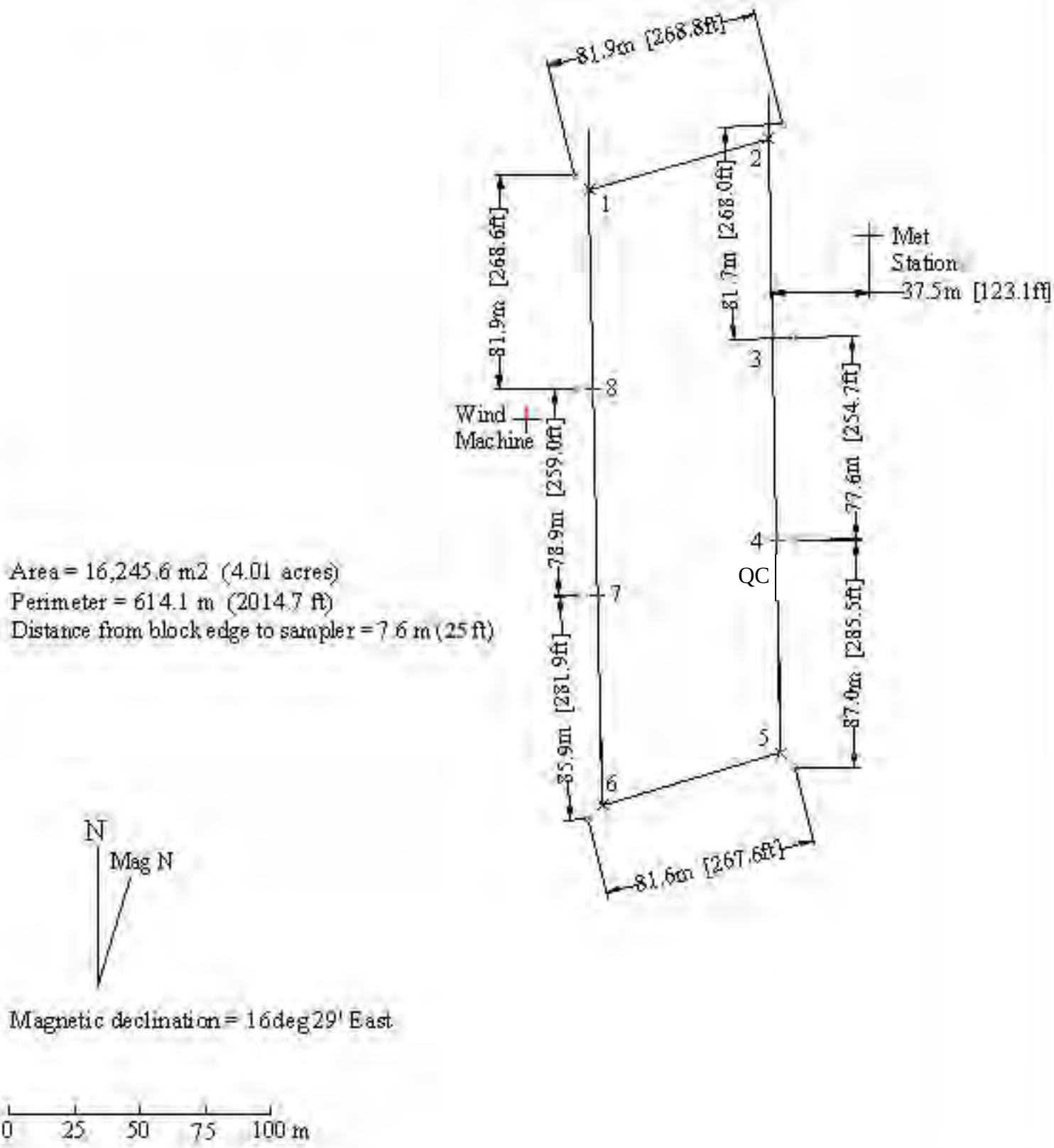
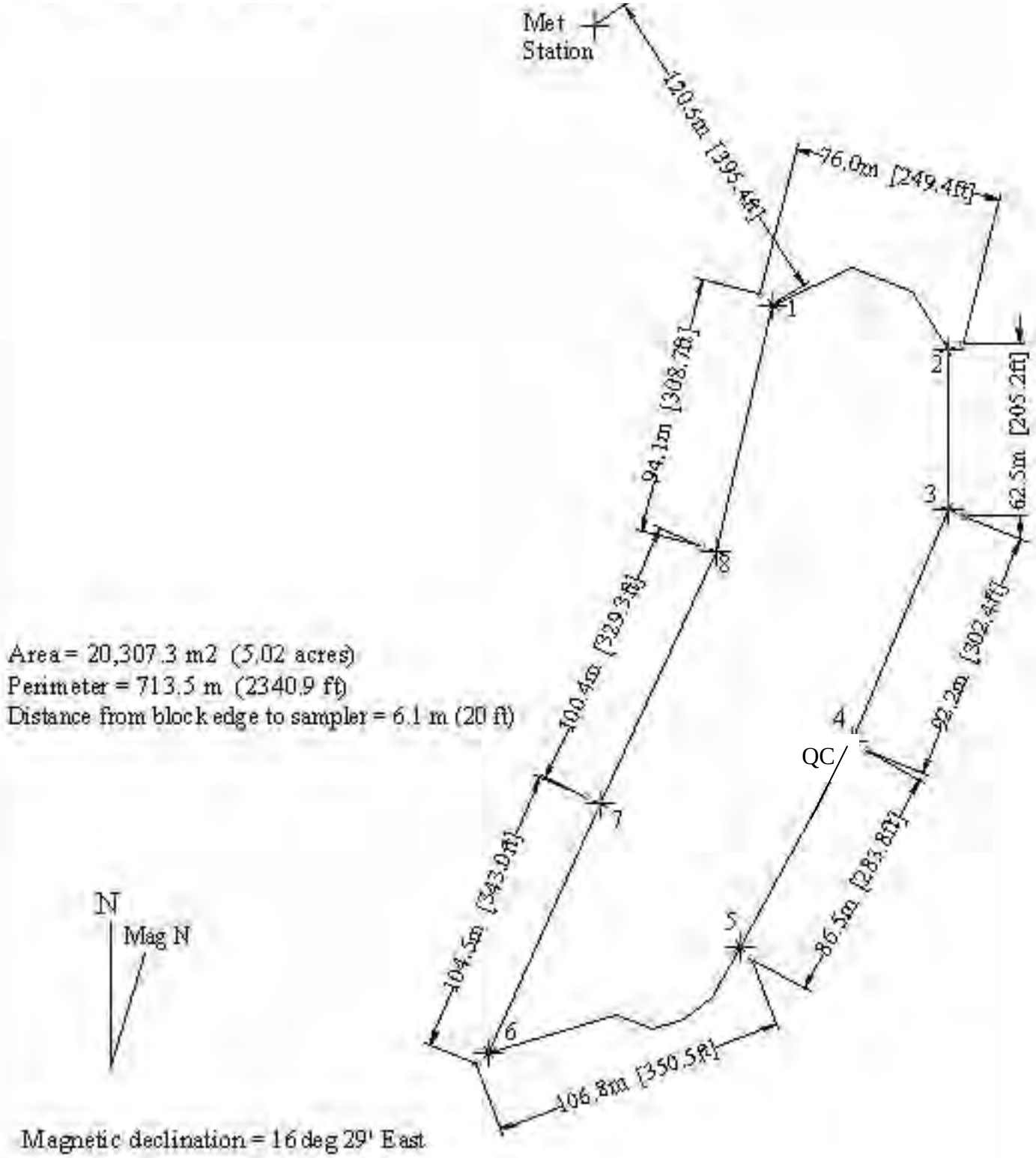


Figure B4: Perimeter Site Layout
Yakima Valley



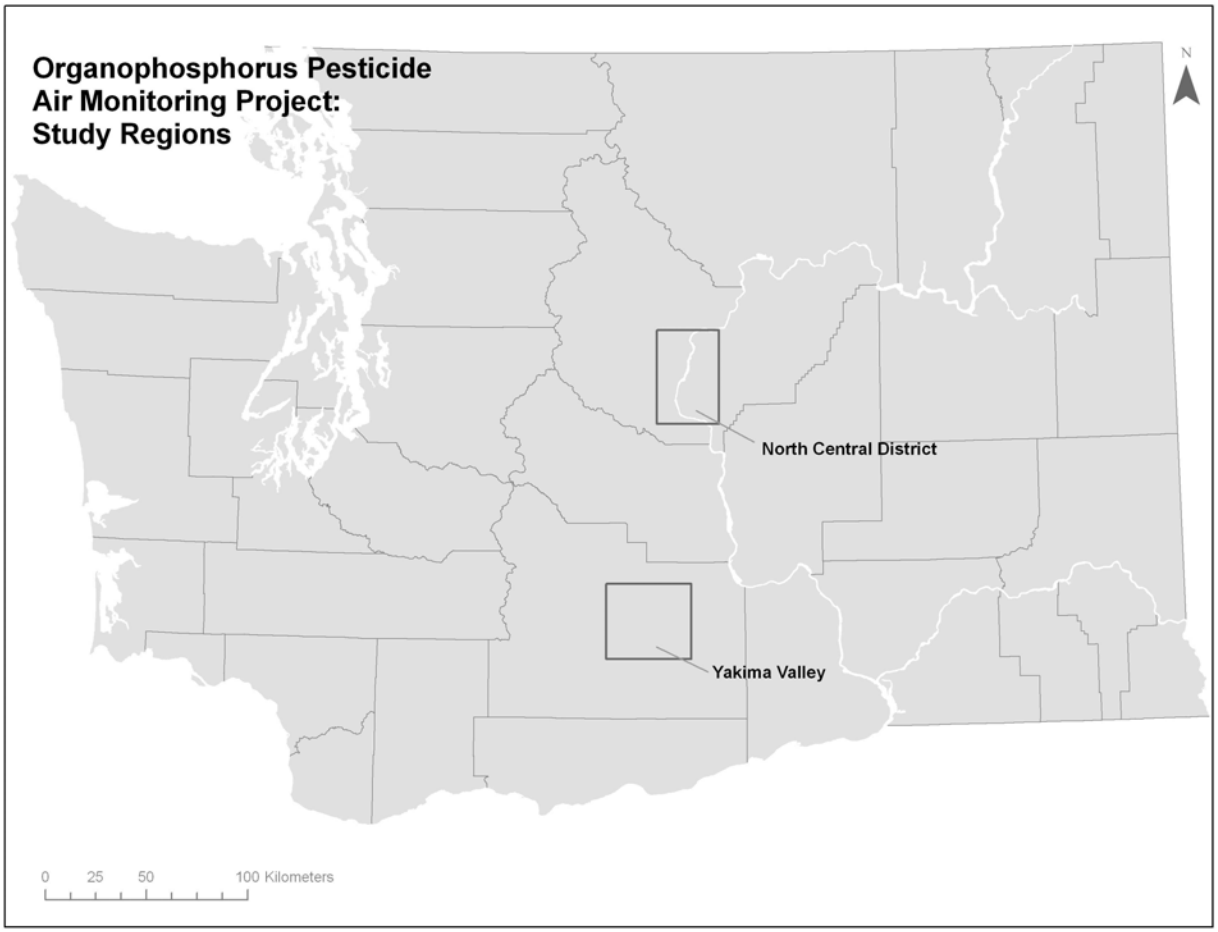


Figure B5. Study Regions Map

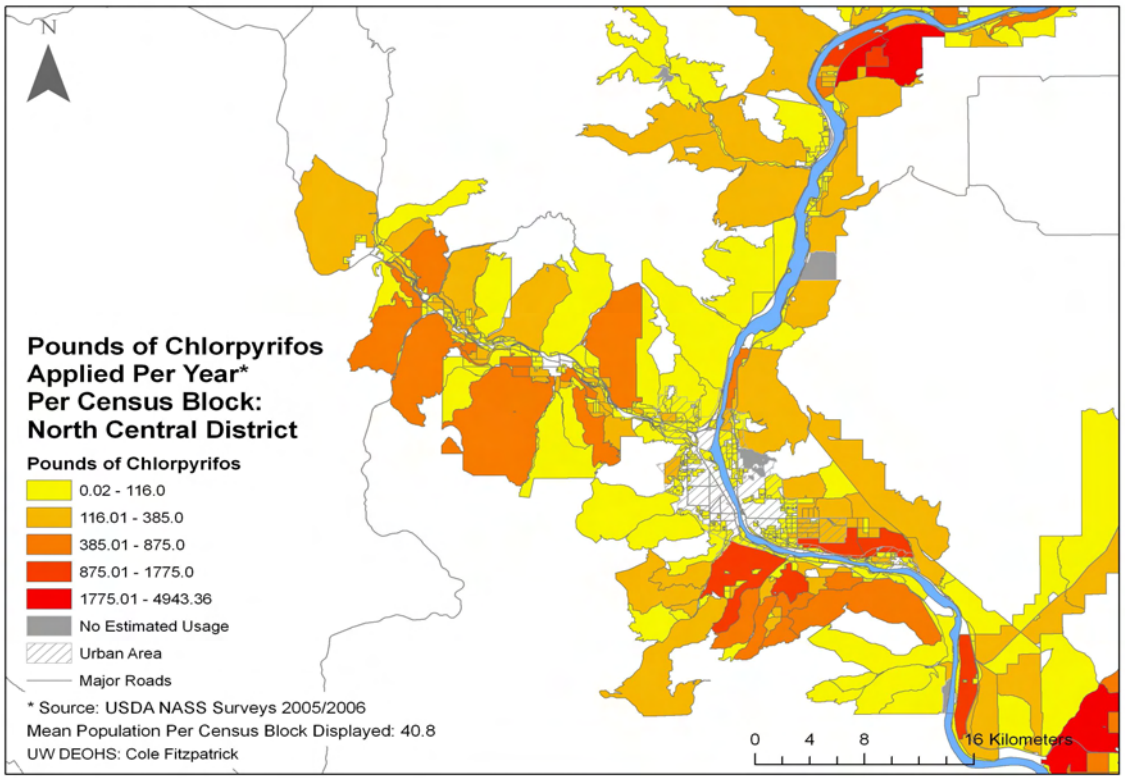


Figure B6. Estimated Pounds of Chlorpyrifos Applied per Year per Census Block: North Central District

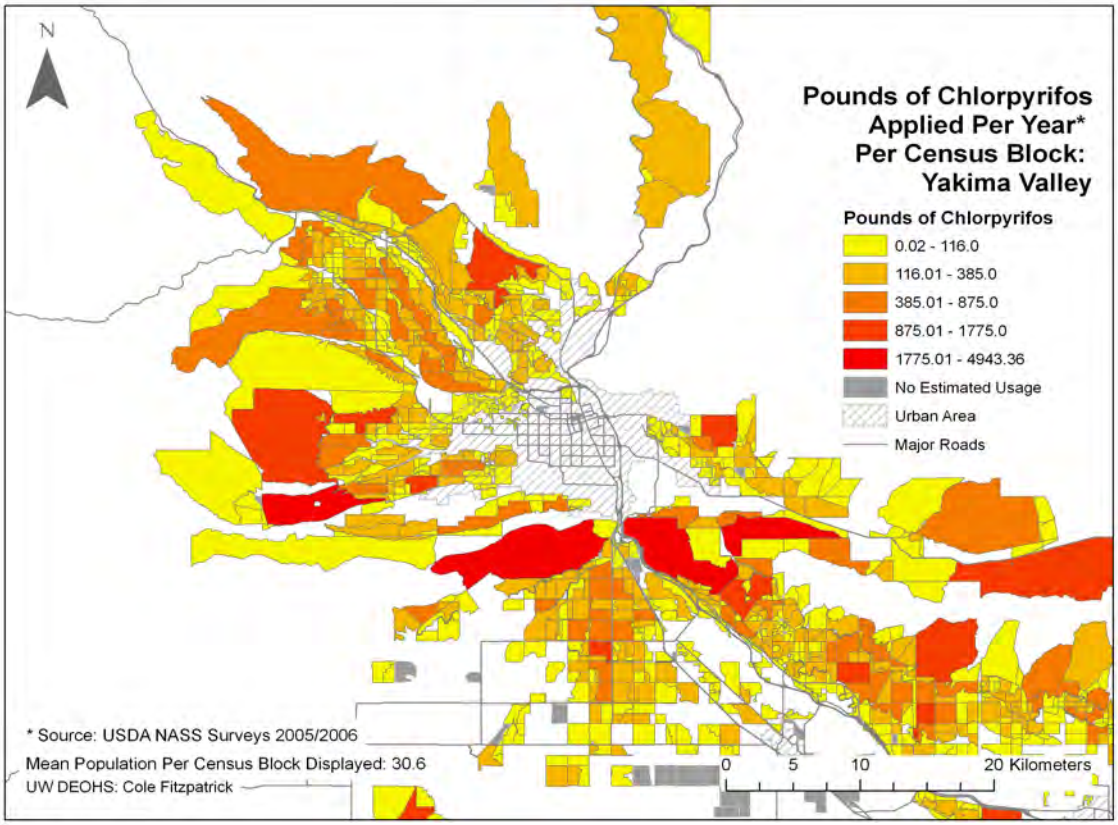


Figure B7. Estimated Pounds of Chlorpyrifos Applied per Year per Census Block: Yakima Valley

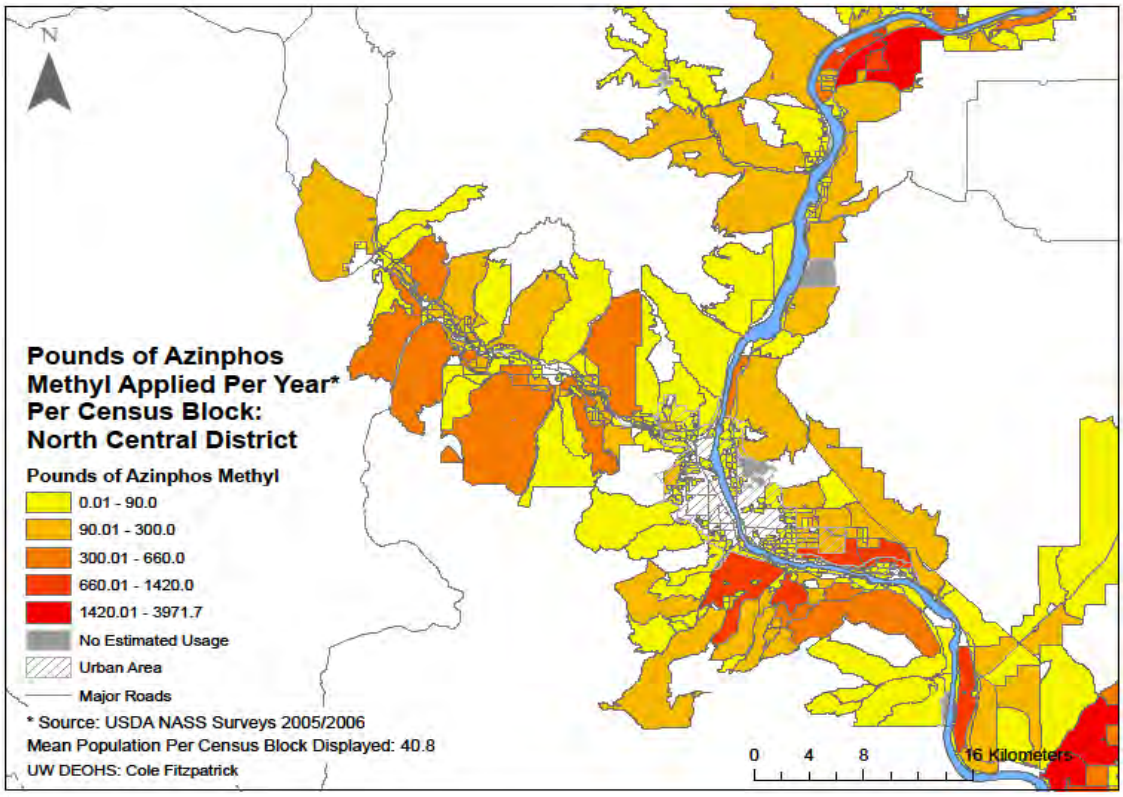


Figure B8. Estimated Pounds of Azinphosmethyl Applied per Year per Census Block: North Central District

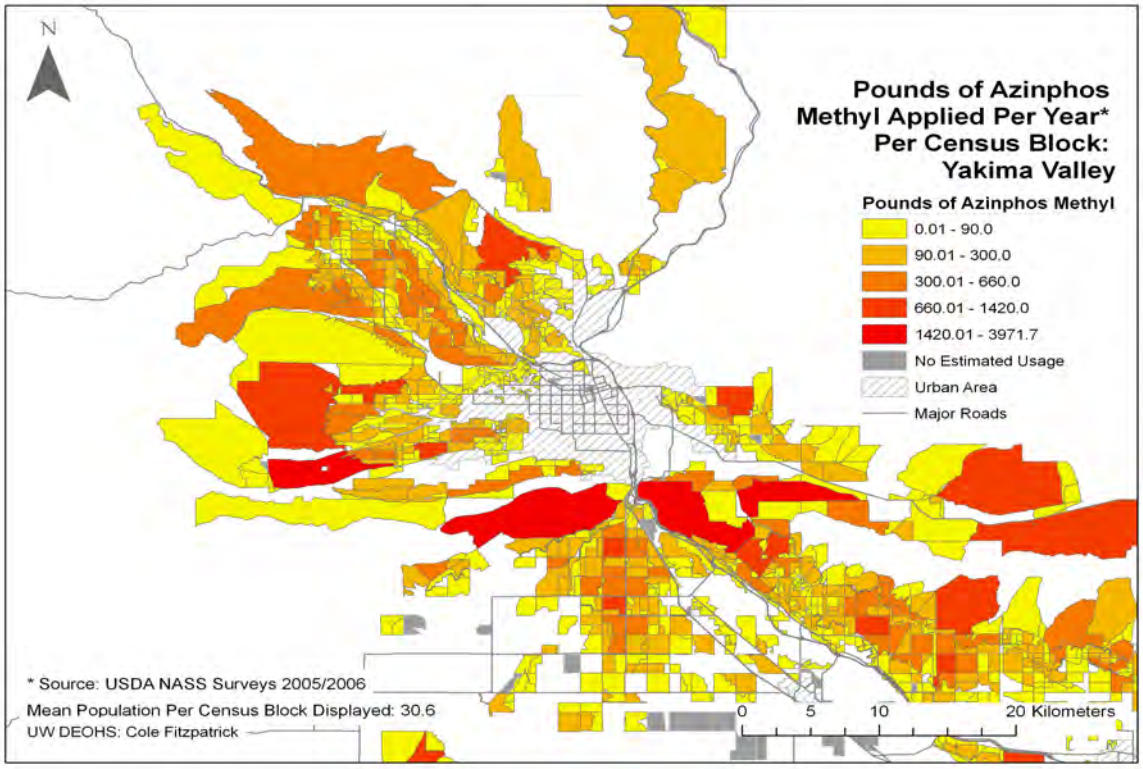


Figure B9. Estimated Pounds of Azinphosmethyl Applied per Year per Census Block: Yakima Valley