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**Analysis of Agricultural Use and Average Concentrations of  
1,3-Dichloropropene in Nine Communities of California in 2006 – 2015,  
and Calculation of a Use Limit (Township Cap)**

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**Abstract**

Ambient air concentrations of 1,3-dichloropropene (1,3-D) have been sampled in nine communities of California in 2006 – 2015. The yearly average concentrations are calculated from these data and paired with 1,3-D annual use in a township-size area around the sampling sites for the analysis on the use-concentration relationship. Because of high concentrations but moderate use reported in December, we analyzed two use scenarios for 1,3-D: Scenario I, factual 12-month use; and Scenario II, 11-month use that hypothetically prohibits use in December. Linear regression cannot explain the relationship between the average concentration and the annual use in both scenarios. The ratios of the yearly average concentration and the adjusted total pounds (ATP) are then calculated. The 95<sup>th</sup> percentile of the ratios is used to estimate a township use cap as 135,785 lbs (ATP) in Scenario II (11-month use) and 92,854 lbs (ATP) in Scenario I (12-month use). These estimates are designed to ensure that the 95% yearly average concentrations of 1,3-D will not exceed the regulatory target concentration of 0.56 ppb in a township applying 1,3-D at the amount of the use cap. A bootstrapping procedure is employed to simulate the 70-year exposure of 1,3-D with the township cap of Scenario II and 100% of the simulated 70-year average concentrations are below 0.56 ppb. All the assumptions and adjustments in this analysis are discussed in the report.

**Introduction**

In California, 1,3-dichloropropene (1,3-D) is registered as a pre-plant soil fumigant used to control certain soil-borne pests such as nematodes, viruses, bacteria, and fungi for vegetables, fruit crops, nut trees, and other food and non-food crops. 1,3-D is listed under Proposition 65 as a chemical known by the State of California to cause cancer. Due to its high vapor pressure (28 mmg Hg at 20°C), 1,3-D is a volatile compound. Volatilization of this chemical creates the opportunity for off-site transport and could cause human exposure. Since 1999, the Department of Pesticide Regulation (DPR) has been implementing a

limit (township cap) on the total amount of 1,3-D that may be applied each year within a township (6 × 6 mile area designated by the Public Lands Survey System) of California to minimize long-term exposures to 1,3-D in the air (Verder-Carlos, 2014).

During the past 10 years, several long-term (>1 year) ambient air monitoring studies for multiple pesticides have been conducted in California. These monitoring studies provide us multiple years of pesticide air concentrations in various areas of the state. It presents a unique opportunity to analyze the relationship between a pesticide's use and its concentration in the ambient air based on many years' worth of data. This report documents our analysis on 1,3-D data and includes:

- (1) Exploratory data analysis for the results of air monitoring studies and the reported use of 1,3-D.
- (2) Statistical analysis on the relationship between the concentrations and the reported use. Since the current use cap is set for the yearly use within a township, we only present the analysis on the relationship between yearly average concentrations and annual total use in a township-size area around the sampling site. In addition, a township cap is calculated using the results of this analysis
- (3) Discussion of our approach along with the limitations of the data and the adjustments and assumptions made during the analysis.

Statistical software R 3.2.4 is used for all the data processing and analysis.

## **1,3-D Air Monitoring Data**

### **Air Monitoring Study**

During 2006 – 2015, 1,3-D ambient air concentrations in nine communities of California were collected through four air monitoring studies conducted by DPR, Air Resource Board (ARB), and Dow AgroSciences (DAS) (Figure 1, Table 1). The first long-term air monitoring study for multiple pesticides was conducted by DPR at Parlier in the San Joaquin Valley in 2006; it was the first of this kind of study that any government agency in the United States had done. In this study, DPR and ARB cooperated on collecting samples of volatile organic compounds (VOC) including 1,3-D in the ambient air once every 6 days. Based on the successful experience of the Parlier study, DPR started an Air Monitoring Network (AMN) study in 2011 to monitor 32 chemicals in the ambient air of three communities: Salinas in the coastal area and Ripon and Shafter in the San Joaquin Valley. In this monitoring project, which has lasted for more than 5 years, one 24-hr air sample is collected at each monitoring site on a randomly chosen day of every week. Samples are then sent to the laboratory of the California Department of Food and Agriculture (CDFA) to analyze pesticide concentrations including 1,3-D. During the same period, ARB has been monitoring 1,3-D concentrations at several communities along the coast of California once every six days. Table 1 includes the links that provide detailed information about these monitoring studies. The DAS Merced study used a different sampling method and continuously collected air samples at the centers of nine townships in Merced for 15 months (Johnson, 2014a). DAS provide DPR its monitoring results as electronic files.

## **Data Preparation**

### Process non-detects

The measured 1,3-D concentrations and sampling dates are extracted from the original dataset of each sampling site and are combined together to build a single concentration dataset with 3,149 observations. About 54% of the total measured concentrations are below the method detection limit (MDL) and are recorded as non-detect (ND). For the purpose of data analysis, all the NDs are substituted by the half values of MDLs (0.0005 – 0.5 ppb) and labeled as adjusted concentrations. Figure 2 shows the distribution of concentrations at different sampling sites after this adjustment. Log-transformed concentrations are used to reduce the data variation and better exhibit the distributions. All the logarithm transformations in this analysis are the natural logarithm. Since half of the data are below MDLs, changing MDLs apparently shapes the data patterns of different studies and a great deal of data cluster at the same low levels.

### Process data from different studies

For the Merced study, DAS conducted 15 months of continuous monitoring at nine locations using different sampling method than that of DPR and ARB. The monitored concentrations in this study exhibit a larger range than those in the other monitoring studies (Figure 2). Nine townships (M06S10E, M06S11E, M06S12E, M07S10E, M07S11E, M07S12E, M08S10E, M08S11E, M08S12E) monitored in Merced are next to each other (Figure 3). Air concentrations sampled in these townships could be somehow correlated since pesticide use occurring in one township could travel to nearby townships depending on weather conditions. For example, M08S10E did not have reported 1,3-D use in 2011 but its yearly average concentration is 0.1 ppb, much higher than the MDL of the Merced study. The presence of 1,3-D in M08S10E could be due to the applications in other townships. This spatial covariation could be affected by meteorological conditions. However, it is hard to estimate this covariation with the current data. To eliminate this effect and for a statistically balanced analysis, we treat the Merced region as one sampling site to be studied along with other communities with a single sampling site. The yearly concentrations and 1,3-D use of the sampling site Merced are calculated by averaging the results of nine townships.

The sampling sites of Camarillo and Oxnard are also located inside two contiguous townships; however monitoring occurred during different time periods. ARB started monitoring the Camarillo site in August 2010, and then moved the site to Oxnard in the middle of October 2011. The Oxnard site has been operating since then. Because the Camarillo site does not have monitoring data for a full calendar year, a yearly average concentration for 2011 is calculated for this site using the concentrations measured from September 2010 to August 2011. Among ARB and DPR sites, Parlier and Camarillo sites operated for about a year, so they have a number of records smaller than six other sites where monitoring has been conducted for 5 years. The highest concentrations monitored at ARB and DPR sites are similar.

### Compare data of different months

Of the 12 months in a year, December had some of the highest 1,3-D concentrations (Figure 4). Two tests are conducted to examine if December data is significantly higher than data from the other months for

both detection probability and adjusted concentrations (Table 2). To analyze detection probability, a new variable “Detect” is created. It is set to 0 when a concentration is recorded as ND and to 1 when a concentration is quantifiable. A generalized linear model (GLM) with a distribution family “binomial” is used to fit a logistic regression for “Detect” with the factor variable “Month”. The logistic regression outputs log(odds ratio) as response, which is log(detection probability/non-detect probability) in this case. Coefficients in the GLM results are estimated for every level of the factor and determine how much other levels of the factor (i.e. Month) can change the average of the response compared to December. A t-test is used to compare the average of log(adjusted concentration) between December and the other months. At significance level  $\alpha = 0.01$  for individual comparison, the probability to detect quantitative concentrations in December is higher than in January – August, similar to that in September and November, and lower than in October. 1,3-D adjusted concentrations are significantly higher in December than in the other months except for November.

## 1,3-D Use Around Air Monitoring Locations

### Pesticide Use Data

Two sources of 1,3-D use data in California are available for the analysis. The first is Pesticide Use Report (PUR) database managed by DPR. All agricultural use of pesticides in California needs to be reported to county agricultural commissioners, who forward the data to DPR. The current use reporting system started in 1990 and collects comprehensive pesticide use information including applied products, applied amounts, application dates, crops, and application locations to a square-mile section. The second source is data submitted by DAS for 1,3-D use since 2011. Besides most of information collected by PUR, this dataset includes the application method for each 1,3-D use record and can be used to assign a variable “application factor” to adjust amount of applied active ingredient (AI) (Appendix I). The application factors range from 0.3x to 2.3x and are used to adjust the amount applied for applications using certain fumigation methods, in certain seasons, with certain tarp types, and inside or outside San Joaquin Valley. The resulting “Adjusted Total Pounds”(ATP) accounts for different mass loadings into the air due to differential cumulative flux fractions of various application methods and is also based on assumptions, judgments, and management directives (Johnson, 2014b). ATP is believed to represent the amount of 1,3-D that is potentially present in the air after an application.

### Data Preparation

1,3-D use within a township size area ( $6 \times 6$  mile) around each sampling site during the period of air monitoring studies are queried from PUR and DAS databases. A Public Land Survey System (PLSS) township is divided into 36 sections (one square mile per section). Since most of the sampling sites are not located in the center of an official township, the use is actually queried for 6 by 6 grids of sections around them, instead of the townships where sampling site are located. Only use data in Merced is queried for the exact PLSS townships since the Merced sampling sites are designed to be located near the center of townships and labeled as township IDs. Appendices II and III present the annual adjusted and unadjusted use maps of  $6 \times 6$  mile area around every monitoring site and also list 1,3-D yearly average concentrations and total use amounts.

Figure 5 shows queried use data and how the use amount varies in different communities and different months. Both ATP and AI amount show a similar season pattern: autumn season (August – October) has highest pesticide use, which explains high detection percentages of 1,3-D in September – October. However, December, in which some of the highest concentrations occur, has moderate 1,3-D use. This may indicate that the meteorological conditions in December assist in retaining 1,3-D in the ambient air. Also communities in coastal areas, such as Santa Maria, Watsonville, and Oxnard, report high use of 1,3-D but concentrations detected at these sites are not higher than those at the other sites. This suggests that the relationship between the pesticide use and the ambient air concentrations could also be affected by geographical characteristics or climate pattern of different regions.

### **Relationship between Yearly Average Concentration and Total Adjusted Use**

Because high concentrations are detected but moderate 1,3-D use are reported in December, we consider two scenarios for yearly use and concentration analysis:

- 1) Scenario I: Factual scenario with year-round 1,3-D use. Annual total use is the sum of 12-month use data and average concentrations are calculated from 12-month monitoring data; and
- 2) Scenario II: Hypothetical scenario excluding 1,3-D use in December. Annual total use is the sum of January – November use. All samples collected in December are assumed to be NDs and the concentrations are replaced by the half of current MDLs. Annual average concentrations are then calculated from the actual concentrations sampled in January – November and pseudo samples in December.

Table 3 summarizes the estimates of yearly average concentrations and ATP for Scenario I (factual 12-month use) and Scenario II (hypothetical 11-month use). There are 31 pairs of use-concentration data for the analysis of each scenario.

Linear regression was first tried but failed to fit 1,3-D average concentrations using annual 1,3-D use (PUR AI amount or DAS ATP amount) in  $6 \times 6$  mile areas. Figure 6 shows that the correlation between 1,3-D average concentration and annual use in  $6 \times 6$  mile area is weak. Several highest average concentrations are paired with low annual total use (<10,000 lbs). Linear regression cannot explain the relationship between these two variables. Figure 6 also demonstrates that removing 1,3-D use in December lowered some of the highest concentrations and changed the direction of correlation between the annual use and average concentration. In addition, ATP exhibits a little stronger correlation (a steeper slope in the 11-month use plots) with the average concentrations than AI amount.

As shown in Figure 6 and Table 3, by hypothetically reducing all concentrations in December to NDs, the highest two average concentration points, 0.54 ppb at Merced in 2011 and 0.57 ppb at Shafter in 2013, disappear from the high concentrations. They both drop to 0.14 ppb, while ATP is only reduced by 32% at Merced and 27% at Shafter by removing the December use. The third highest average concentration, 0.48 ppb of Parlier, drops 30% to 0.34 ppb when the December use, accounting for 14% of the total adjusted pounds, is removed in Scenario II. On the other hand, all the noticeable reductions only happened at the inland sampling sites: Parlier, Merced, Ripon, and Shafter (Figure 7). The sampling sites

in the coastal region have less than 6% reduction in both ATP and yearly average concentrations after excluding 1,3-D use in December. This suggests that Scenario II (11-month use) would greatly benefit the inland area, but would not bring much change to the current 1,3-D use in the coastal area. There is no 1,3-D use within  $6 \times 6$  grid area around the Shafter sampling site in December of 2014 and 2015 but reduction is still positive for the concentration. This is evidence that the 1,3-D ambient air concentration could come from the use farther than 36 mile<sup>2</sup> around a sampling site.

Since the variation of yearly average concentrations cannot be explained by a linear model with 1,3-D use in a township area, the paired two variables could be a random combination. Ratios of yearly average concentrations and annual ATP amounts for each sampling site in each year are calculated to represent this combination. Their percentile ranks are calculated to study the variable's distribution for both use scenarios (Table 4). The distributions of these ratios are close to log-normal (Figure 8):

1) Scenario I (12-month use):  $\log(\text{Average Concentration} / \text{annual ATP}) \sim N(-13.604, 0.937)$

2) Scenario II (11-month use):  $\log(\text{Average Concentration} / \text{annual ATP}) \sim N(-13.642, 0.829)$

Scenario II fits the estimated distribution better than Scenario I. Two estimated log-normal distributions have similar means, which indicates that the geometric means of two scenarios are close to each other. But the distribution of Scenario I exhibit a larger variance, which is consistent with the impact of December. The estimated percentiles and log-normal distribution for the ratios of concentration and use then can be used to compute the annual use amount of 1,3-D in a  $6 \times 6$  mile area for certain 1,3-D average concentrations.

DPR's 1,3-D risk management directive (RMD) document (DPR, 2016) sets a regulatory target concentration at 0.56 ppb and requires that the 70-year average concentration in a township will not exceed the target when 1,3-D is used at the level of the township cap. Since the 70-year data are not available, the ratios of yearly average concentration and ATP are used to estimate the township cap. The 95<sup>th</sup> percentiles of concentration/ATP ratios are 4.12E-06 in the Scenario II and 6.03E-06 in Scenario I. With a 1,3-D regulatory target concentration of 0.56 ppb, the township cap is estimated to be 135,785 lbs (ATP) for Scenario II (11-month use) and 92,854 lbs (ATP) for Scenario I (12-month use). These estimates are designed to ensure that the 95% yearly average concentrations of 1,3-D will not exceed the regulatory target concentration in a township using 1,3-D ATP under a township cap.

## Discussion

In this report, we analyze the relationship between 1,3-D ambient air concentration and its use in a township-size area. A township cap is estimated using the analysis result of yearly average concentration and annual ATP. Data from several different sources are combined together to build up a dataset for this analysis. Because of this combination and the limitation of individual data sources, many adjustments and assumptions have been made during the data analysis procedure and caused a couple of uncertainties in the analysis, which we discuss here.

### MDL and Non-detects

The MDL is defined as the lowest concentration of a pesticide that the analytical method could reliably detect. This definition and the determination procedure of MDL refer to USEPA (1984) 40 CFR, Part 136, Appendix B (DPR, 1995). To determine a MDL, the laboratory analyzes a standard of each analyte at a concentration with a signal to noise ratio of 2.5 to 5 at least 7 times.

the MDL

is determined by calculating the 99% confidence interval:

$$MDL = s \times t_{(n-1, 1-\alpha=0.99)}$$

Where

$n$  = number of replicate spikes,  $n \geq 7$ ,

$s$  = standard deviation of measured concentrations of  $n$  spikes,

$t$  = Student's  $t$  value at  $n-1$  degree of freedom and  $1-\alpha$  (99%) confidence level,

$\alpha$  = level of significant.

The MDL is a characteristic of both the method and the chemical. That is, different methods can have different MDLs for the same chemical. Similarly, one method can have different MDLs for different chemicals. Also the MDL is determined by a statistical analysis procedure, which means it is an estimate from an assumed distribution instead of a single absolute value.

Besides the limitation of individual MDL, various MDLs used in different studies brought more complexity to the data analysis. Also in the AMN study, the CDFFA laboratory has improved their chemical analysis method and lowered the MDL of 1,3-D twice since 2011 (Table 1). The first MDL of the AMN study was much higher than the subsequent others and only used for 5 months. The second MDL was the same with the ARB's level and used for about 28 months. The third MDL has been used since October 2013. The chemical concentration reported as ND may contain a concentration at any value between zero and the MDL. For combined data like the one in this study, the information hidden behind the records of NDs are actually changing from time to time because of multiple MDLs.

NDs are substituted by the half of the MDL values to calculate average concentrations in this data analysis. Substitution is usually not an effective way to analyze NDs because it loses the uncertainty information in the data (Helsel, 2012). Several statistical methods, both parametric (e.g. maximum likelihood estimation, regression on order statistics) and non-parametric (e.g. Kaplan-Meier survival analysis), have been developed to handle NDs measured in environmental data. Unfortunately, these methods are only applicable for the data with at least 20% quantitative observations that can be used to estimate an assumed distribution or a meaningful data order (Helsel, 2012). Table 5 lists the percentages of quantitative measurements in the data of each site for each year. 1,3-D monitoring data from most of ARB and DPR sites cannot meet the 20% requirement (Table 5). The violin plot shown in Figure 2 is

similar to a boxplot but captures the shape of the density mass. It starts with a box plot then adds a rotated kernel density plot to each side (Hintze and Nelson, 1998). Kernel density is a data smoothing tool to estimate the probability density of a variable. In Figure 2, the changing values of NDs apparently determine the density shape of the data. About 58 – 100% of measurements in ARB and DPR sites are reported as NDs and these data cluster at the half values of the MDLs in the violin plot.

The Merced data has the lowest MDL and total 88% quantitative measurements so presents a different shape from other sites with a much larger data range. Although the average concentration of Merced is much higher, its median and geometric mean is actually close to other sites (Table 5). Figure 9 overlaps the probability density of log-transformed concentrations of Merced with another two sites in the San Joaquin Valley. It reveals that the most frequently detected concentrations were close in three sites although they have very different percent of substituted data. Therefore, substituting NDs with half values of MDLs is considered to be appropriate for the current analysis. With the improved air sampling and chemical analysis methods, the MDL could be decreased and the air monitoring could achieve more detections. After the MDL of the AMN study was lowered in 2013, the detection percentages of Shafter and Ripon sites were increased by 60 – 100% from 2013 to 2015 (Table 5) while the use amount in both 6 × 6 mile areas was decreased by 45% during this period (Table 3b). With more quantitative data are collected, better statistical methods can be applied in this analysis and may present clearer distribution of the 1,3-D concentrations in the ambient air of California communities in the future.

Table 5 shows that samples collected in Ripon in 2012 and Shafter in 2011 have no quantitative concentrations and some of the other sites also have detections lower than 10% in some years. This analysis does not exclude any year's data at any site because of its high percentages of NDs. Usually no measurements should be removed from a data for a statistical analysis unless they are proved to be invalid samples or measured mistakenly. The MDL and NDs do not imply the accuracy of the measurements. There is no way to determine that the data with more detections has better quality than the data with fewer detections. High concentrations usually attract researchers' attention and are not treated as outliers in environmental data because they are the interest in the environmental study. However in statistical analysis, low concentrations and high concentrations contain equally important information about the data distribution. High percentages of NDs illustrate that the 1,3-D concentration in the ambient air is most likely below some level even with some amount of pesticide use. The pesticide may not reach a detectable concentration until its use exceeds a certain amount under certain meteorological condition. So NDs contain the information about the relationship between the concentration and the use although the signal is not as clear as quantitative measurements. In this study, we decided to use the substitution method to handle NDs and all the NDs should be treated equally. Therefore, all the measurements in the original dataset have been used to estimate the yearly average for further analysis.

### **Yearly Average Concentration**

It is assumed that the data collected from different years are independent. One of subjects of this report, “yearly average concentration”, is an arithmetic mean of concentrations sampled at each site in each year. It is calculated by adding all the numerical values together and dividing by the number of the values. Arithmetic mean is not an effective way to summarize highly skewed data like 1,3-D data because it is easily impacted by extreme data points as shown in Table 5. The values could become even more arbitrary with the substituted NDs. Arithmetic means are used in this study because: (1) there is no other



effective way to estimate a mean for the data with high percentages of NDs as discussed above; (2) compared to the median or the geometric mean (the  $n$ th root of a product of  $n$  numbers), the arithmetic mean has a higher value, and thus is considered to be more conservative for environmental and public health protection; and (3) arithmetic mean is currently used by the DPR to evaluate the long-term, cumulative exposure of 1,3-D and is also easily understood by the public.

### **Averaging Merced data**

Nine townships (M06S10E, M06S11E, M06S12E, M07S10E, M07S11E, M07S12E, M08S10E, M08S11E, M08S12E) are monitored in Merced and their data are averaged to represent the Merced region in 2011. The yearly average concentration and ATP for each sampling site of the DAS Merced study is plotted on Figure 10. All of the yearly average concentrations, total PUR AI amount, and total DAS AI and ATP amount of nine sites are also listed under the Merced use maps in Appendices II and III. As shown in Figure 10, the yearly average concentrations were low and constant around 0.19 ppb at the sites whose townships applied 1,3-D ATP less than 120,000 lbs. When ATP reached more than 150,000 lbs, the yearly average concentrations rapidly increased to 0.69 – 1.92 ppb. This pattern also indicates that the average pesticide concentration in the ambient air may stay low and not be affected by the use amount as long as the amount remains under a certain level. When the use exceeds this level, the concentration could increase with the use amount. However, comparing Figure 10 with Figure 6, this rapid increase pattern with ATP over 150,000 lbs is not consistent with the multiple-year data collected in other communities. Among all the monitored communities, only Merced had multiple sampling sites but the data was only collected for a year. Because there is no data available from other contiguous townships and in other years to compare, it is impossible to evaluate the spatial covariation between Merced sites and also test if their pattern exists in other years. Since the data collected in Merced can only represent a one year average of this region, averaging nine townships is a strategy to include the information from all sampled locations. Averaging data from adjacent townships has been also used in a previous study to evaluate a use cap for methyl bromide (Fan et al., 2010).

### **AI pounds and ATP**

Pesticide use data were queried from two different sources. PUR is the best available and the most complete pesticide use reporting database of California. It has been widely used by DPR for risk assessment, analyzing human exposure patterns, promoting farm worker health and safety, monitoring and investigating environmental issues, and improving pest management. The data is also extensively used by other state agencies, U.S. governments, universities, farmer organizations, the pesticide industry, and public interest groups. PUR data is considered to be reliable, yet a complex and continuously growing system like this can never achieve 100% accuracy. Errors can occur during data entering and processing. There are 80 error codes used in PUR processing to flag all types of possible errors. More than 50,000 errors (about 2% records) can be identified each year and most of the detected errors are corrected in the final version of PUR (Wilhoit, 2002). Still it is impossible to know the true error rate. The capacity of the PUR loader program to detect and correct errors is restricted by the quality of the data being entered at the beginning. As for application rates, the error handling system only tries to identify the extreme high values. Therefore, any entering error that looks to be within a “normal” range or some extremely low rates cannot be detected.

1,3-D use data from DAS reports application methods and the calculated ATP is used for this data analysis along with AI from PUR. It needs to be noted that the DAS dataset is sent to DPR in Excel files without complete documentation. The details of the loading and quality control procedure used in this dataset are currently unknown. The AI amount queried from the PUR and DAS datasets shows some discrepancy. The discrepancy is largest in 2011 – 2012 and the ratios between annual AI amounts in 6×6 mile area range from 0.57 – 3.77 (Table 6). In the queried data that are limited to the sampling locations and periods, DAS reports higher 1,3-D AI amount in Merced but lower amount in all the other areas than the PUR. But more importantly, the discrepancy between queried data significantly declines over time and the ratio between two sources in 2015 is close to 1 in all queried areas (Table 6).

Although ATP is practically considered to represent 1,3-D concentration in the ambient air and compared with the township cap, the application factors used to calculate ATP were not completely developed based on scientific data. The adjusted factors were initially established in the mid-1990s in order to reflect different amounts of volatilization from various application methods. A deep shank study conducted in Salinas was the base line to quantify volatilization and the factor 1.0 corresponds to 35% volatilization (Johnson, 2013). Adjusted factors also attempted to account for meteorological impacts on air concentrations however these impacts were not well evaluated (Johnson, 2013). Even before the ambient air concentrations were extensively collected, the phenomenon that 1,3-D applications in winter may result in higher concentrations than applications in other time of the year had been noticed. The greater values of adjusted factors in December and January are designed to discourage such applications, rather than to accurately reflect meteorological enhancements of 1,3-D air concentrations. All the details about the development of 1,3-D adjusted factors can be found in the documents of DPR (Johnson, 2013; Johnson, 2014b). Table 6 includes the ratios of yearly ATP amount and AI amount reported in DAS dataset. Ratios of ATP/AI in Salinas, Santa Maria, and Watsonville are less than 1 in 2013 – 2015. These ratios range from 0.39 to 0.77 and indicate low adjusted factors related to tarp and application methods used in these communities.

### **Prohibiting 1,3-D Use in December**

Two scenarios are analyzed for the use-concentration relationship in this report. Scenario II assumes that the December use of 1,3-D is prohibited in California. This hypothetical scenario is set up to evaluate (1) if 11-month use could help eliminate some highest concentrations measured in December and consequently reduce the yearly average concentration; and (2) if air concentrations could be better explained by the use amount in 6×6 mile area after removing the meteorological impact of December. When developing 1,3-D adjusted factors, higher factor values have been assigned to discourage 1,3-D use in December and January (Johnson, 2013). However, although 1,3-D use in December was lower than peak months (Figure 5), some of the highest concentrations were still monitored in the inland communities during this month. The current data does not show significantly high concentrations in January hence the hypothetical scenario only studies prohibiting the use in December.

In the calculation for Scenario II (11-month use), the use amounts (AI and ATP) in December are simply removed from the annual totals but the concentration measurements have different processing. Assuming that 1,3-D concentration in the ambient air was zero when the use was prohibited in December, the air monitoring studies would still collect air samples and the result of the chemical analysis would report NDs, instead of zero, for samples detecting nothing. Additionally, applications made in late-November

may continue to off-gas in December. For these reasons, all of the original concentrations in December are replaced with NDs for Scenario II. To calculate yearly averages, half values of MDLs are then used to substitute these pseudo NDs. The MDL has been changed twice in the AMN study. Considering Scenario II is developed as a reference for the future regulation and NDs reported in the future will be based on a MDL equal to or lower than the current MDL, half value of the current MDL (0.01 ppb) is applied to all the pseudo samples no matter what MDL was originally used in the actual monitoring. The result shows that Scenario II only affects the use and concentrations in the inland communities and reduces the highest yearly average concentrations at Merced and Shafter (Figure 7). As for the ATP-concentration relationship, the slope of the average concentrations and annual total use in Scenario II is higher than that in Scenario I, although the linear regression is not significant.

### **Linear regression analysis**

Linear regression models have been tried to fit the air monitoring results with 1,3-D use for both use scenarios (Table 7). The responses of the models are yearly average concentrations or log-transformed average concentrations. The only independent variable is 1,3-D total use (10,000 lbs) of each year, which is the AI amount queried from the PUR or the ATP from the DAS dataset. P-values of the fitted models ranging from 0.07 to 0.80 suggest that none of these models are statistically significant. The low  $R^2$ s (0.05 – 11.1%) further confirm that simple linear regression cannot explain the variation of 1,3-D yearly average concentrations. Data points in Figure 6 show two different patterns: one group of data displays sharply increased concentrations within low use range, and another group has a larger range of 1,3-D use but gently increased concentrations. These two groups can be roughly distinguished by the regions where sampling sites are located. For this reason, 31 data points are divided into 12 inland data points (Merced, Parlier, Ripon, and Shafter) and 19 coastal data points (Camarillo, Oxnard, Salinas, Santa Maria, and Watsonville). Linear regression is then applied to the two groups of data. With this separation, the models achieve p-value less than significance level  $\alpha = 0.05$  and enhanced  $R^2$ . Although these models are made from limited data points and still not successful with 25% and 45%  $R^2$ , they showed that the concentrations are more likely associated with the use when analyzing them location-specifically. The slope of inland regression is 5 times the slope of coastal regression. The results suggest that the concentrations and the uses may have stronger correlation in the inland communities. As more years of data are collected in different regions, these relationships may be confirmed more.

Linear regression model on pesticide use and concentration was used to develop a use cap for methyl bromide (Li et al., 2005; Fan et al., 2010). These previous analyses were conducted for the monthly or 8-week average concentrations and have overlooked some residue problems in the modeling or excluded parts of data to achieve significant regression. Although the air concentration of a pesticide must be caused by the use of this pesticide, it is a complex process that a pesticide volatilizes from an application, disperses in the air, travels to a certain location, and reaches some concentration. Usually function models with hourly weather profiles are needed to simulate such a procedure for a specific application, but may not work for yearly total use in a township and for chronic concentrations. Statistical models such as linear regression are applicable in this case but these models cannot explain causality and are only used to estimate variables' relationships empirically. A 6×6 mile area is used in this analysis because of the need of regulation, but may not be a correct use area to be connected with the average concentration. The failure of a simple linear regression model illustrates that: (1) linear association is not a good explanation

for the yearly township use-concentration relationship; and (2) more data needs to be collected and other factors may need to be considered to build up a statistical model for this case.

### **Application of Concentration/Use Ratio**

Although the yearly average concentration and the use in a township size area cannot be fitted with a linear regression model, the ratios of these two variables exhibit a pattern close to log-normal distributions in both use scenarios. This result further suggests that the combination of average concentrations and 1,3-D use amounts in townships could be random. Both the cumulative density of ratios and a fitted log-normal distribution are plotted in Figure 8 and they have the same uncertainties: (1) the sampled data series may not be representative of the real population; and (2) a change of environmental conditions or monitoring methods in the future may cause a change in the probabilities of occurrence of the phenomenon. Percentiles calculated from the fitted distributions are slightly different with the results shown in Table 4. For example, the 95<sup>th</sup> percentiles of concentration/ATP ratios are 6.03E-06 for Scenario I and 4.12E-06 for Scenario II. When calculating quantiles for the cumulative density 0.95 of the log-normal distributions, the values are 5.77E-06 for Scenario I and 4.65E-06 for the Scenario II. When the assumption of a log-normal distribution is true, the estimates based on the fitted distributions can be more accurate since they represent a population better than 31 data points.

In Scenario I, the lowest 8 concentration/use ratios fall in the coastal communities, the highest 6 ratios belong to the inland sampling sites, and the middle 17 ratios are a mix of two regions (Table 4b). For Scenario II, the lowest 15 ratios belong to the coastal sampling sites and the highest 16 ratios are a mix of the coastal and inland sampling sites (Table 4a). The result of a t-test shows that the means of log-transformed ratios are significantly different between two groups (Table 8). The geometric mean of coastal ratios is about  $e^{-1}$  or 0.36 times of the geometric mean of inland ratios. The means of log-transformed ratios between the two use scenarios are not significantly different, especially for the coastal sampling sites. Table 8 shows that the log-transformed ratios of the inland sampling sites have much lower variation in Scenario II than in Scenario I. This indicates that the 11-month use reduces the probability of the high concentration/ATP ratios in the inland communities.

DPR's RMD (2016) sets the regulatory target concentration at 0.56 ppb for the 70-year exposure. An estimate by calculating a township cap for the 95% yearly average concentrations is actually very protective compared to the 70-year average as 0.56 ppb. A bootstrapping method is applied to simulate the 70-year exposure with the estimated 1,3-D township cap (Table 9). First, the yearly average concentrations are calculated by multiplying the township cap of 135,785 lbs with the concentration/ATP ratios of Scenario II (11-month use). Then 70 values are randomly sampled from the calculated yearly concentrations as a 70-year sample and the sampling procedure is repeated for 100,000 times. The mean of each of 100,000 samples is calculated as a 70-year average concentration and the percentiles (50%, 95%, and 100%) are summarized for 100,000 70-year average concentrations. Besides total 31 ratios, this procedure is also applied to the inland ratios only to test if the inland area could have a risk exceeding the regulatory target concentration. Two types of Merced ratios are used for the inland simulation: the ratio calculated by the averaged Merced data, and the ratios of 8 individual Merced townships (excluding the township M08S10E). The results show that the highest 70-year average concentration is 0.46 ppb, lower than the regulatory target concentration.

## Conclusion

This report summarizes the data analysis on the relationship between 1,3-D use in a township-size area and its yearly average concentrations. The results of the analysis are used to calculate a township use cap ensuring that the 1,3-D 70-year average concentration of a township will not exceed the regulatory target concentration of 0.56ppb. 1,3-D ambient air concentrations have been collected in nine communities of California during 2006 – 2015. These data are compiled to calculate the yearly average concentrations that are paired with 1,3-D use amount in a township size area around sampling sites to study the relationship between the two variables. Because some of the highest concentrations have been monitored in December, two scenarios are set up for the data analysis: Scenario I, factual 12-month use, and Scenario II, hypothetical 11-month use excluding December. Prohibiting 1,3-D use in December could only affect the inland region since December use was not found in the coastal communities during the period of the air monitoring. Linear regression models cannot explain the relationships between 31 pairs of yearly average concentration and 1,3-D total use in both scenarios. The ratios of the yearly average concentrations and ATP exhibit a probability distribution close to log-normal. The relationship between 1,3-D yearly average concentration and the use in a township could vary in different regions because: (1) the linear association is estimated more significantly for the data separated by regions than their combination. The slope of the inland regression is 5 times the slope of the coastal regression; and (2) the geometric mean of concentration/ATP ratios of the inland sampling sites is significantly higher than that of the coastal sampling sites. Using the 95<sup>th</sup> percentiles of concentration/ATP ratios and a 1,3-D regulatory target concentration of 0.56 ppb, the township use cap is estimated at 135,785 lbs (ATP) in Scenario II (11-month use) and 92,854 lbs (ATP) in Scenario I (12-month use). The bootstrapping simulation shows that 100% 70-year average concentrations of townships applying 1,3-D under the use cap do not exceed the regulatory target concentration.

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## Figures

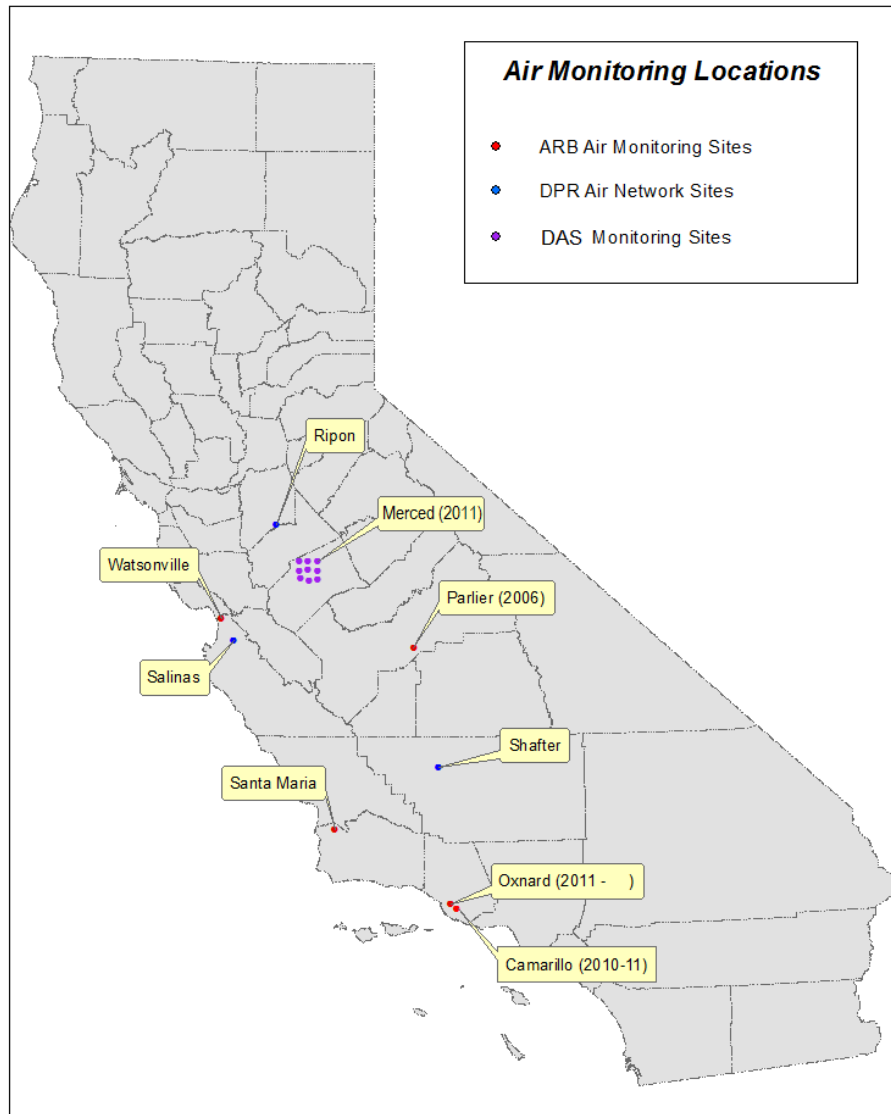


Figure 1. Locations of 1,3-D Air Monitoring Sites in California (2006-2015).

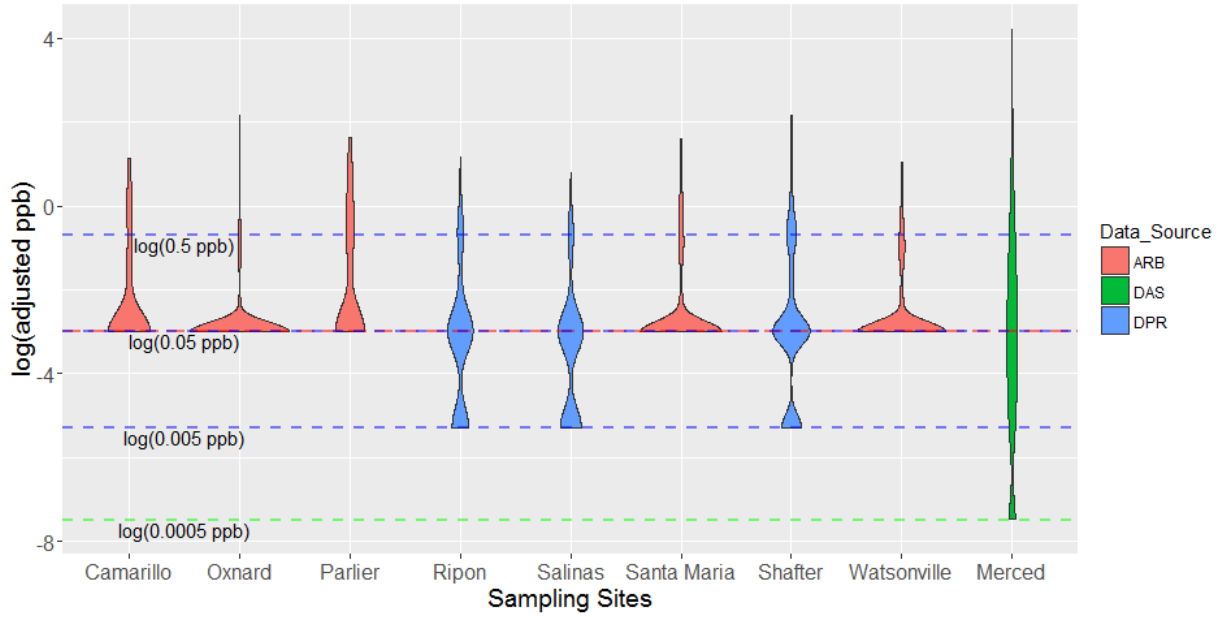


Figure 2. Violin plot for log-transformed 1,3-D concentrations sampled in the ambient air of California. About 54% samples are measured as NDs and substituted by the values of half the method detection limits (0.5- 0.0005 ppb) for data analysis.



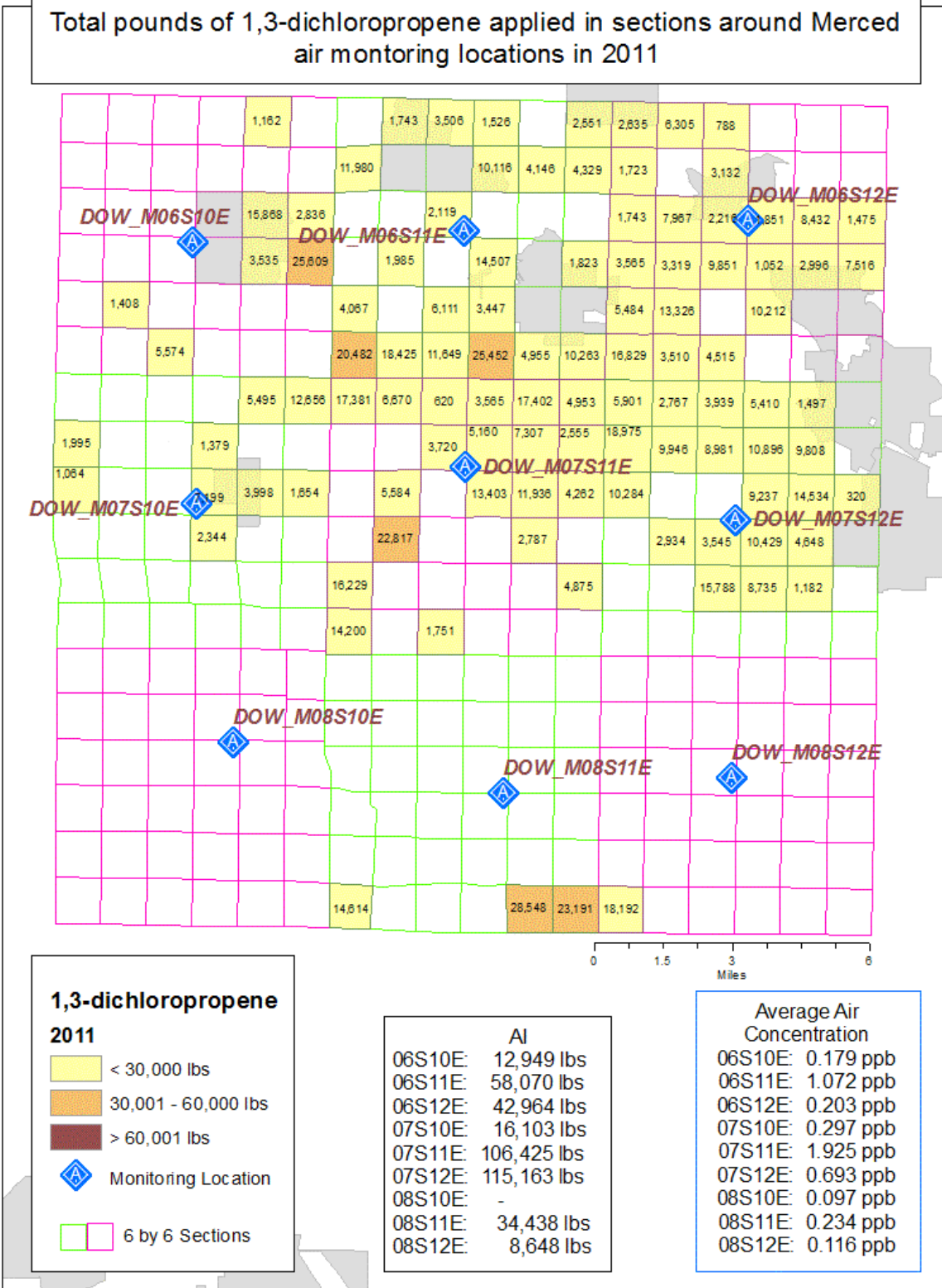


Figure 3. Map of 1,3-D air monitoring sites in 2011 DAS's Merced study and 1,3-D active ingredient (AI) amount queried from the PUR for nine townships where monitoring sites are located.

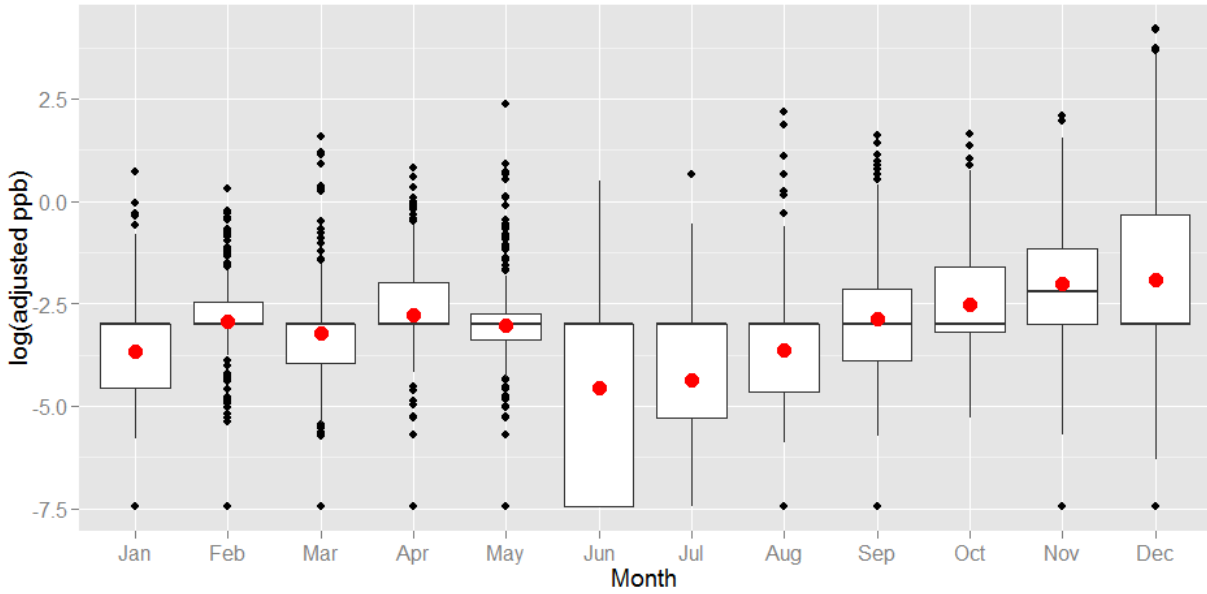


Figure 4. Boxplot of log-transformed 1,3-D concentrations over the months of the sampled years. Red points are means of log-transformed concentrations sampled in each month.

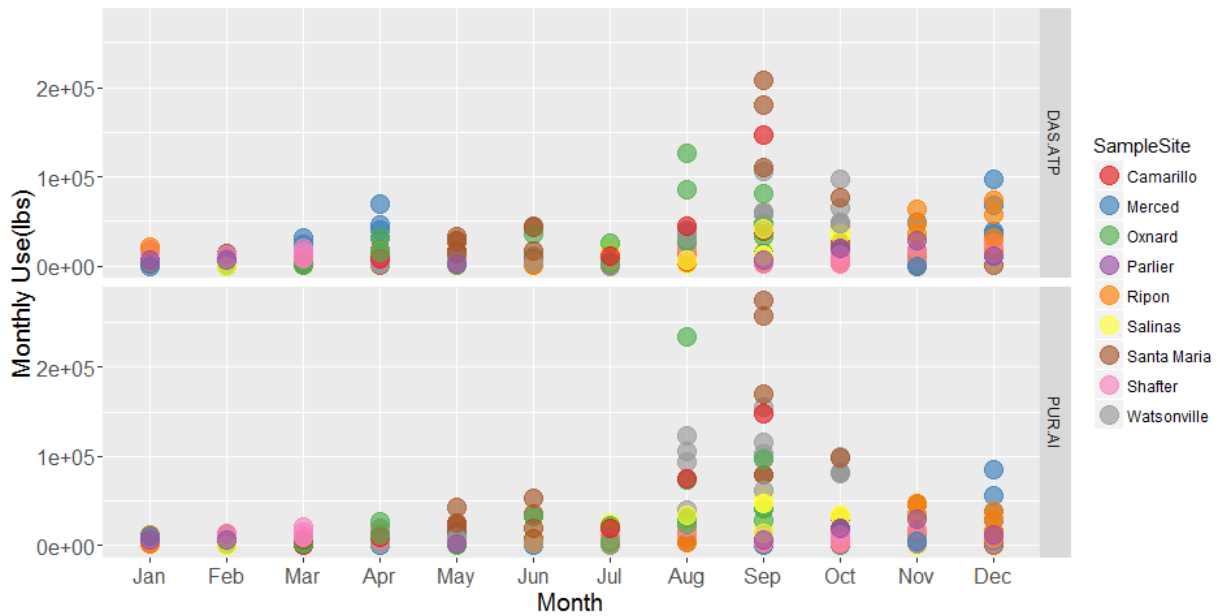


Figure 5. Monthly adjusted total pounds (DAS.ATP, lbs) and active ingredient use amount (PUR.AI, lbs) of 1,3-D in  $6 \times 6$  mile areas around sampling sites during the period of air monitoring studies.

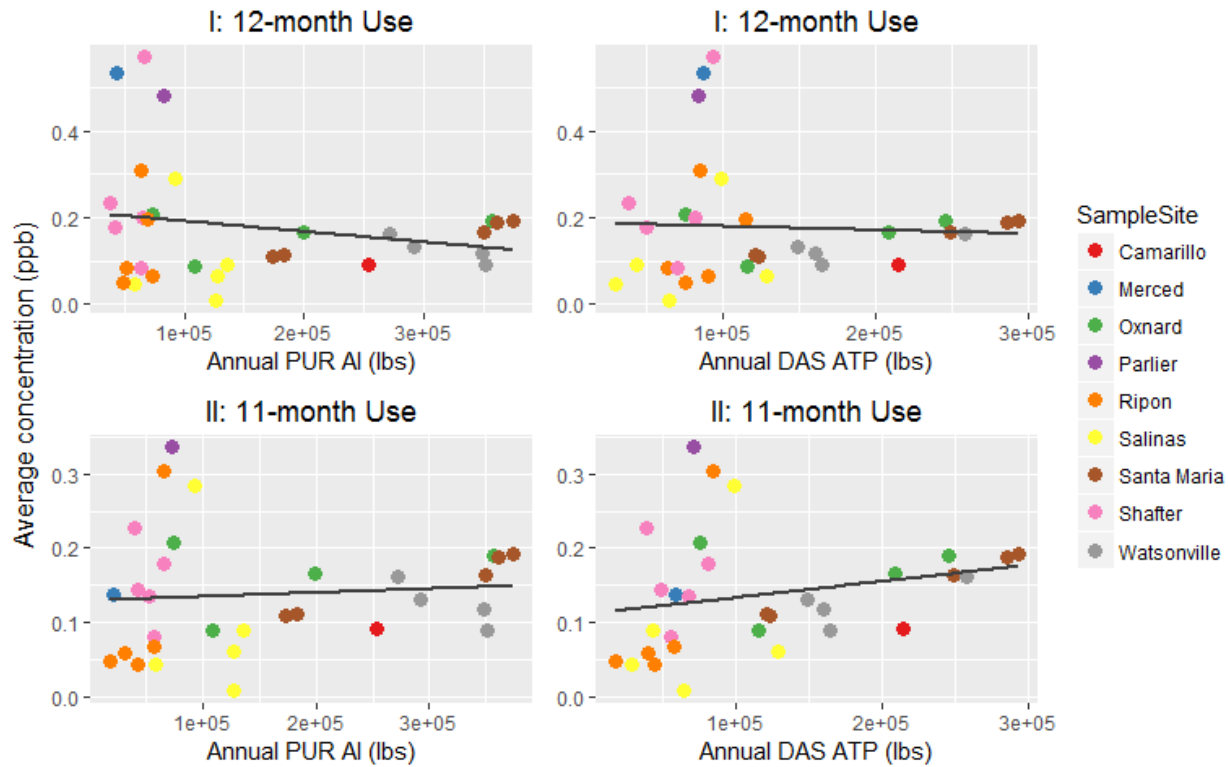


Figure 6. Scatterplot of 1,3-D yearly average concentrations and annual total uses in  $6 \times 6$  mile areas. Use are calculated from active ingredient (AI, lbs) reported in the PUR and adjusted total pounds (ATP, lbs) reported in the DAS data. Two use scenarios are included: Scenario I, factual 12-month use; and Scenario II, 11-month use, assuming no 1,3-D use and concentration measured as NDs in December. Linear regressions are plotted and estimated but not statistically significant.



Figure 7. Reduction (%) of annual adjusted total pounds (ATP) and yearly average concentration (ppb) by hypothetically prohibiting 1,3-D use and sampling only non-detects in December. All the sampling sites of the coastal area are not shown because these sites have less than 6% reduction in the use and the concentrations when comparing Scenario II (11-month use) to Scenario I (12-month use).

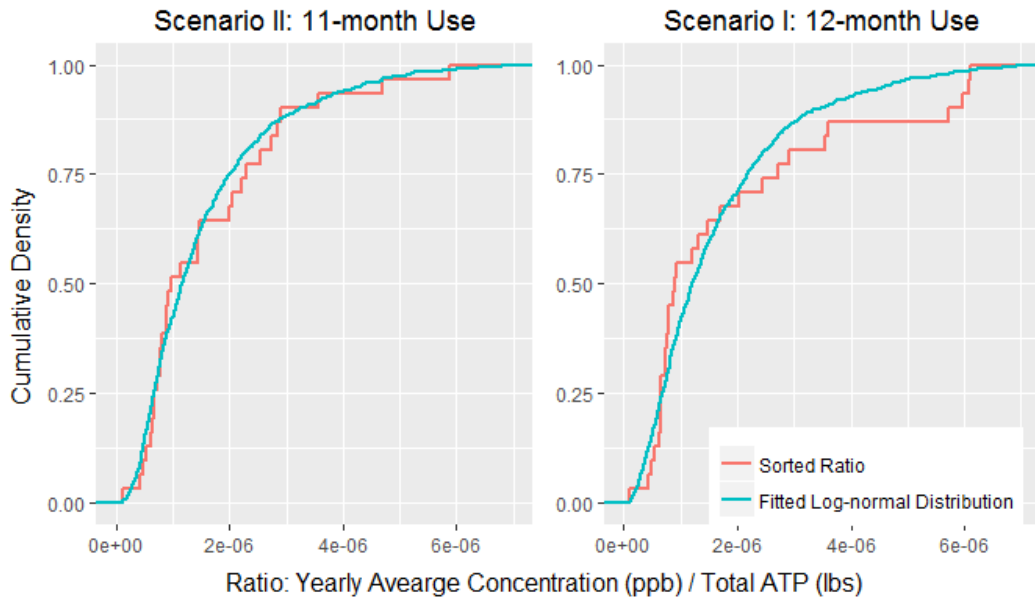


Figure 8. Cumulative density plot for ratios of 1,3-D yearly average concentration (ppb) and adjusted total pounds (ATP) in Scenario I (12-month use) and Scenario II (11-month use).

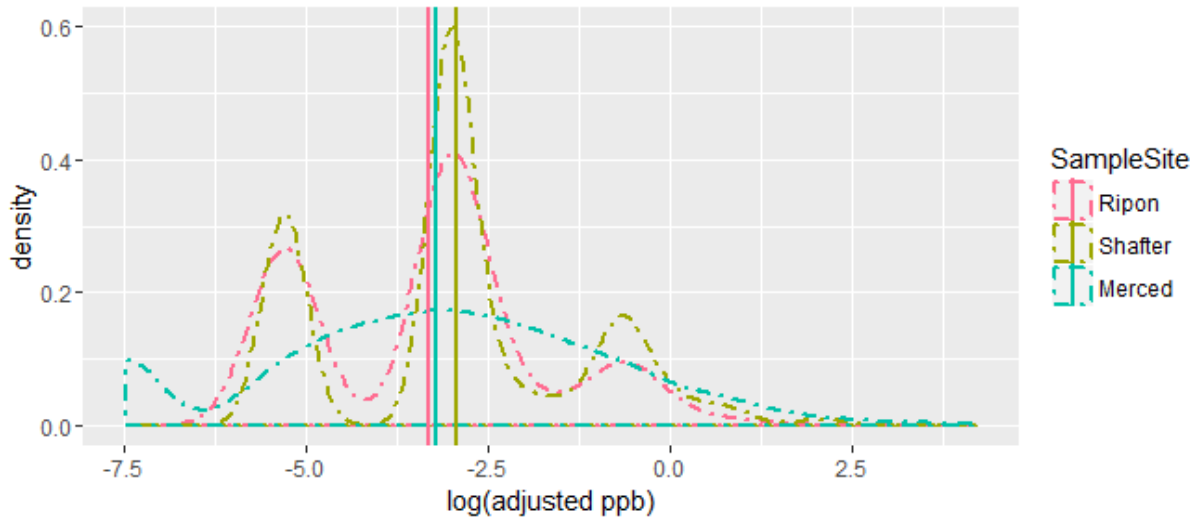


Figure 9. Density plot of log-transformed 1,3-D concentrations sampled in Ripon, Shafter, and Merced. The solid lines are means of log-transformed concentrations (ppb) of three sites, whose natural exponential estimates are equal to geometric means.

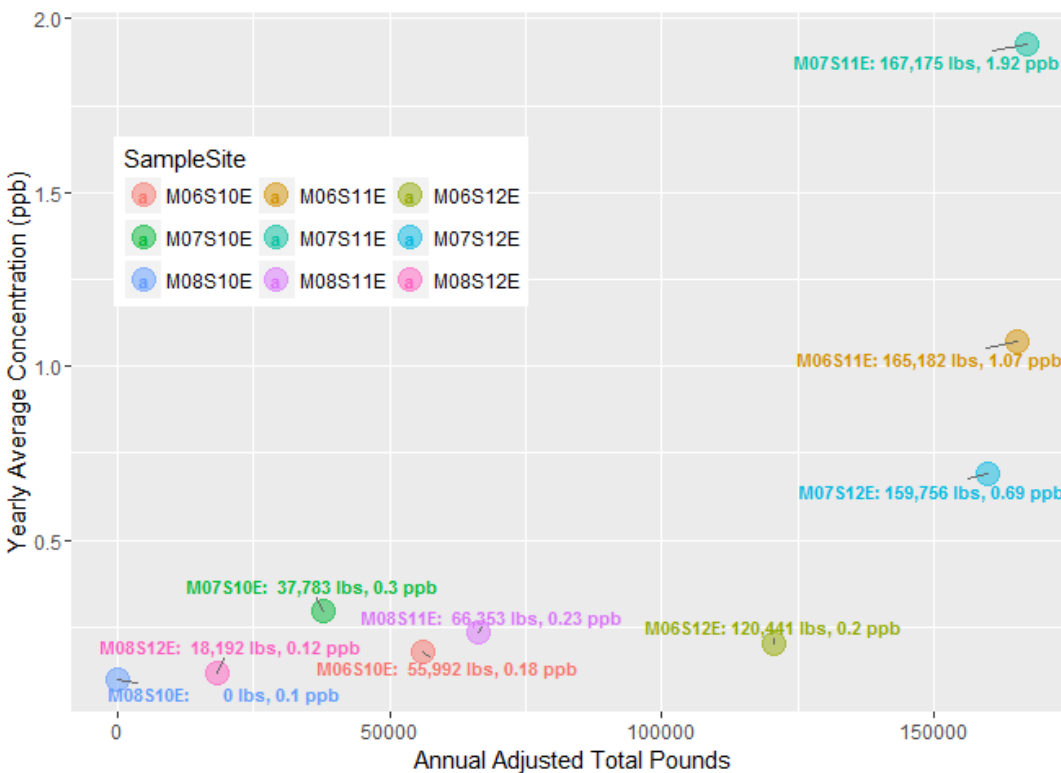


Figure 10. 1,3-D yearly average concentrations(ppb) and adjusted total pounds in nine townships of Merced in October 2010 – December 2011. The legend of sampling sites reflects the relative locations of nine townships.

## Tables

Table 1. Summary of ambient air monitoring studies conducted by Department of Pesticide Regulation (DPR), Air Resource Board (ARB), and Dow AgroSciences (DAS) involving pesticide 1,3-D.

Study	Community	Duration	Number of Sampling Sites	Sampling Method	Sampling Frequency	Method Detection Limit	Study Reports
<b>DPR: Air Monitoring Network</b>	Salinas Shafter Ripon	Feb 2011 – now	One at each community	Canister	24 hr every week	1 ppb: Feb – Jun 2011 0.1 ppb: Jun 2011 – Oct 2013 0.01 ppb: Oct 2013 – now	<a href="http://www.cdpr.ca.gov/docs/emon/airinit/air_network.htm">http://www.cdpr.ca.gov/docs/emon/airinit/air_network.htm</a>
<b>ARB: Toxic Air Contaminant Monitoring</b>	Camarillo Oxnard Santa Maria Watsonville	Aug 2010 – Oct 2011 Oct 2011 – now Aug 2010 – now Nov 2011 – now	One at each community	Canister	24 hr every 6 days	0.1 ppb	<a href="http://www.arb.ca.gov/adam/toxics/toxics.html">http://www.arb.ca.gov/adam/toxics/toxics.html</a>
<b>ARB &amp; DPR: Pesticide Air Monitoring in Parlier, CA</b>	Parlier	Jan 2006 – Jan 2007	One	Canister	24 hr every 6 days	0.1 ppb	<a href="http://cdpr.ca.gov/docs/envjust/pilot_proj/index.htm">http://cdpr.ca.gov/docs/envjust/pilot_proj/index.htm</a>
<b>DAS: 1,3-D Air Monitoring in Merced, CA</b>	Merced	Oct 2010 – Dec 2011	Nine at the approximate center of nine contiguous townships	Charcoal Tubes	Continuous sampling. Change tubes every 72 hours	0.001 ppb	

Table 2. Comparison results of 1,3-D detection probability and concentrations between December and the other Months. The probability of 1,3-D detections in December are significant higher than January – August. October has the highest detection probability, but its concentrations are lower than December. Analysis is originally done on log-transformed data therefore differences between months are estimated as ratio.

Ratio between Months	Detect Probability / Non-detect Probability Method: logistic regression		Adjusted Concentration (ppb) Method: t test	
	Estimate	P-value*	Estimate	P-value*
<b>December</b>	1.49	0.00	0.15	0.00
<b>January / December</b>	0.46	0.00	0.17	0.00
<b>February / December</b>	0.48	0.00	0.36	0.00
<b>March / December</b>	0.44	0.00	0.27	0.00
<b>April / December</b>	0.45	0.00	0.42	0.00
<b>May / December</b>	0.41	0.00	0.33	0.00
<b>June / December</b>	0.09	0.00	0.07	0.00
<b>July / December</b>	0.21	0.00	0.09	0.00
<b>August / December</b>	0.40	0.00	0.18	0.00
<b>September / December</b>	1.02	0.91	0.39	0.00
<b>October / December</b>	1.90	0.00	0.55	0.00
<b>November / December</b>	1.32	0.08	0.90	0.41

\* The difference between two months is considered to be significant if p-value < individual  $\alpha$  0.01

Table 3a. 1,3-D yearly average concentrations (ppb) of scenario I (12-month Use) and scenario II (11-month Use) at nine sampling sites.

Sample Site	Year													
	2006		2011		2012		2013		2014		2015		Average	
	I	II	I	II	I	II	I	II	I	II	I	II	I	II
<b>Camarillo</b>			0.091	0.091									0.091	0.091
<b>Merced</b>			0.535	0.137									0.535	0.137
<b>Oxnard</b>					0.191	0.191	0.167	0.167	0.089	0.089	0.207	0.207	0.164	0.164
<b>Parlier</b>	0.479	0.337											0.479	0.337
<b>Ripon</b>			0.308	0.304	0.050	0.047	0.195	0.060	0.067	0.067	0.084	0.044	0.141	0.104
<b>Salinas</b>			0.288	0.284	0.064	0.060	0.090	0.090	0.007	0.007	0.044	0.044	0.099	0.097
<b>Santa Maria</b>			0.165	0.165	0.192	0.192	0.189	0.189	0.112	0.112	0.109	0.109	0.153	0.153
<b>Shafter</b>			0.232	0.228	0.085	0.081	0.571	0.136	0.200	0.180	0.176	0.145	0.253	0.154
<b>Watsonville</b>					0.161	0.161	0.132	0.132	0.090	0.090	0.117	0.117	0.125	0.125

Table 3b. 1,3-D yearly adjusted total pounds of scenario I (12-month Use) and scenario II (11-month Use) within 6 × 6 mile areas around sampling sites.

Sample Site	Year													
	2006		2011		2012		2013		2014		2015		Average	
	I	II	I	II	I	II	I	II	I	II	I	II	I	II
<b>Camarillo</b>			215,230	215,230									215,230	215,230
<b>Merced</b>			87,875	59,793									87,875	59,793
<b>Oxnard</b>					246,171	246,171	209,043	209,043	115,579	115,579	76,100	76,100	161,723	161,723
<b>Parlier</b>	83,704	71,825											83,704	71,825
<b>Ripon</b>			85,484	85,484	75,583	18,253	114,589	40,953	90,448	58,465	64,028	45,138	86,026	49,658
<b>Salinas</b>			99,525	99,525	129,381	129,381	43,972	43,972	65,013	65,013	29,926	29,926	73,563	73,563
<b>Santa Maria</b>			249,007	249,007	293,210	293,210	286,272	286,272	121,531	121,531	123,956	123,559	214,795	214,716
<b>Shafter</b>			38,855	38,855	70,665	56,086	93,312	67,875	81,734	81,734	49,689	49,689	66,851	58,848
<b>Watsonville</b>					258,512	258,512	148,813	148,813	164,697	164,697	160,841	160,841	183,216	183,216



Table 4a. Ratio of 1,3-D yearly average concentration and adjusted total pounds (ATP) in 36 mile<sup>2</sup> area for Scenario I (12-month use).

Sample Site	Year	Average	ATP (lbs)	Ratio 1	Ratio1 Percentile Rank	Ratio 2	Ratio 2 Percentile Rank
		Concentration (ppb)		ATP / Concentration		Concentration / ATP	
Shafter	2013	0.57	93312	1.64E+05	0.00	6.12E-06	1.00
Merced <sup>1</sup>	2011	0.54	87875	1.64E+05	0.03	6.09E-06	0.97
Shafter	2011	0.23	38855	1.67E+05	0.07	5.97E-06	0.93
Parlier	2006	0.48	83704	1.75E+05	0.10	5.73E-06	0.90
Ripon	2011	0.31	85484	2.77E+05	0.13	3.60E-06	0.87
Shafter	2015	0.18	49689	2.82E+05	0.17	3.55E-06	0.83
Salinas	2011	0.29	99525	3.45E+05	0.20	2.90E-06	0.80
Oxnard	2015	0.21	76100	3.67E+05	0.23	2.72E-06	0.77
Shafter	2014	0.20	81734	4.08E+05	0.27	2.45E-06	0.73
Salinas	2013	0.09	43972	4.90E+05	0.30	2.04E-06	0.70
Ripon	2013	0.19	114589	5.89E+05	0.33	1.70E-06	0.67
Salinas	2015	0.04	29926	6.76E+05	0.37	1.48E-06	0.63
Ripon	2015	0.08	64028	7.65E+05	0.40	1.31E-06	0.60
Shafter	2012	0.08	70665	8.34E+05	0.43	1.20E-06	0.57
Santa Maria	2014	0.11	121531	1.09E+06	0.47	9.19E-07	0.53
Watsonville	2013	0.13	148813	1.13E+06	0.50	8.85E-07	0.50
Santa Maria	2015	0.11	123956	1.13E+06	0.53	8.81E-07	0.47
Oxnard	2013	0.17	209043	1.25E+06	0.57	7.99E-07	0.43
Oxnard	2012	0.19	246171	1.29E+06	0.60	7.77E-07	0.40
Oxnard	2014	0.09	115579	1.30E+06	0.63	7.68E-07	0.37
Ripon	2014	0.07	90448	1.36E+06	0.67	7.36E-07	0.33
Watsonville	2015	0.12	160841	1.37E+06	0.70	7.28E-07	0.30
Ripon	2012	0.05	75583	1.51E+06	0.73	6.62E-07	0.27
Santa Maria	2011	0.16	249007	1.51E+06	0.77	6.61E-07	0.23
Santa Maria	2013	0.19	286272	1.52E+06	0.80	6.59E-07	0.20
Santa Maria	2012	0.19	293210	1.53E+06	0.83	6.55E-07	0.17
Watsonville	2012	0.16	258512	1.60E+06	0.87	6.24E-07	0.13
Watsonville	2014	0.09	164697	1.84E+06	0.90	5.44E-07	0.10
Salinas	2012	0.06	129381	2.03E+06	0.93	4.92E-07	0.07
Camarillo <sup>2</sup>	2011	0.09	215230	2.37E+06	0.97	4.23E-07	0.03
Salinas	2014	0.01	65013	8.84E+06	1.00	1.13E-07	0.00

1. Merced is the average of nine sampling sites; 2. Camarillo 2011 is the estimates of data during September 2010 – August 2011.

Table 4b. Ratio of 1,3-D yearly average concentration and adjusted total pounds(ATP) in 36 mile<sup>2</sup> area for scenario II (11-month use).

Sample Site	Year	Average	ATP (lbs)	Ratio 1	Ratio1 Percentile Rank	Ratio 2	Ratio 2 Percentile Rank
		Concentration (ppb)		ATP / Concentration		Concentration / ATP	
Shafter	2011	0.23	38855	1.70E+05	0.00	5.87E-06	1.00
Parlier	2006	0.34	71825	2.13E+05	0.03	4.69E-06	0.97
Ripon	2011	0.30	85484	2.81E+05	0.07	3.56E-06	0.93
Shafter	2015	0.14	49689	3.43E+05	0.10	2.91E-06	0.90
Salinas	2011	0.28	99525	3.51E+05	0.13	2.85E-06	0.87
Oxnard	2015	0.21	76100	3.67E+05	0.17	2.72E-06	0.83
Ripon	2012	0.05	18253	3.92E+05	0.20	2.55E-06	0.80
Merced <sup>1</sup>	2011	0.14	59793	4.35E+05	0.23	2.30E-06	0.77
Shafter	2014	0.18	81734	4.55E+05	0.27	2.20E-06	0.73
Salinas	2013	0.09	43972	4.90E+05	0.30	2.04E-06	0.70
Shafter	2013	0.14	67875	5.00E+05	0.33	2.00E-06	0.67
Salinas	2015	0.04	29926	6.76E+05	0.37	1.48E-06	0.63
Ripon	2013	0.06	40953	6.88E+05	0.40	1.45E-06	0.60
Shafter	2012	0.08	56086	6.90E+05	0.43	1.45E-06	0.57
Ripon	2014	0.07	58465	8.78E+05	0.47	1.14E-06	0.53
Ripon	2015	0.04	45138	1.03E+06	0.50	9.73E-07	0.50
Santa Maria	2014	0.11	121531	1.09E+06	0.53	9.19E-07	0.47
Watsonville	2013	0.13	148813	1.13E+06	0.57	8.85E-07	0.43
Santa Maria	2015	0.11	123559	1.13E+06	0.60	8.84E-07	0.40
Oxnard	2013	0.17	209043	1.25E+06	0.63	7.99E-07	0.37
Oxnard	2012	0.19	246171	1.29E+06	0.67	7.77E-07	0.33
Oxnard	2014	0.09	115579	1.30E+06	0.70	7.68E-07	0.30
Watsonville	2015	0.12	160841	1.37E+06	0.73	7.28E-07	0.27
Santa Maria	2011	0.16	249007	1.51E+06	0.77	6.61E-07	0.23
Santa Maria	2013	0.19	286272	1.52E+06	0.80	6.59E-07	0.20
Santa Maria	2012	0.19	293210	1.53E+06	0.83	6.55E-07	0.17
Watsonville	2012	0.16	258512	1.60E+06	0.87	6.24E-07	0.13
Watsonville	2014	0.09	164697	1.84E+06	0.90	5.44E-07	0.10
Salinas	2012	0.06	129381	2.15E+06	0.93	4.65E-07	0.07
Camarillo <sup>2</sup>	2011	0.09	215230	2.37E+06	0.97	4.23E-07	0.03
Salinas	2014	0.01	65013	8.84E+06	1.00	1.13E-07	0.00

1. Merced is the average of nine sampling sites; 2. Camarillo 2011 is the estimates of data during September 2010 – August 2011.

Table 5. Percentages of quantitative measurements in each year and summary statistics of adjusted concentrations (ppb).

Sample Site	Quantitative Measurements (%)							Statistics of Adjusted Concentrations (ppb)		
	2006	2010	2011	2012	2013	2014	2015	Arithmetic Mean	Geometric Mean	Median
<b>Camarillo</b>		31.6 <sup>1</sup>	21.7 <sup>1</sup>					0.25	0.09	0.05
<b>Oxnard</b>				9.9	15.7	5.8	6.5	0.16	0.06	0.05
<b>Parlier</b>	34.3							0.48	0.13	0.05
<b>Ripon</b>			4.3	0.0	15.4	18.9	31.4	0.14	0.04	0.05
<b>Salinas</b>			6.3	1.9	15.7	3.8	19.2	0.10	0.03	0.05
<b>Santa Maria</b>		28.6	11.9	27.4	19.2	8.6	13.1	0.16	0.07	0.05
<b>Shafter</b>			0.0	5.8	26.4	36.5	42.3	0.25	0.05	0.05
<b>Watsonville</b>			16.7 <sup>1</sup>	13.0	21.1	10.3	20.3	0.12	0.07	0.05
<b>Merced</b>		97.9 <sup>1</sup>	85.8					0.62	0.04	0.04

1. Estimated from measurements less than a year.

Table 6. Discrepancy between 1,3-D use amounts in 6x6 grid area queried from the PUR and DAS databases and ratios of annual adjusted total pounds (ATP) to active ingredient(AI) amount.

Sample Site	Annual Discrepancy: DAS AI / PUR AI					Annual Adjust Factor: DAS ATP / DAS AI				
	2011	2012	2013	2014	2015	2011	2012	2013	2014	2015
<b>Oxnard</b>		0.57	1.00	0.99	1.00		1.22	1.04	1.08	1.04
<b>Santa Maria</b>	0.62	0.70	1.03	1.01	0.98	1.15	1.12	0.77	0.66	0.73
<b>Watsonville</b>		0.91	1.03	1.01	1.00		1.05	0.50	0.46	0.46
<b>Ripon</b>	1.07	0.99	0.99	0.99	0.99	1.24	1.56	1.65	1.23	1.24
<b>Salinas</b>	0.98	0.97	0.83	1.21	1.02	1.09	1.04	0.39	0.42	0.50
<b>Shafter</b>	1.00	1.00	1.09	1.20	0.99	1.00	1.11	1.29	1.03	1.17
<b>Merced<sup>1</sup></b>	1.30 – 3.77					1.00-1.15				

1. 1,3-D use around Merced sampling sites is queried for nine townships and this table lists a range based on eight townships. According to both PUR and DAS data, township M08S10E did not have reported use of 1,3-D in 2011 so does not have discrepancy ratio and adjust factor.

Table 7. Results of linear regression analysis on yearly average concentration (ppb) and total use (10,000 lbs).

Scenario	Model	Intercept	Slope	P-value	R <sup>2</sup> (%)
<b>I:</b>	Average concentration (ppb) ~ DAS ATP (10,000 lbs)	0.19	-0.00087	0.80	0.24
<b>12-month Use</b>	Average concentration (ppb) ~ PUR AI (10,000 lbs)	0.22	-0.0024	0.25	4.47
	Log (average concentration (ppb)) ~ DAS ATP (10,000 lbs)	-2.23	0.017	0.40	2.42
	Log (average concentration (ppb)) ~ PUR AI (10,000 lbs)	-1.99	-0.0016	0.90	0.05
<b>II:</b>	Average concentration (ppb) ~ DAS ATP (10,000 lbs)	0.11	0.0022	0.22	5.21
<b>11-month Use</b>	Average concentration (ppb) ~ PUR AI (10,000 lbs)	0.13	0.00053	0.65	0.70
	Log (average concentration (ppb)) ~ DAS ATP (10,000 lbs)	-2.55	0.030	0.07	11.1
	Log (average concentration (ppb)) ~ PUR AI (10,000 lbs)	-2.37	0.012	0.31	3.61
<b>Inland Only<sup>1</sup></b>	Log (average concentration (ppb)) ~ DAS ATP (10,000 lbs)	-3.52	0.246	0.02	44.9
<b>Coast Only<sup>2</sup></b>	Log (average concentration (ppb)) ~ DAS ATP (10,000 lbs)	-3.01	0.049	0.03	25.1

1. Use 12 data points of sampling site Merced, Parlier, Ripon, and Shafter; 2. Use 19 data points of sampling site Camarillo, Oxnard, Salinas, Santa Maria, and Watsonville.

Table 8. Comparison of the log-transformed ratios of yearly average concentration and adjusted total pounds between the coastal and inland sampling sites.

Region	Scenario II: 11-month Use				Scenario I: 12-month Use		
	N	Mean	St. Dev.	95% CI of Difference	Mean	St. Dev.	95% CI of Difference
<b>Coast</b>	19	-14.046	0.718	(-1.512, -0.575)	-14.042	0.717	(-1.740, -0.523)
<b>Inland</b>	12	-13.003	0.549		-12.911	0.835	

Table 9. 1,3-D 70-year average concentrations with the township cap 135,785 lbs of Scenario II (11-month use) estimated by a bootstrapping method.

<b>Yearly Avg Concentration/ATP Ratios</b>	<b>Estimates of Yearly Average Concentrations (ppb) With the Township Cap 135785 lbs</b>	<b>Bootstrap Sample Size (Year)</b>	<b>Bootstrap Sampling Times</b>	<b>Percentiles of 100,000 70-year averages</b>		
<b>11-month Use:</b>	<b>135,785 lbs * (Yearly Avg Concentration/Annual ATP Ratios)</b>			<b>50%</b>	<b>95%</b>	<b>100%</b>
	0.80 0.64 0.48 0.40 0.39 0.37 0.35 0.31 0.30 0.28 0.27 0.20 0.20 0.20					
31 ratios from all the monitored locations	0.15 0.13 0.12 0.12 0.12 0.11 0.11 0.10 0.10 0.09 0.09 0.09 0.08 0.07 0.06 0.06 0.02			0.22	0.26	0.32
12 ratios from the Inland locations only (Average Merced townships)	0.80 0.64 0.48 0.40 0.35 0.31 0.30 0.27 0.20 0.20 0.15 0.13	70	100,000	0.35	0.39	0.46
19 ratios from the Inland locations only (Individual Merced townships)	0.17 0.10 0.13 0.57 0.53 0.37 0.39 0.52 0.80 0.64 0.48 0.40 0.35 0.30 0.27 0.20 0.20 0.15 0.13			0.35	0.39	0.46

## Appendix I

### Application Factors to Calculate 1,3-Dichloropropene Adjusted Total Pounds (Source: Pesticide Use Enforcement Program Standards Compendium V3, Restricted Materials and Permitting. Appendix J: 1,3-Dichloropropene Pesticides (Field Fumigant) Recommended Permit Conditions)

Location	Tarp Type	Months	Fumigation Method*	Application Factor
Within San Joaquin Valley	non-60% credit	Dec or Jan	Shallow	Prohibited
			Deep	1.9
			Drip	1.16
		Feb-Nov	Shallow	1.9
			Deep	1.0
			Drip	1.16
	60% credit	Dec or Jan	Shallow	0.6
			Deep	0.6
			Strip	1.2
			Drip	1.16
		Feb-Nov	Shallow	0.3
			Deep	0.3
Outside San Joaquin Valley	non-60% credit	Dec or Jan	Shallow	2.3
			Deep	1.2
			Drip	1.16
		Feb-Nov	Shallow	1.9
			Deep	1.0
			Drip	1.16
	60% credit	Dec or Jan	Shallow	0.6
			Deep	0.6
			Strip	1.2
			Drip	1.16
		Feb-Nov	Shallow	0.3
			Deep	0.3
Feb-Nov	Strip	0.6		
	Drip	1.16		

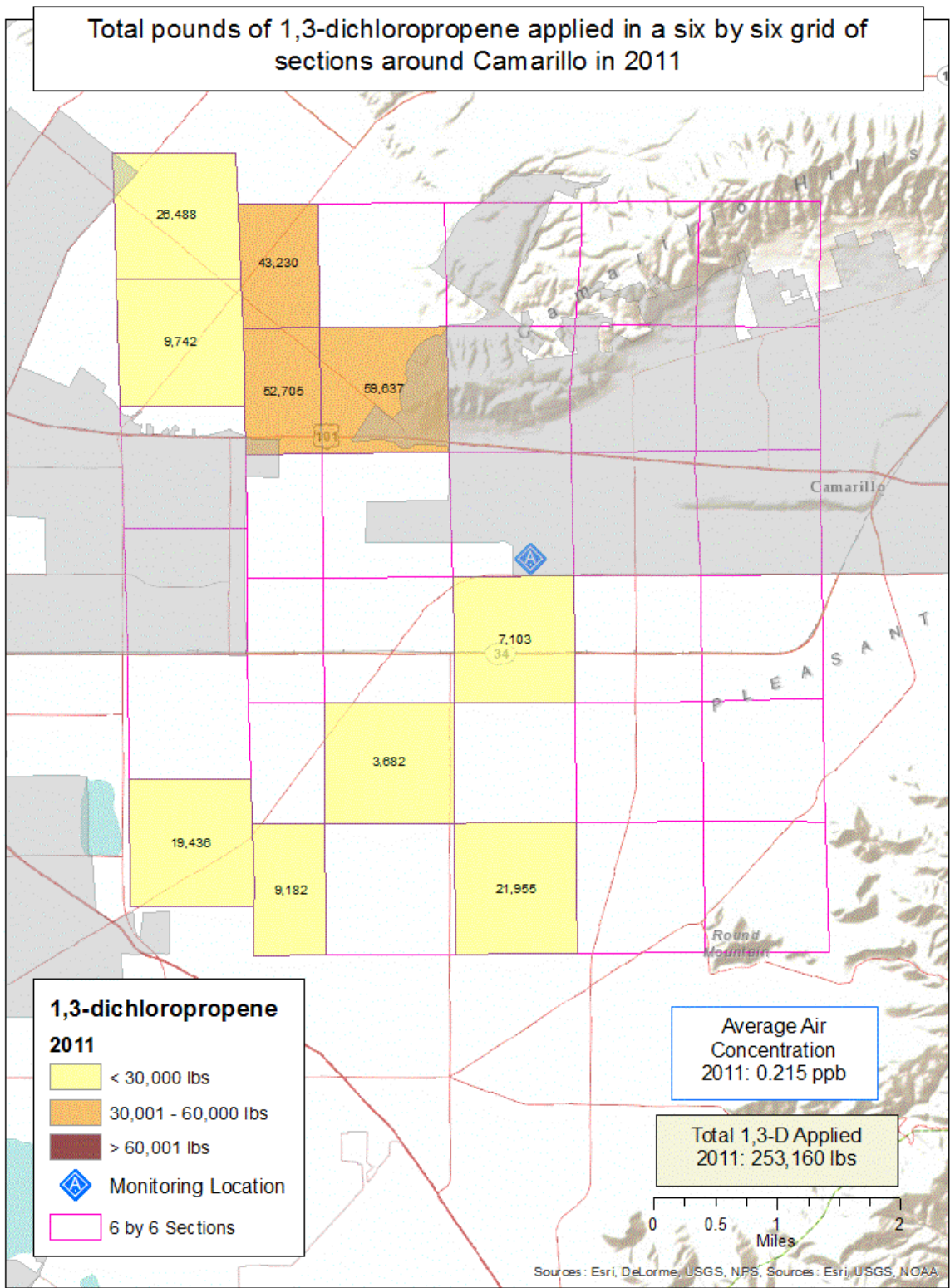
\*Fumigation methods consist of:

- Shallow – shank injection less than 18 inches deep;
- Deep – shank injection 18 inches or deeper;
- Strip – shank injection alternating with untreated area;
- Drip – chemigation using drip irrigation system. Drip irrigation applications shall use an application factor of 1.16, regardless of depth

## **Appendix II**

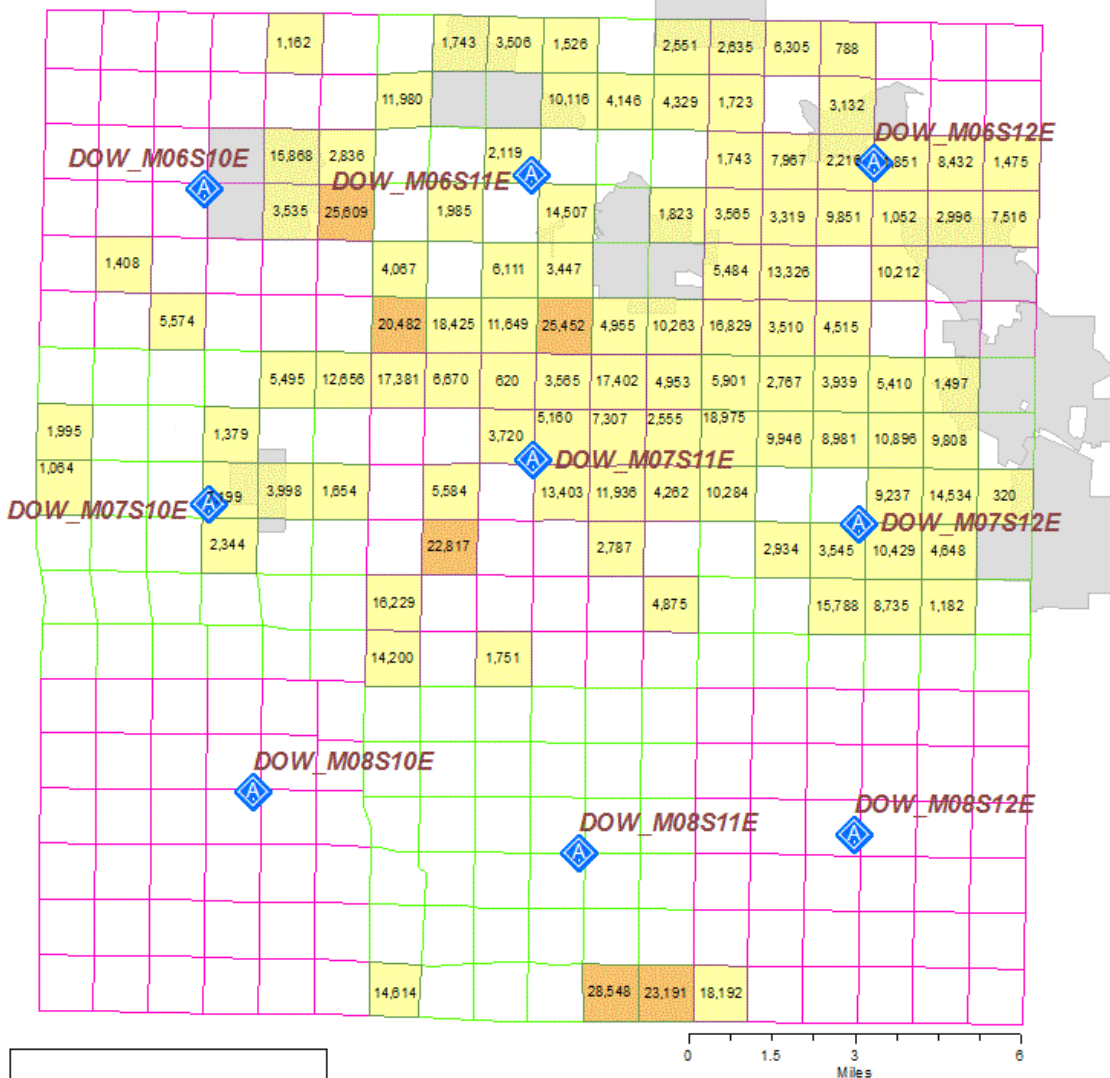
### **PUR Use Map of 1,3-Dichloropropene in 6 × 6 Mile Area around Air Monitoring Stations in 2006 – 2015**

**(Source: Rosemary Neal, Senior Environmental Scientist, DPR)**





**Total pounds of 1,3-dichloropropene applied in sections around Merced  
air monitoring locations in 2011**



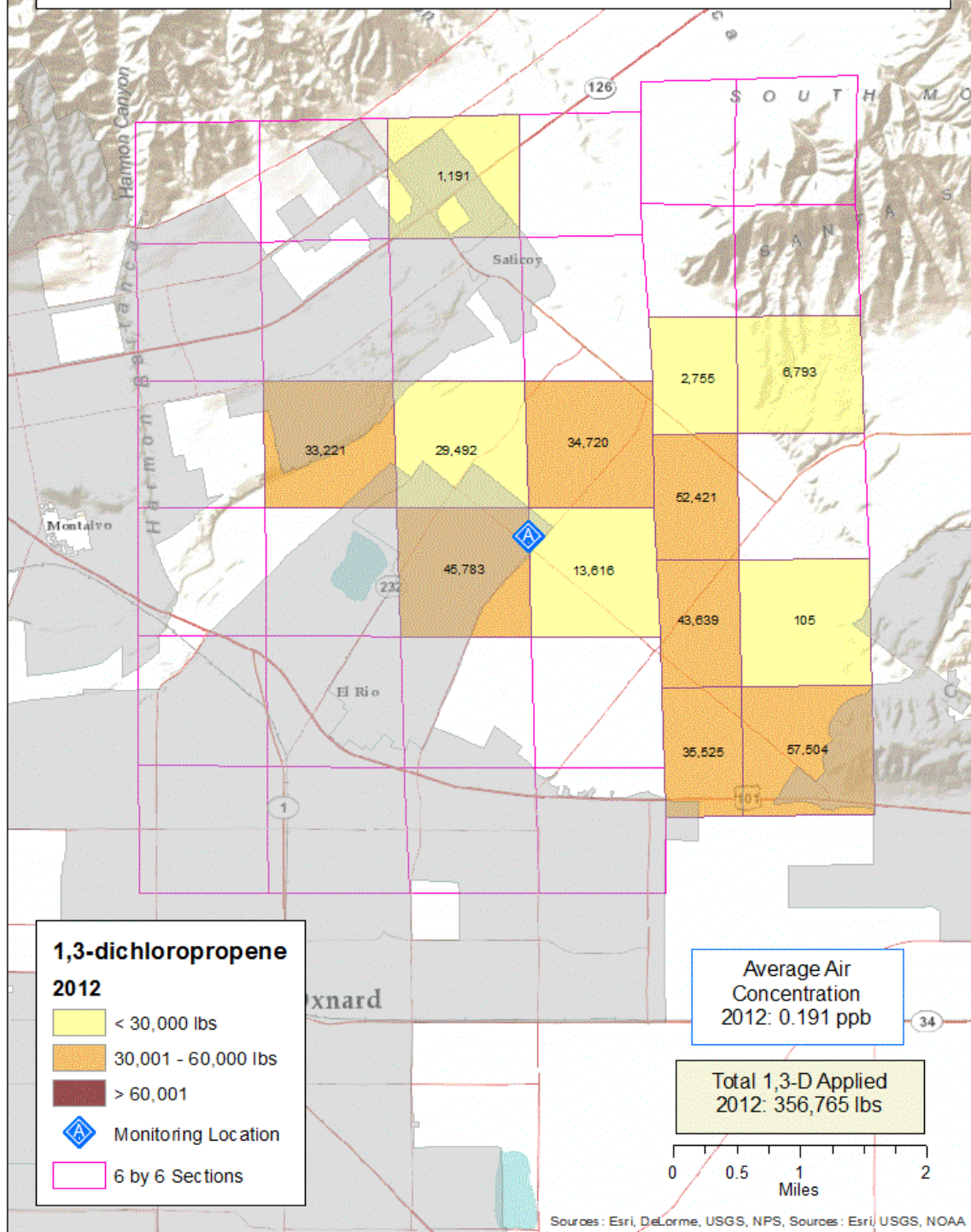
**1,3-dichloropropene  
2011**

- < 30,000 lbs
- 30,001 - 60,000 lbs
- > 60,001 lbs
- Monitoring Location
- 6 by 6 Sections

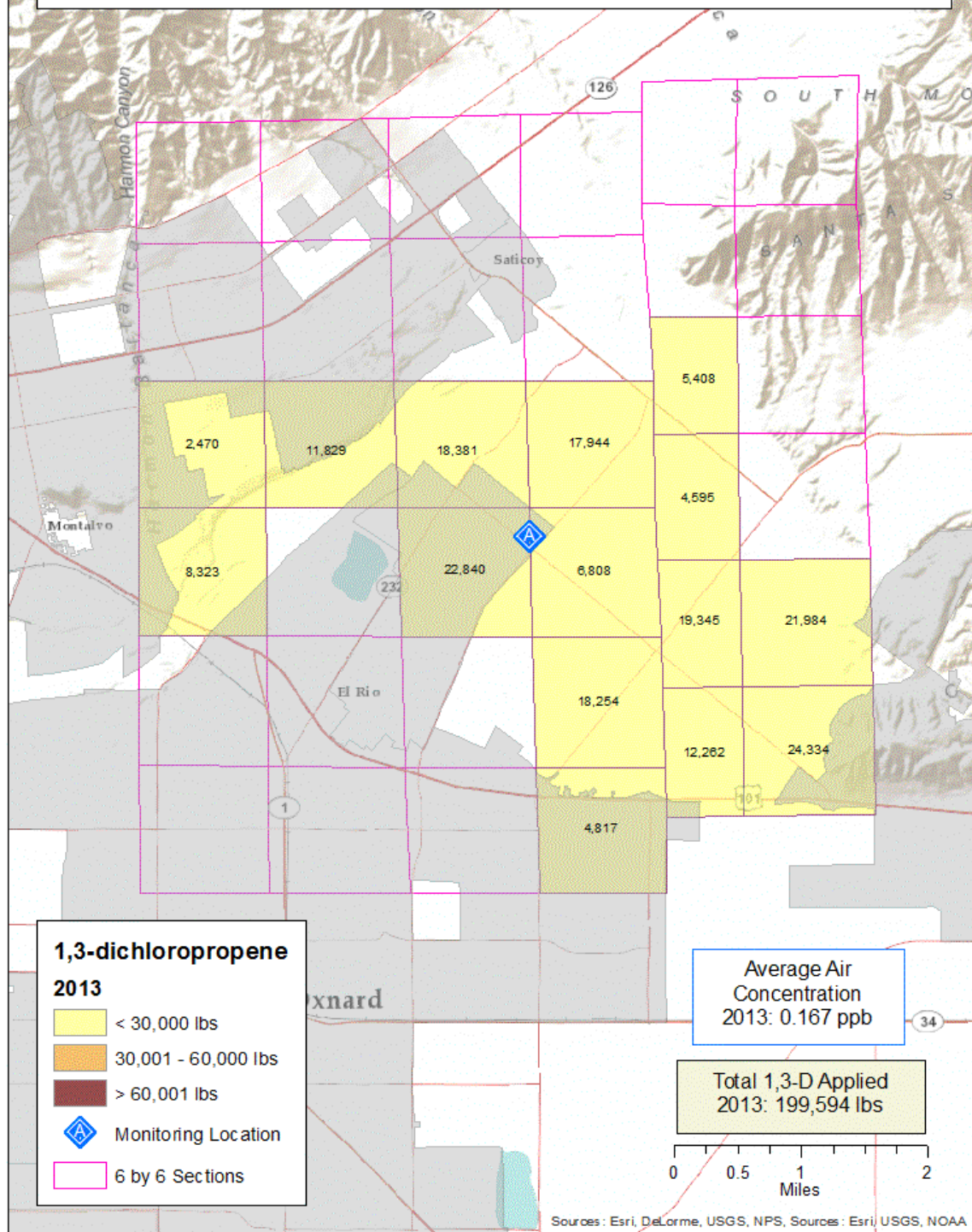
AI	
06S10E:	12,949 lbs
06S11E:	58,070 lbs
06S12E:	42,964 lbs
07S10E:	16,103 lbs
07S11E:	106,425 lbs
07S12E:	115,163 lbs
08S10E:	-
08S11E:	34,438 lbs
08S12E:	8,648 lbs

Average Air Concentration	
06S10E:	0.179 ppb
06S11E:	1.072 ppb
06S12E:	0.203 ppb
07S10E:	0.297 ppb
07S11E:	1.925 ppb
07S12E:	0.693 ppb
08S10E:	0.097 ppb
08S11E:	0.234 ppb
08S12E:	0.116 ppb

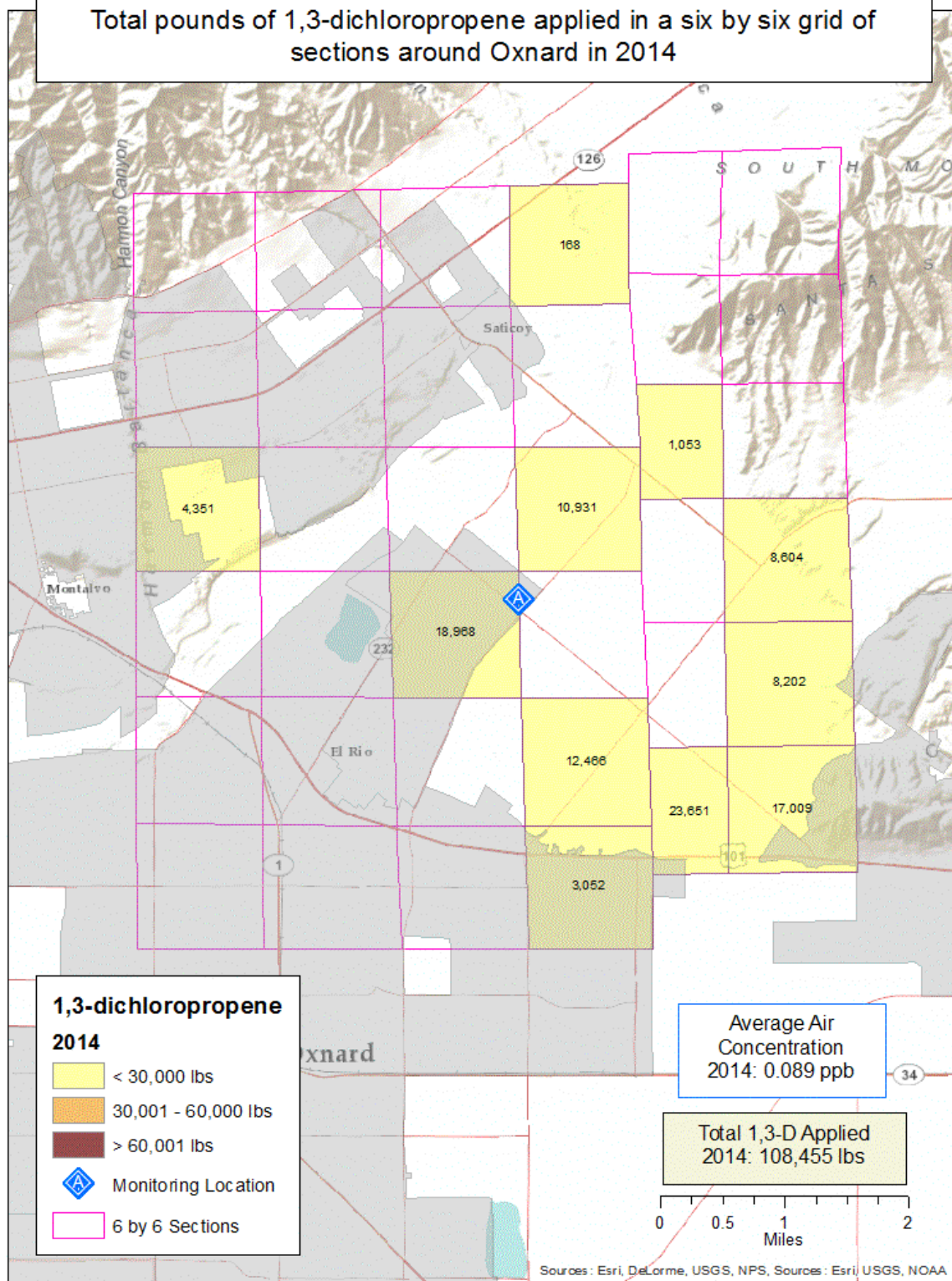
Total pounds of 1,3-dichloropropene applied in a six by six grid of sections around Oxnard in 2012



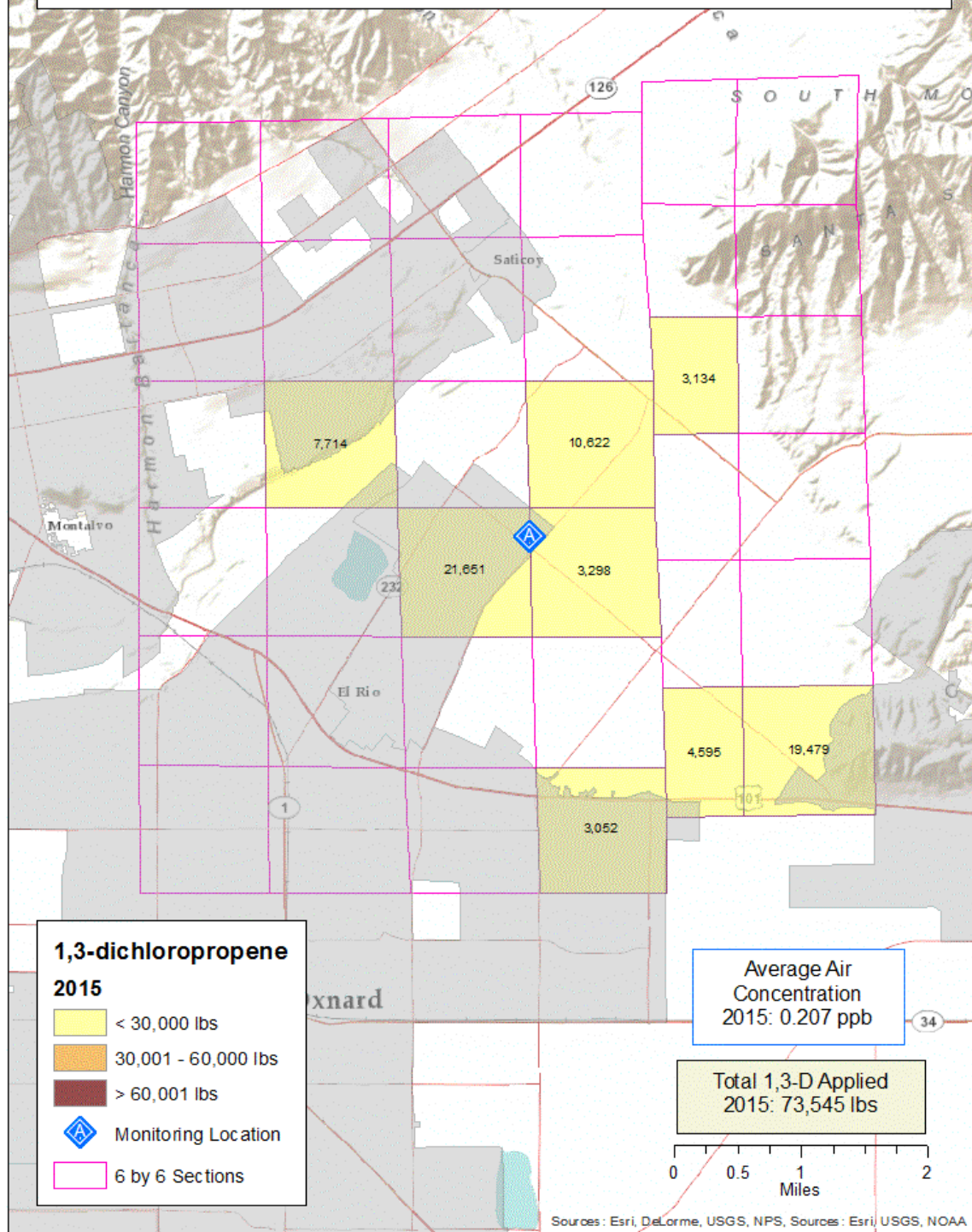
Total pounds of 1,3-dichloropropene applied in a six by six grid of sections around Oxnard in 2013



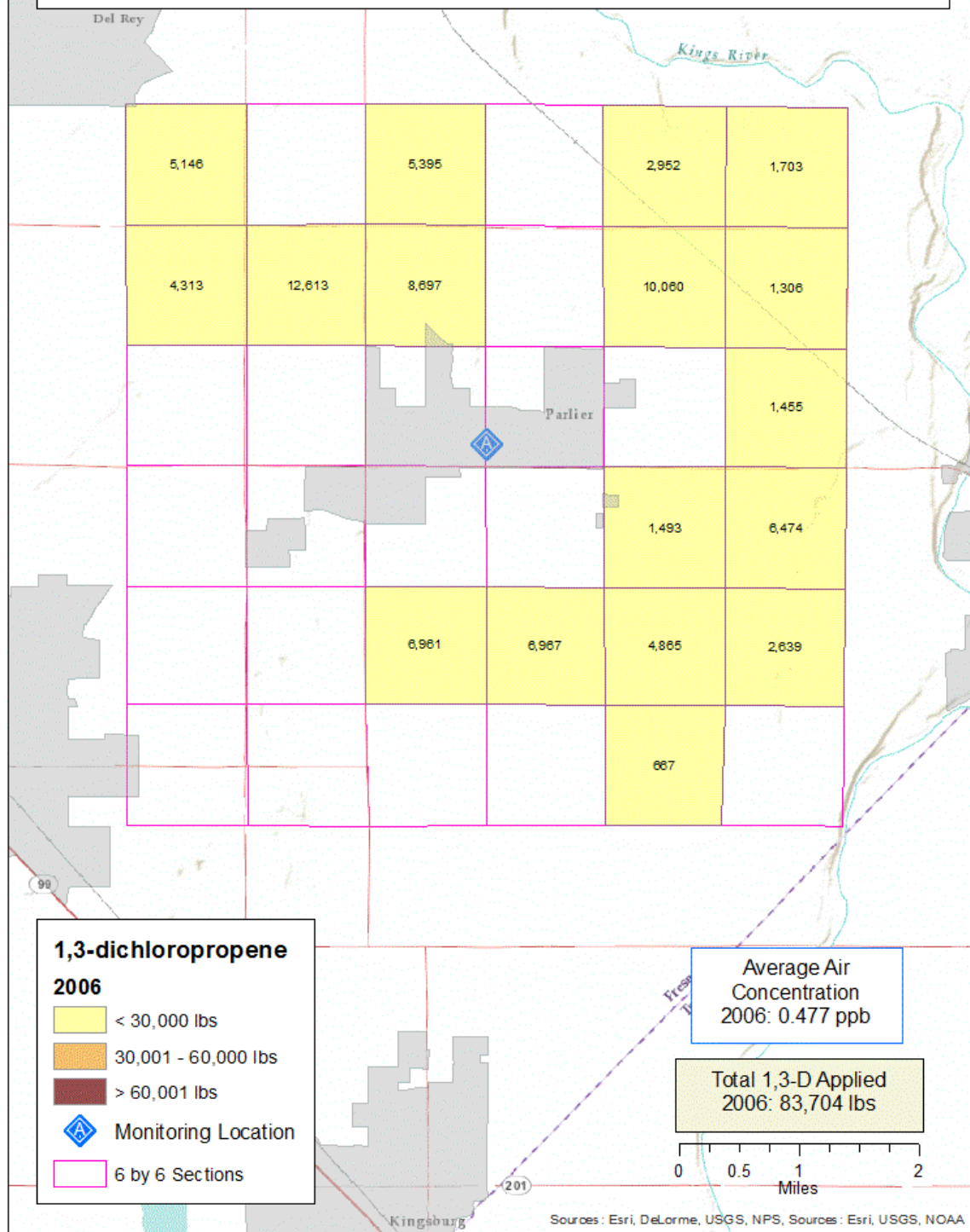
Total pounds of 1,3-dichloropropene applied in a six by six grid of sections around Oxnard in 2014

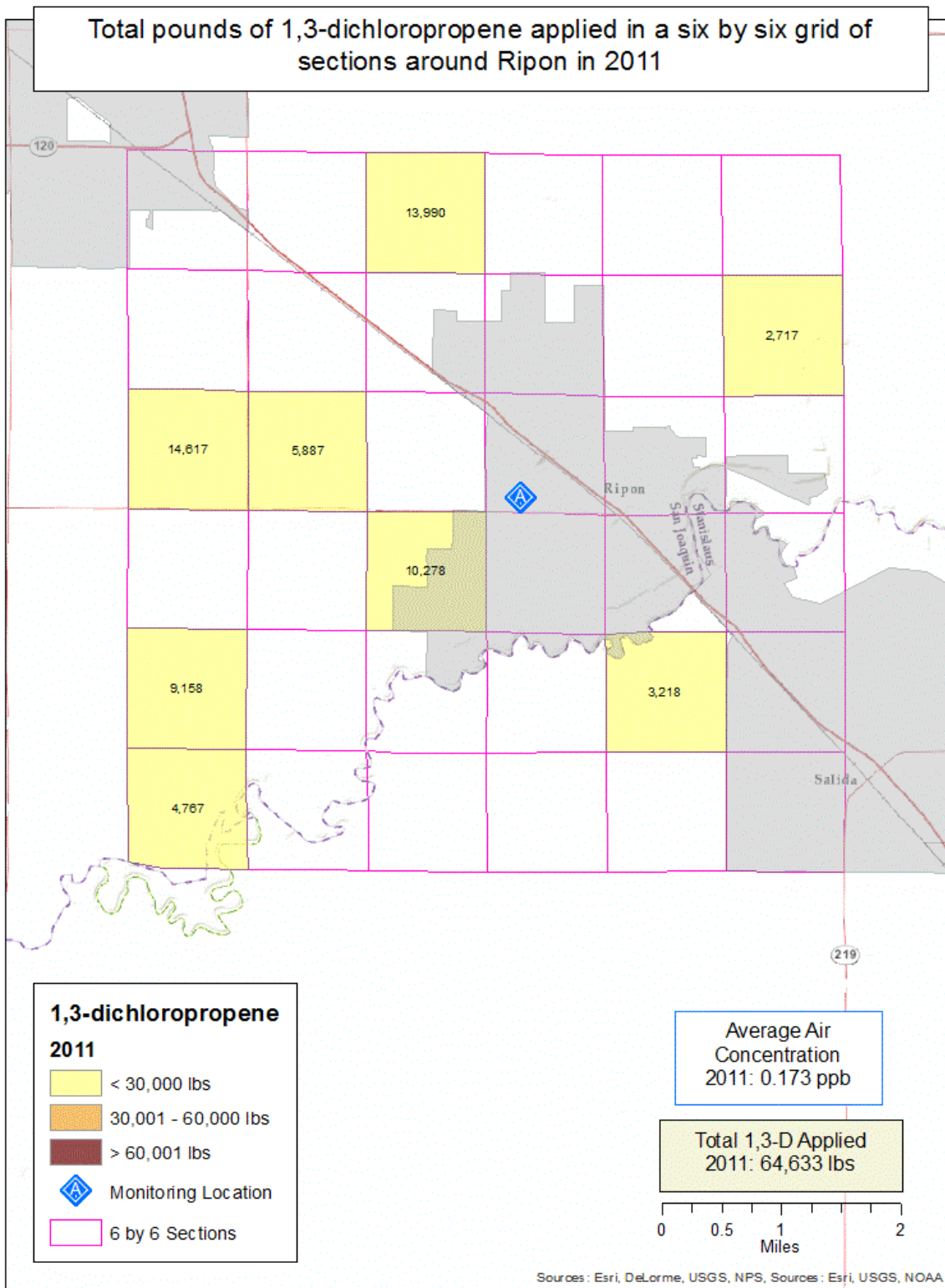


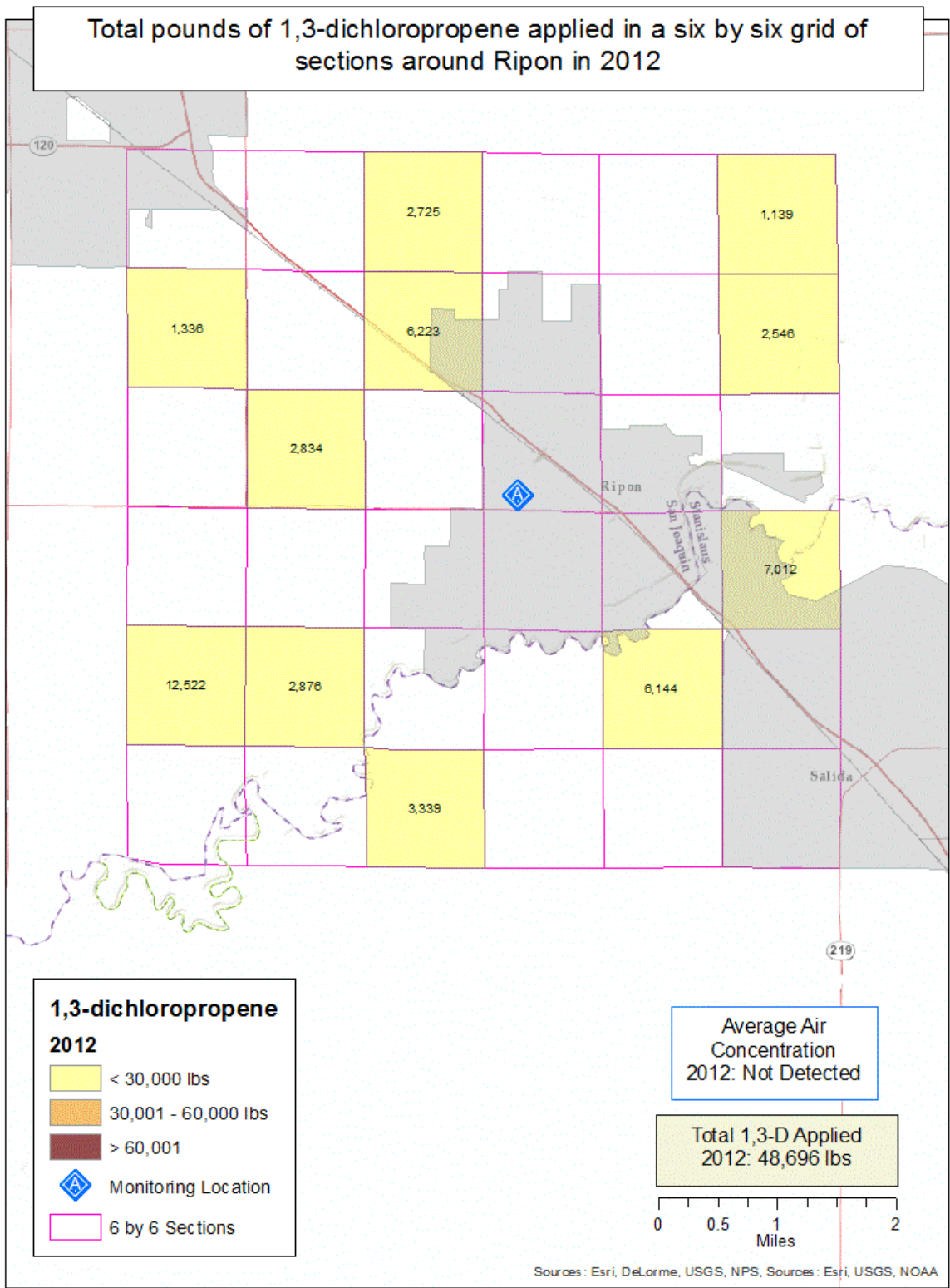
Total pounds of 1,3-dichloropropene applied in a six by six grid of sections around Oxnard in 2015



**Total pounds of 1,3-dichloropropene applied in a six by six grid of sections around Parlier in 2006**

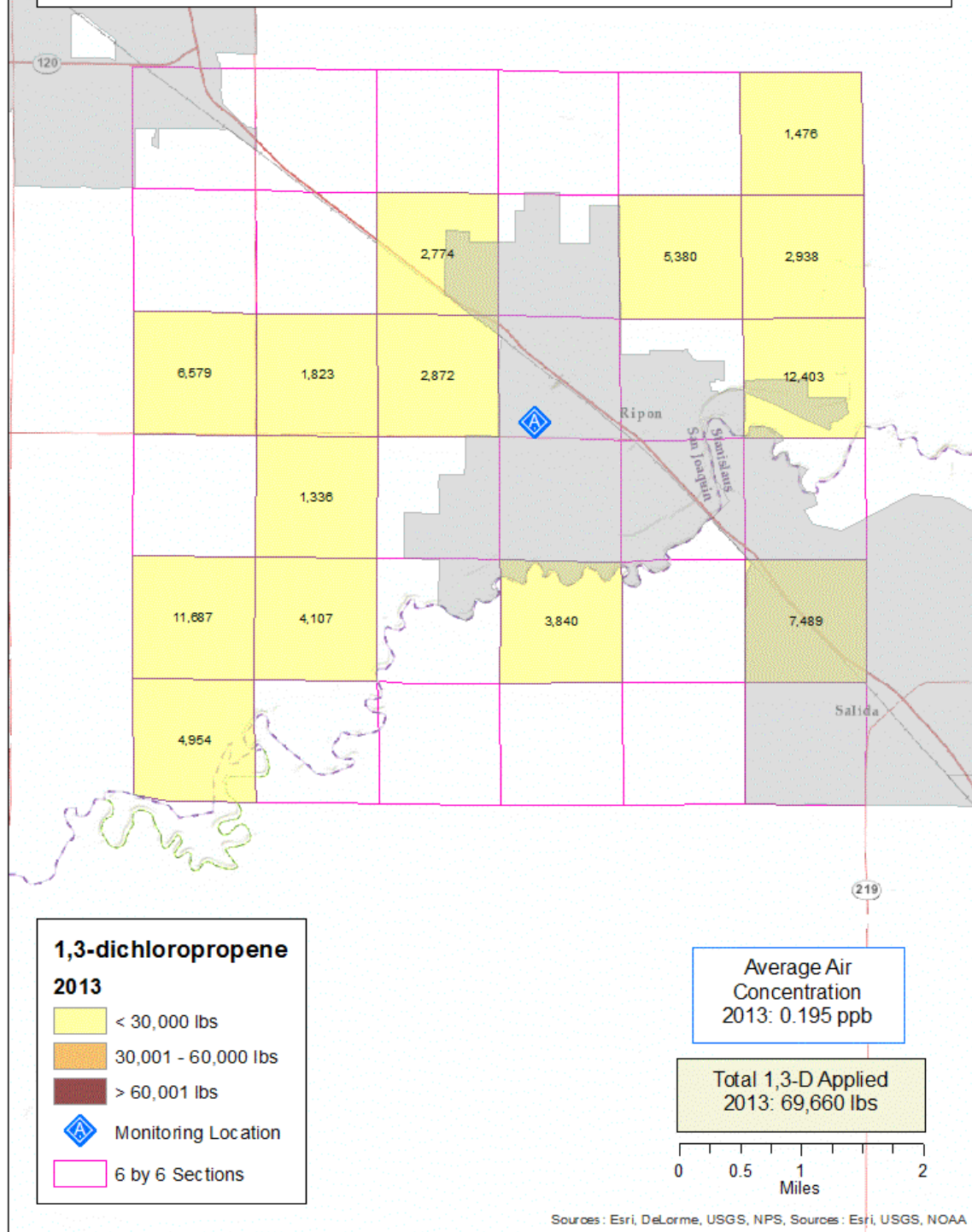


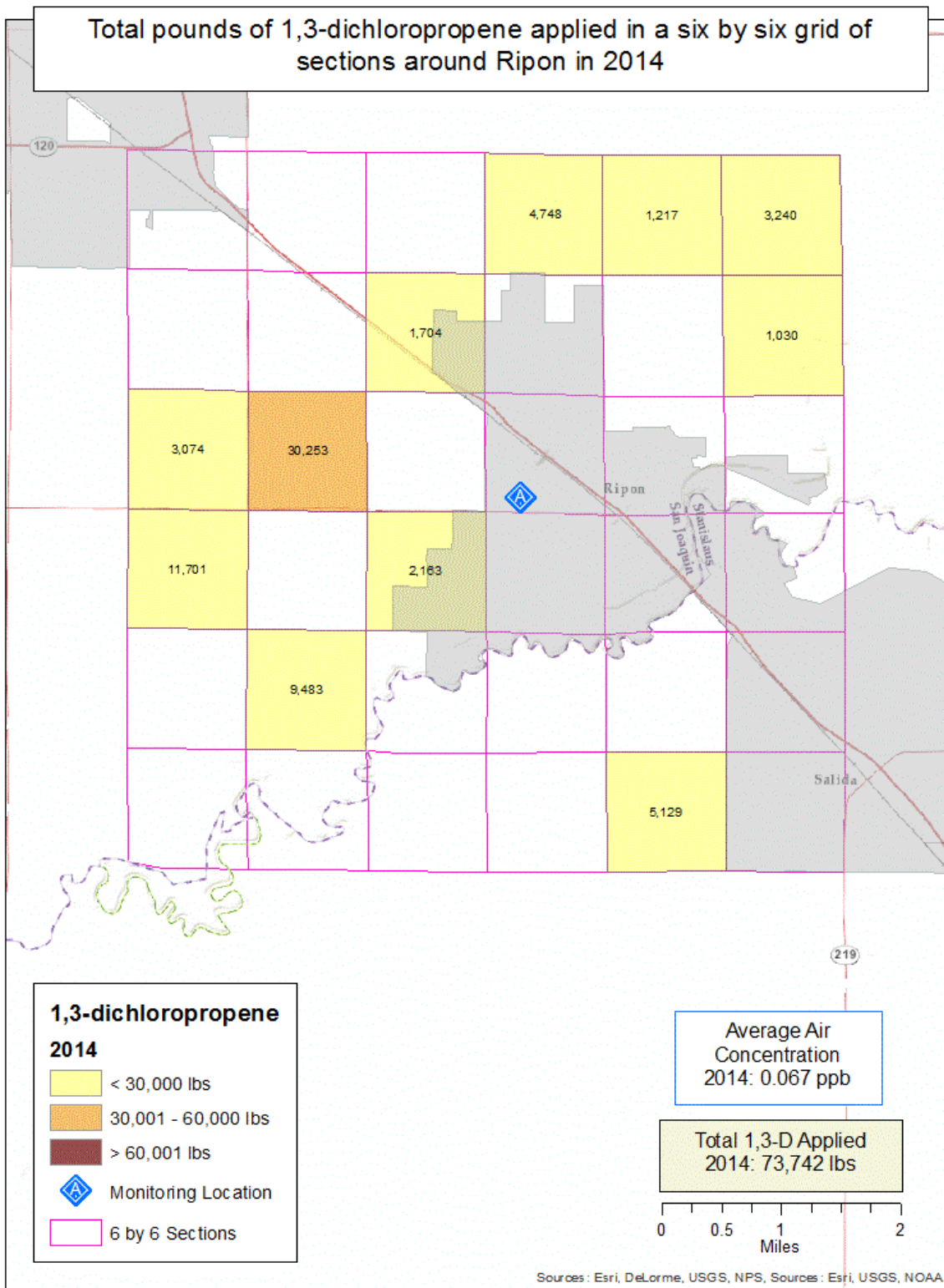




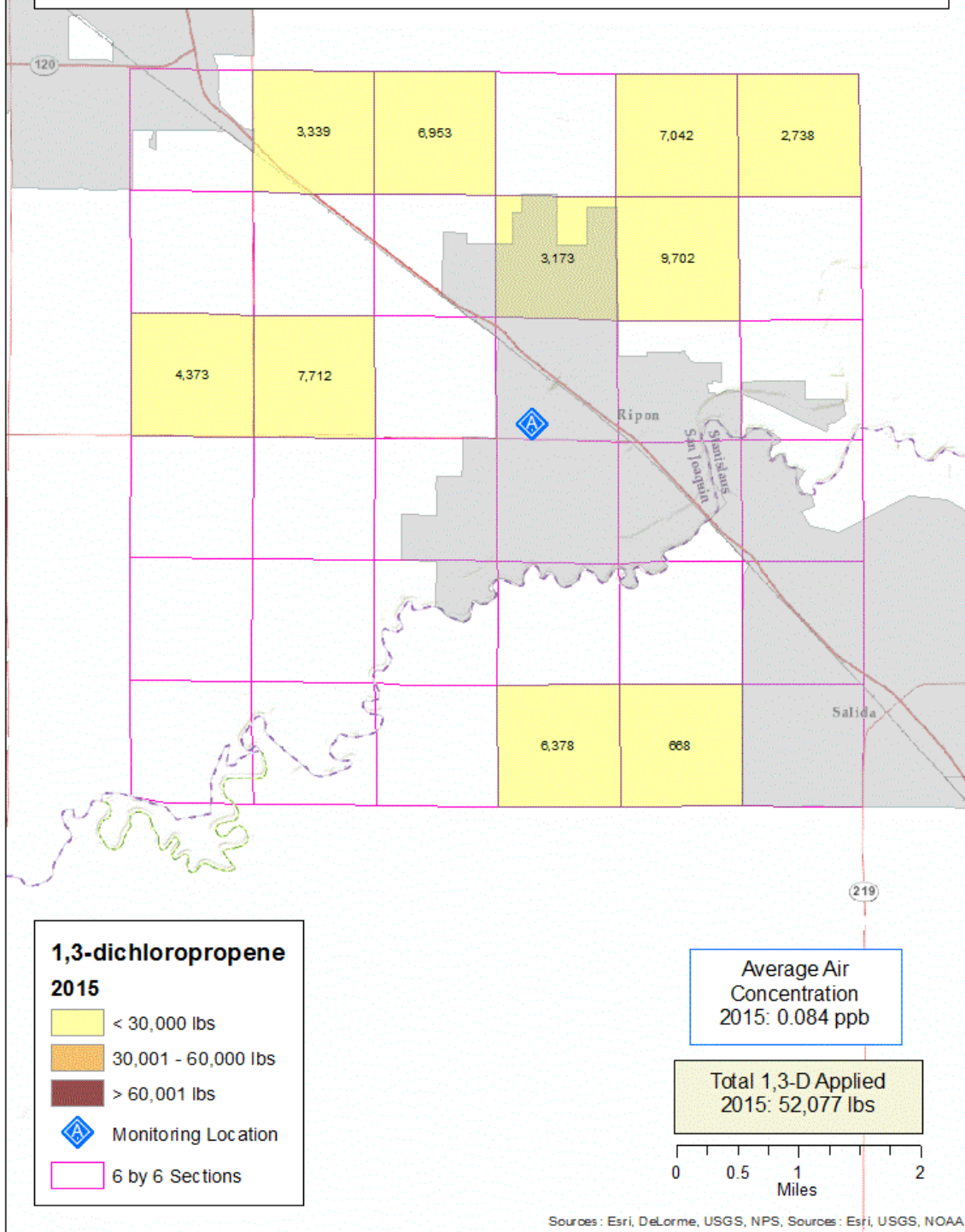


Total pounds of 1,3-dichloropropene applied in a six by six grid of sections around Ripon in 2013

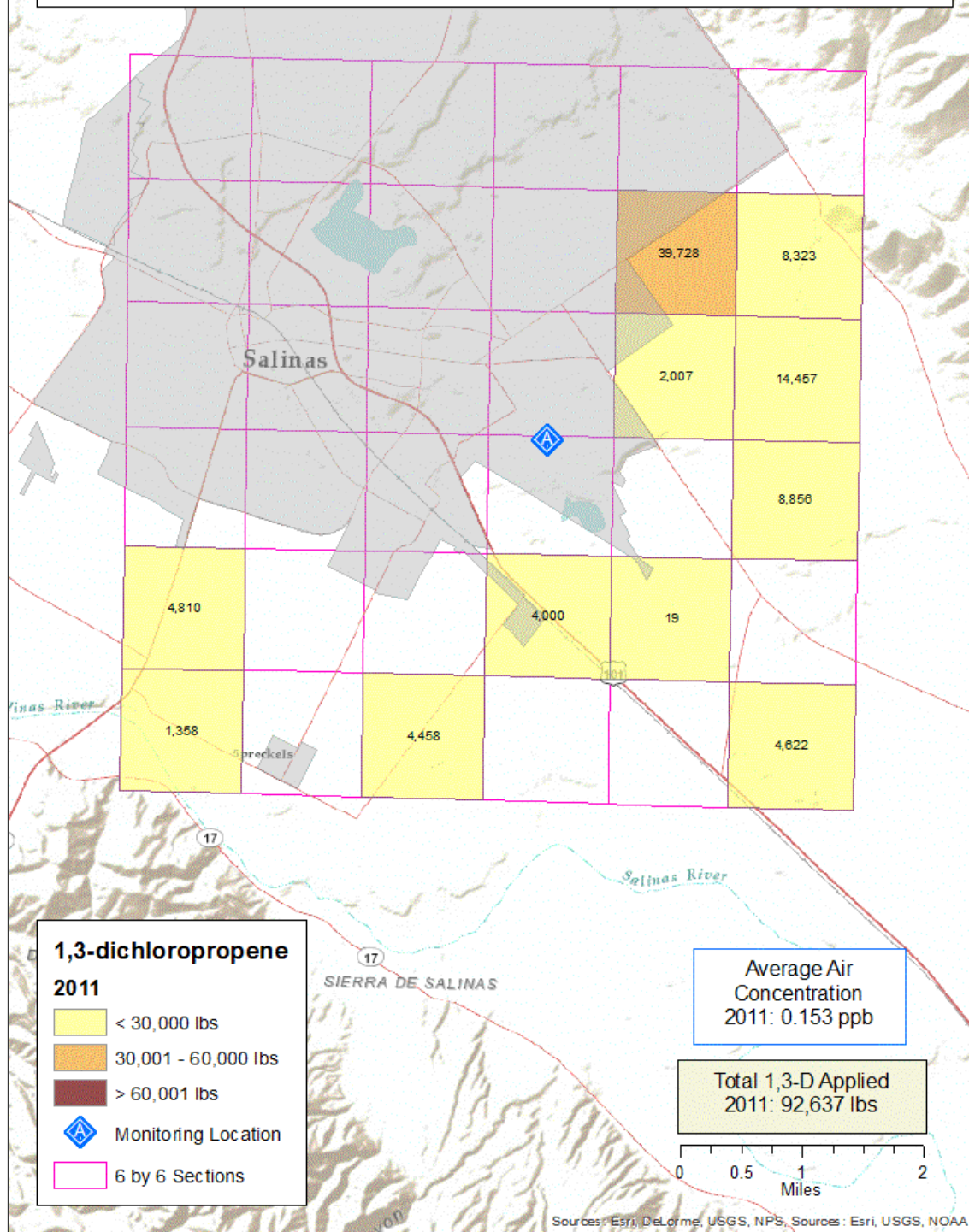




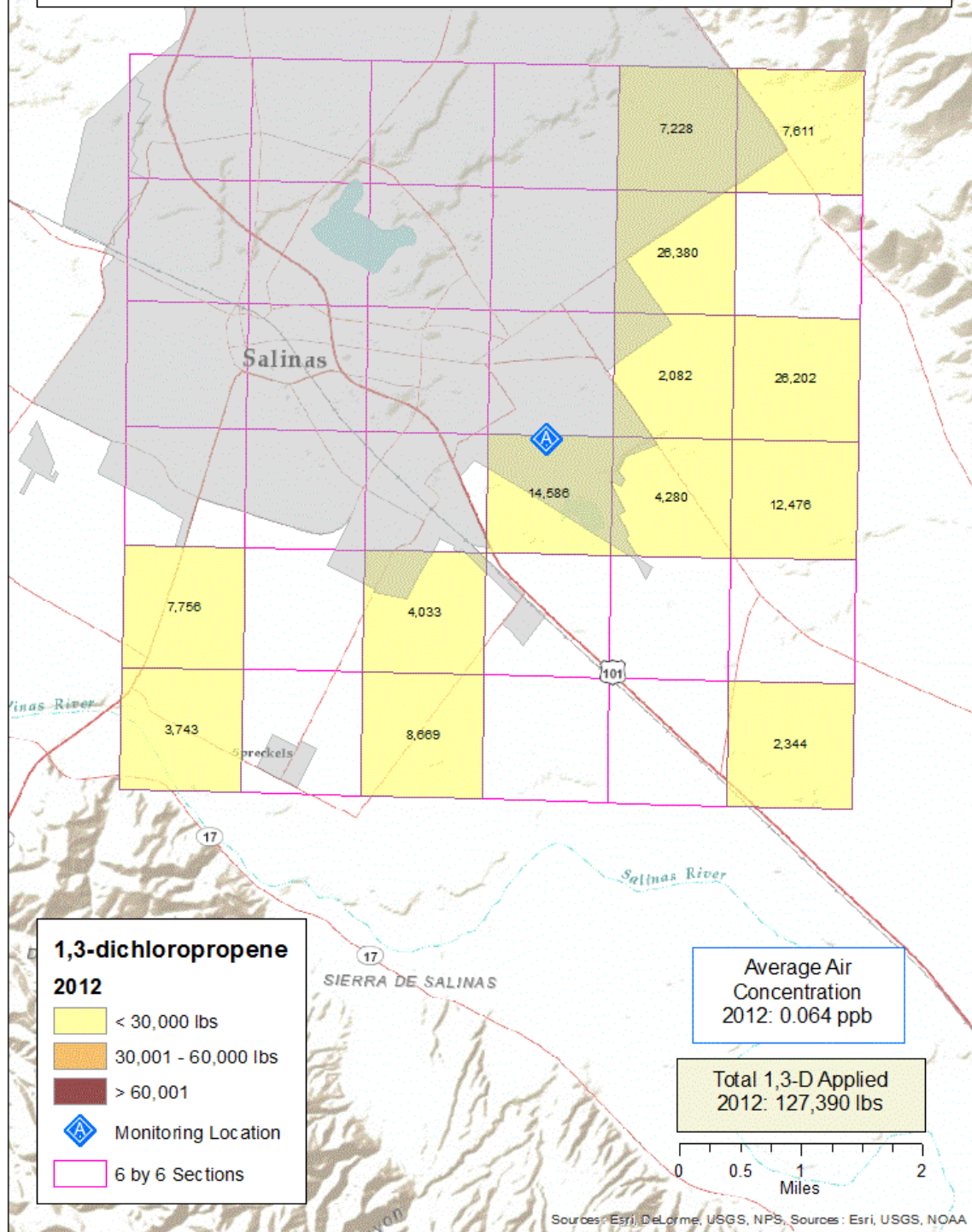
Total pounds of 1,3-dichloropropene applied in a six by six grid of sections around Ripon in 2015



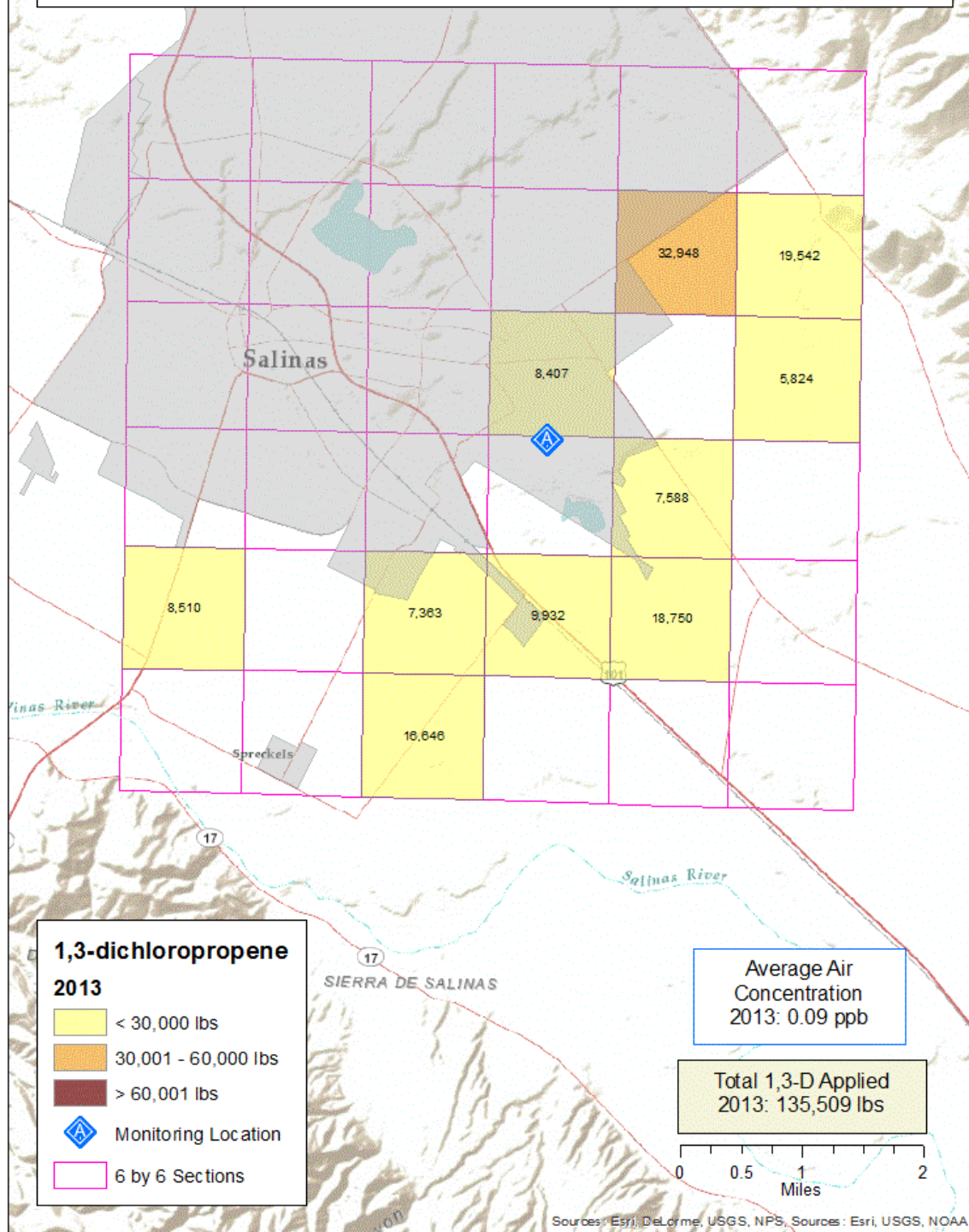
Total pounds of 1,3-dichloropropene applied in a six by six grid of sections around Salinas in 2011



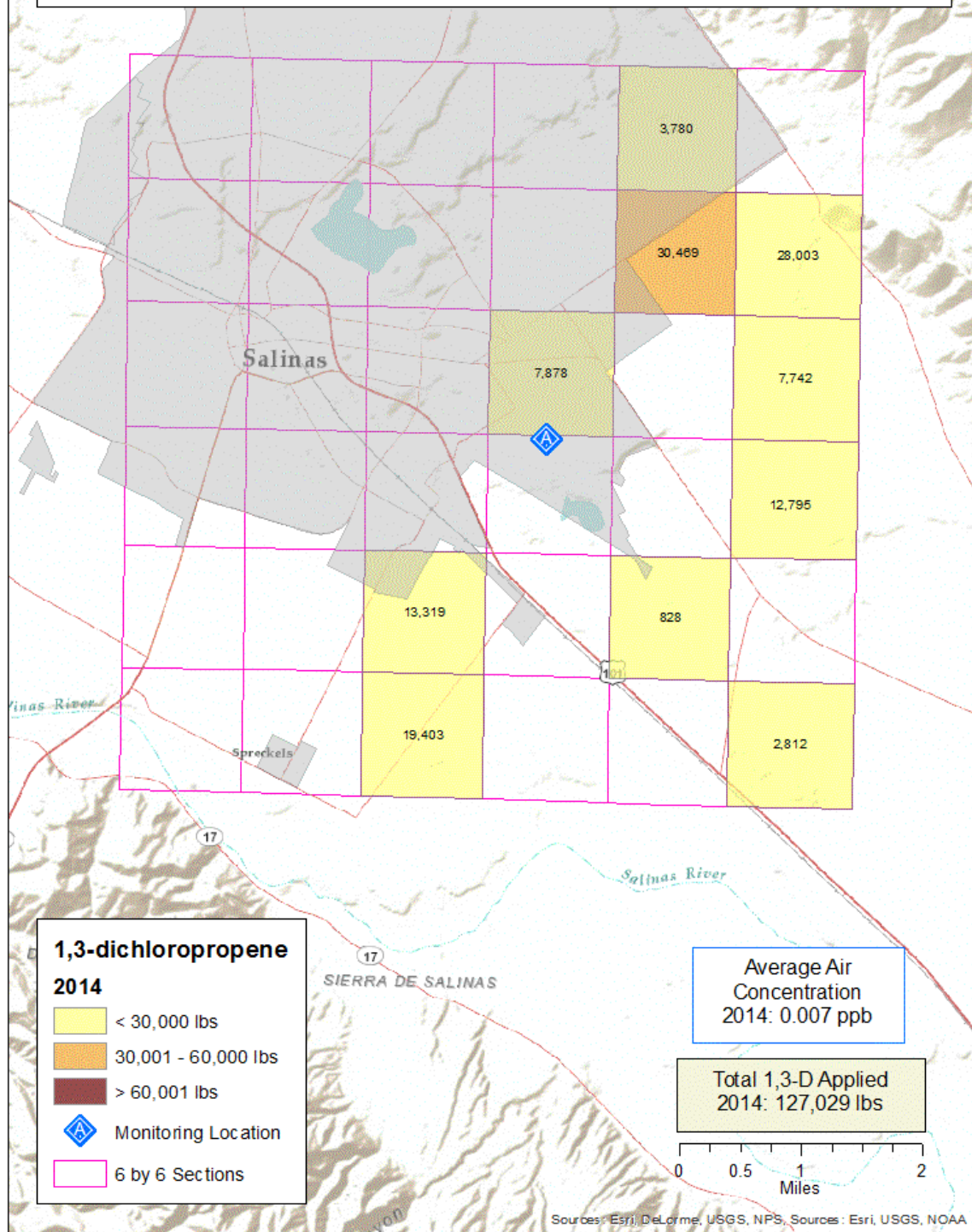
Total pounds of 1,3-dichloropropene applied in a six by six grid of sections around Salinas in 2012



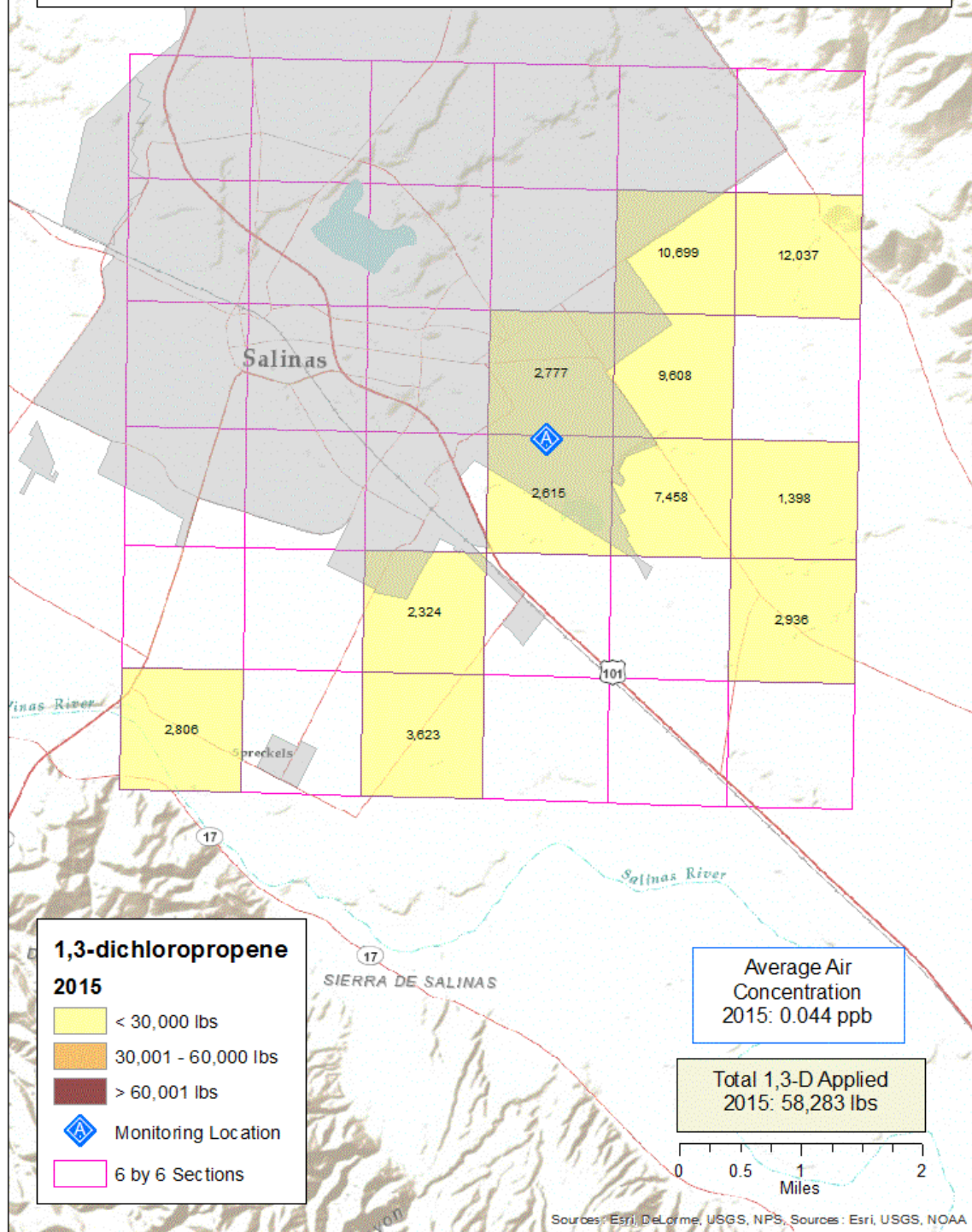
Total pounds of 1,3-dichloropropene applied in a six by six grid of sections around Salinas in 2013



Total pounds of 1,3-dichloropropene applied in a six by six grid of sections around Salinas in 2014

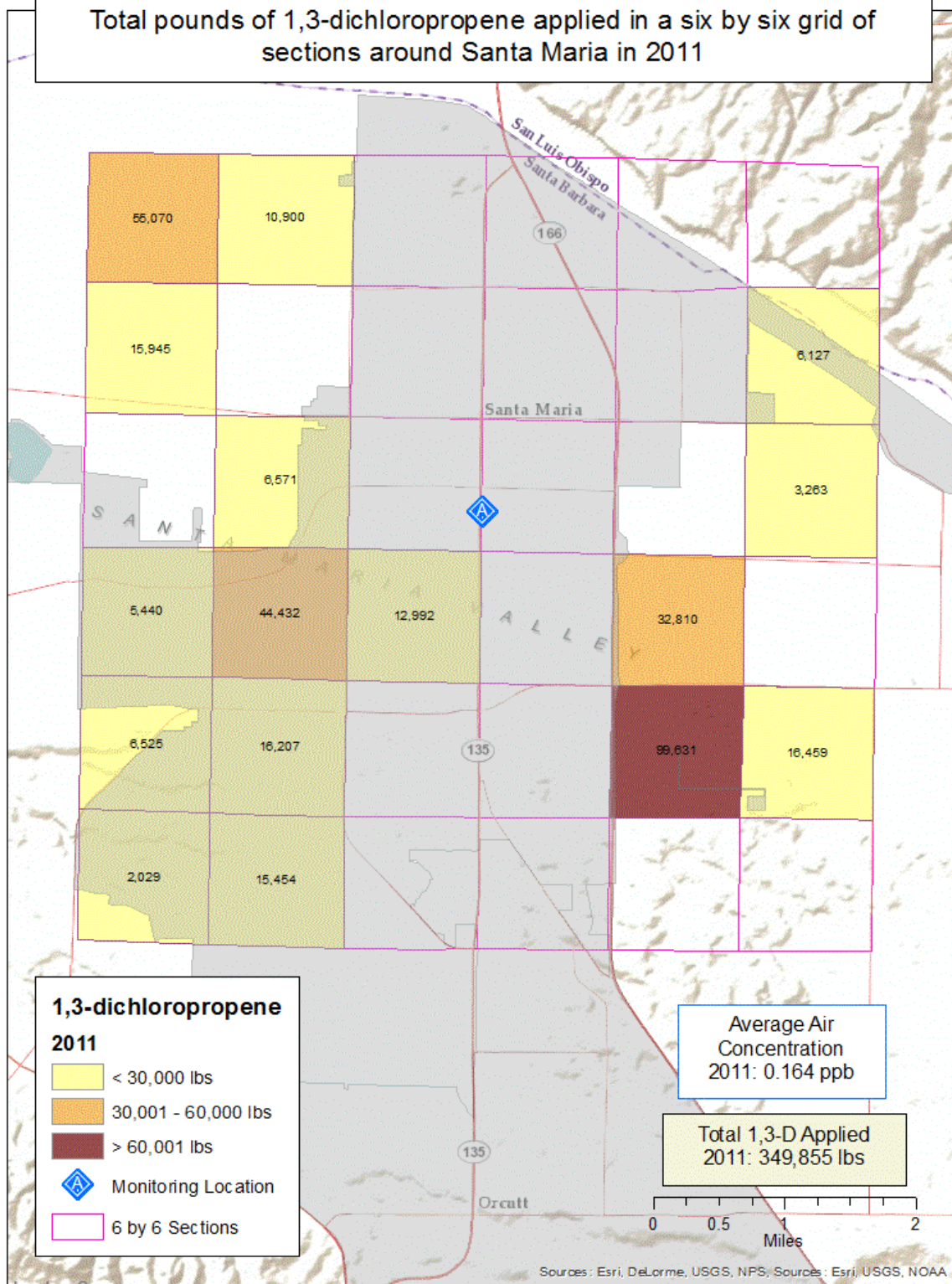


Total pounds of 1,3-dichloropropene applied in a six by six grid of sections around Salinas in 2015

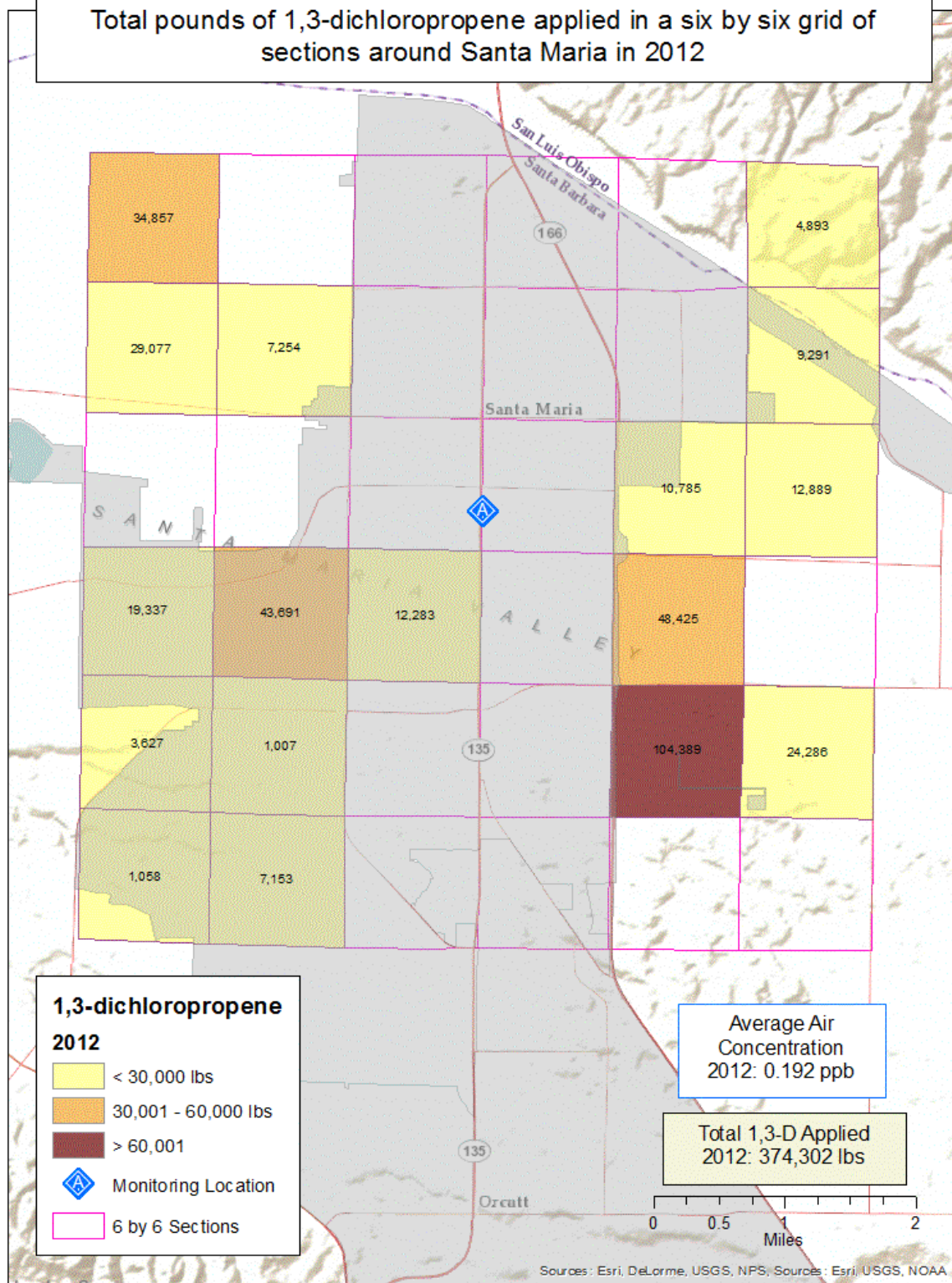


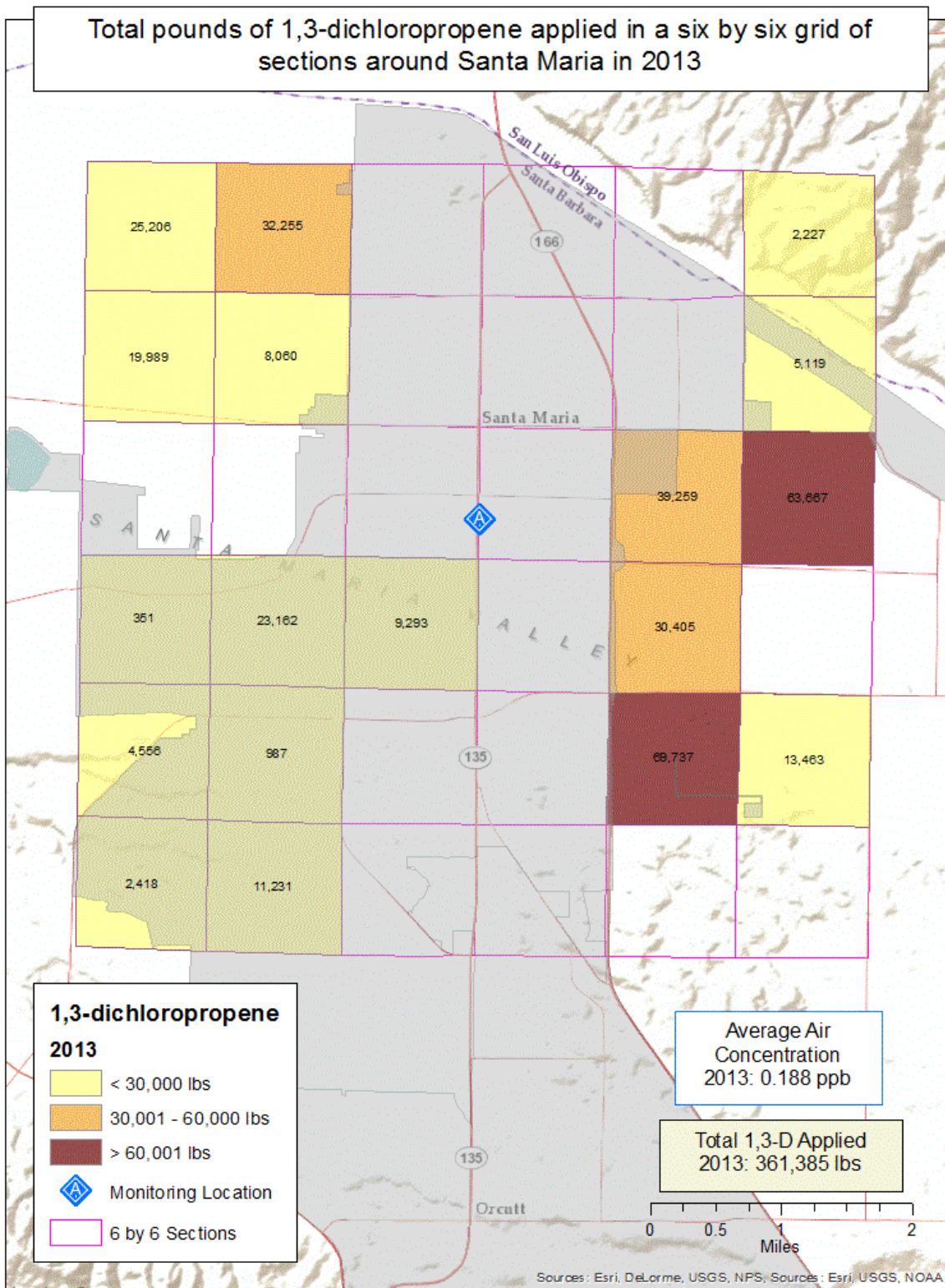


Total pounds of 1,3-dichloropropene applied in a six by six grid of sections around Santa Maria in 2011

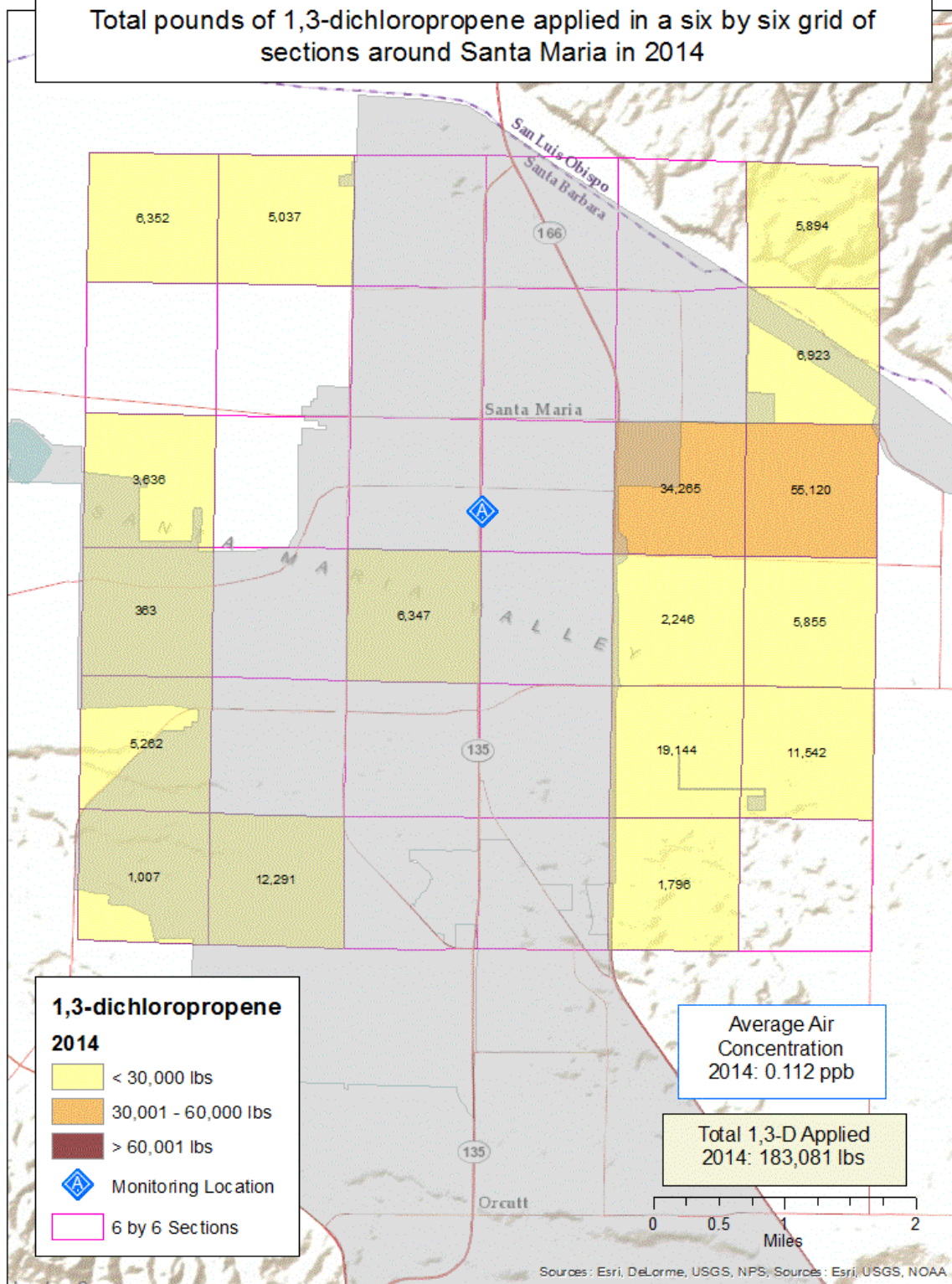


Total pounds of 1,3-dichloropropene applied in a six by six grid of sections around Santa Maria in 2012

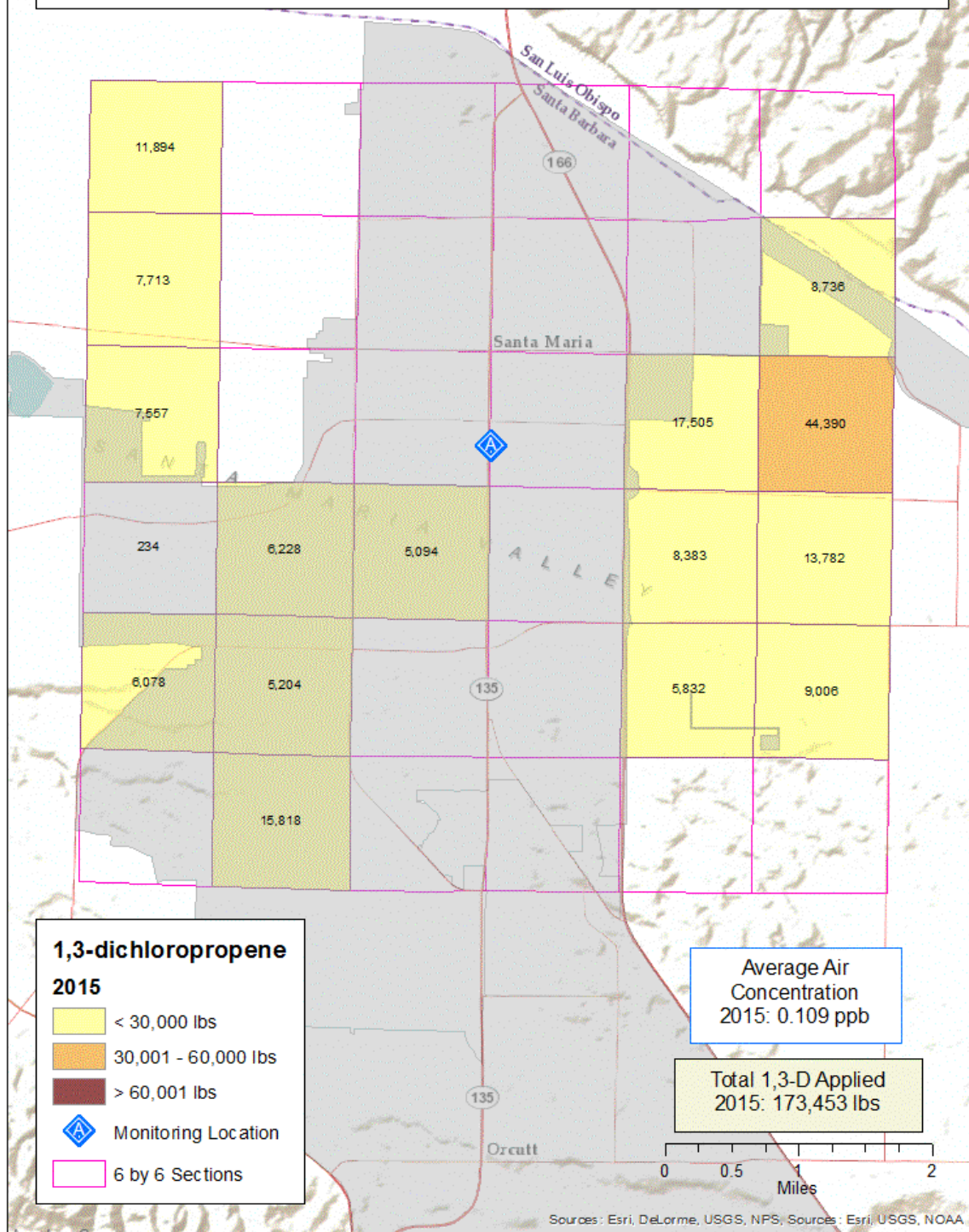




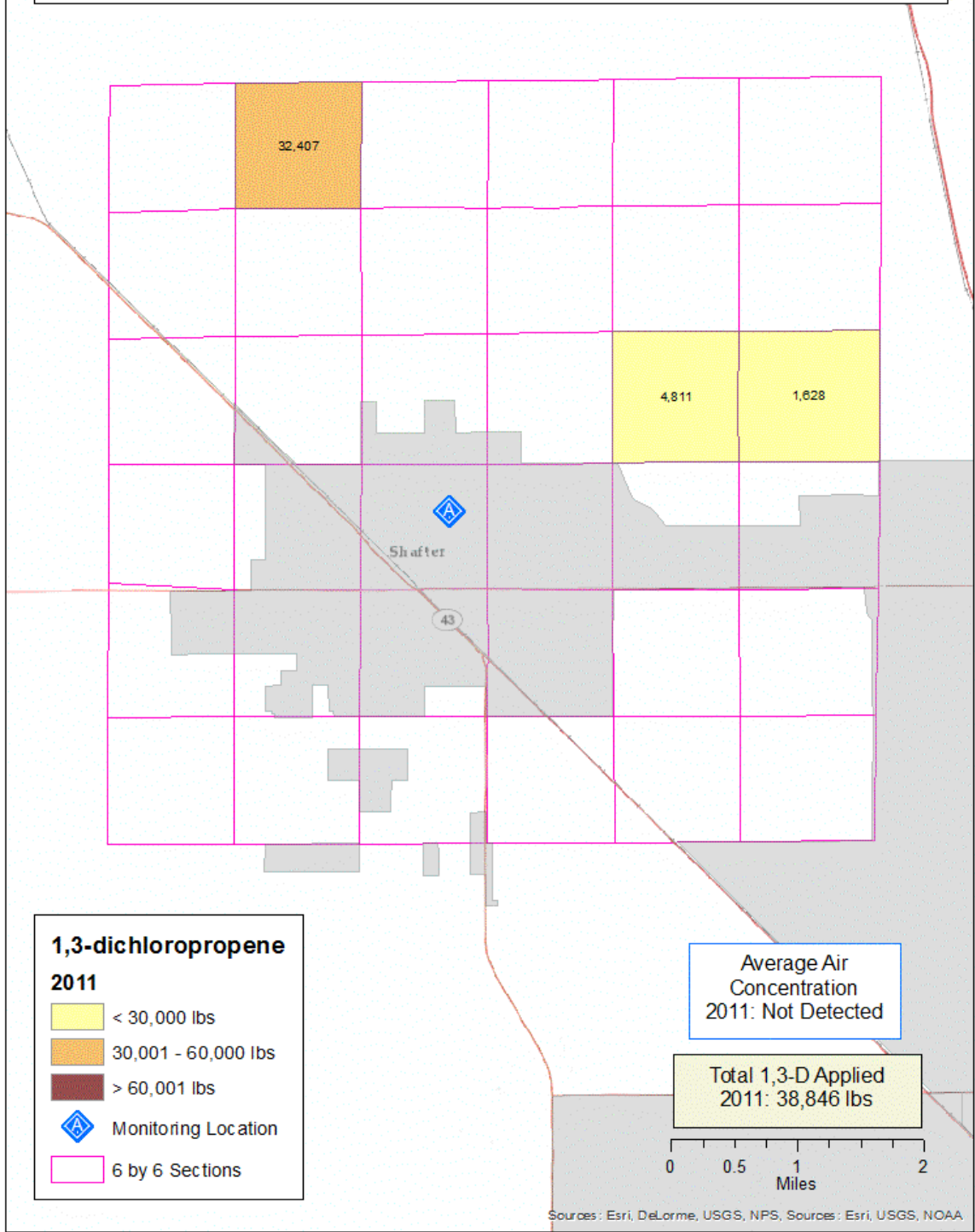
Total pounds of 1,3-dichloropropene applied in a six by six grid of sections around Santa Maria in 2014



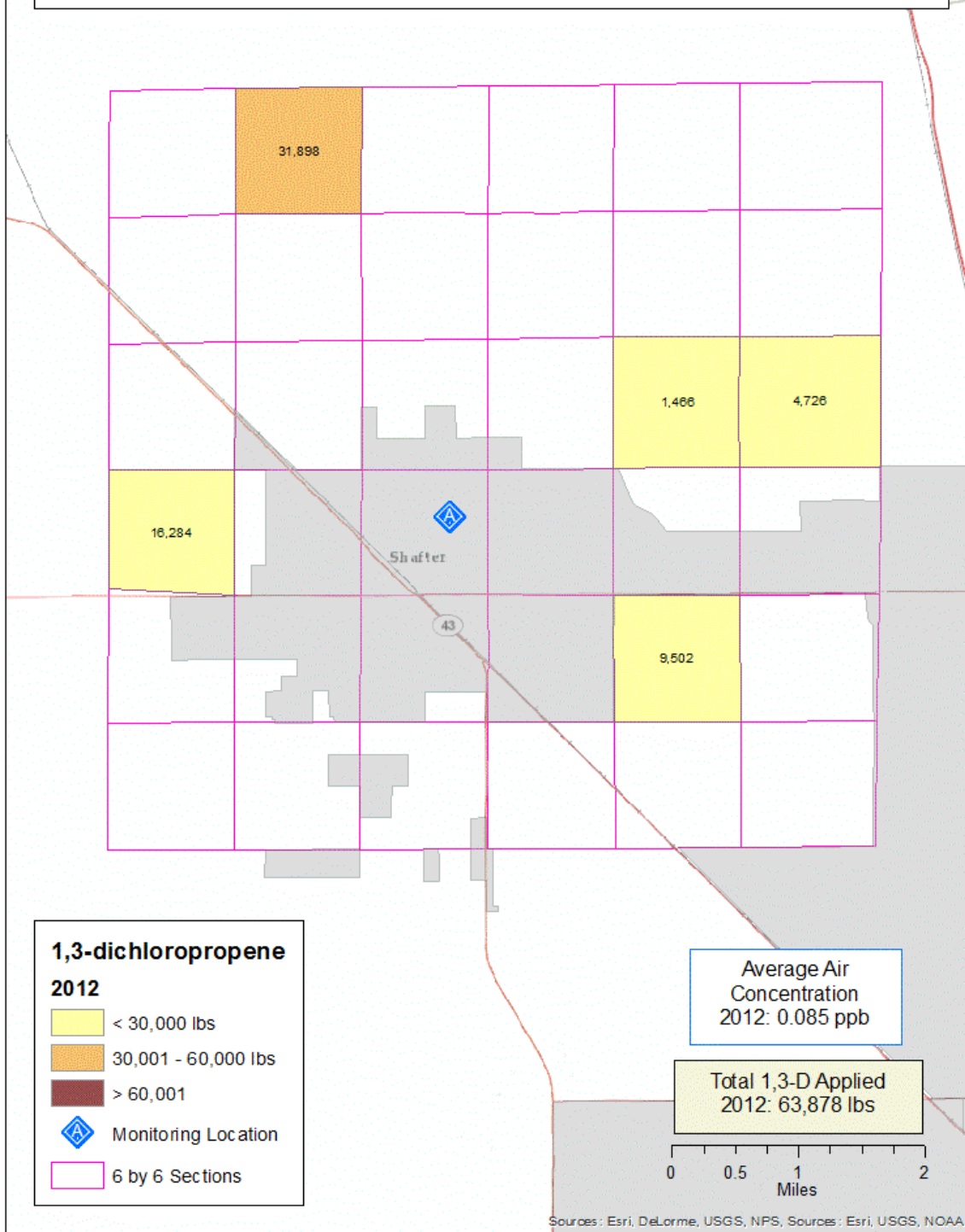
Total pounds of 1,3-dichloropropene applied in a six by six grid of sections around Santa Maria in 2015



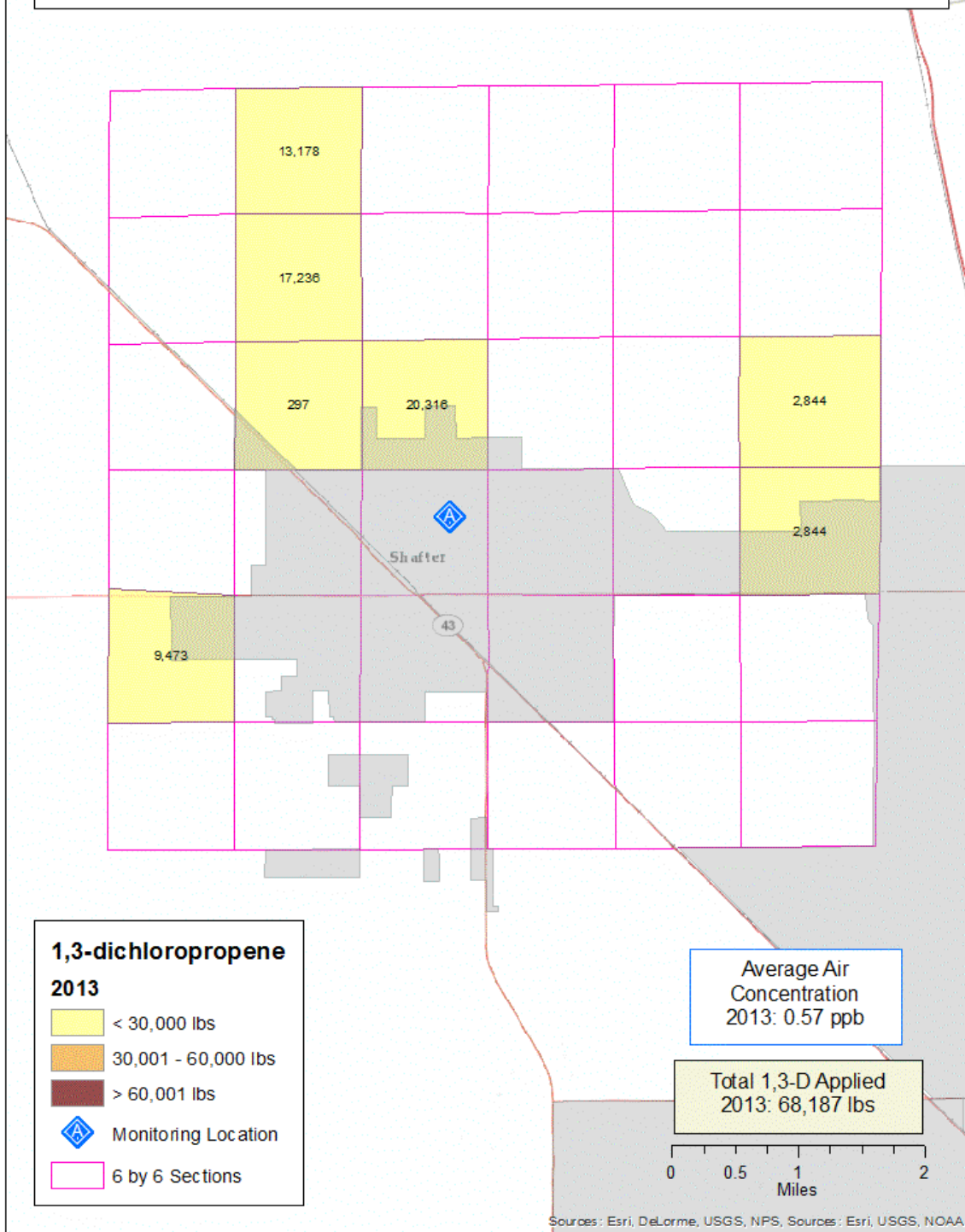
Total pounds of 1,3-dichloropropene applied in a six by six grid of sections around Shafter in 2011



Total pounds of 1,3-dichloropropene applied in a six by six grid of sections around Shafter in 2012

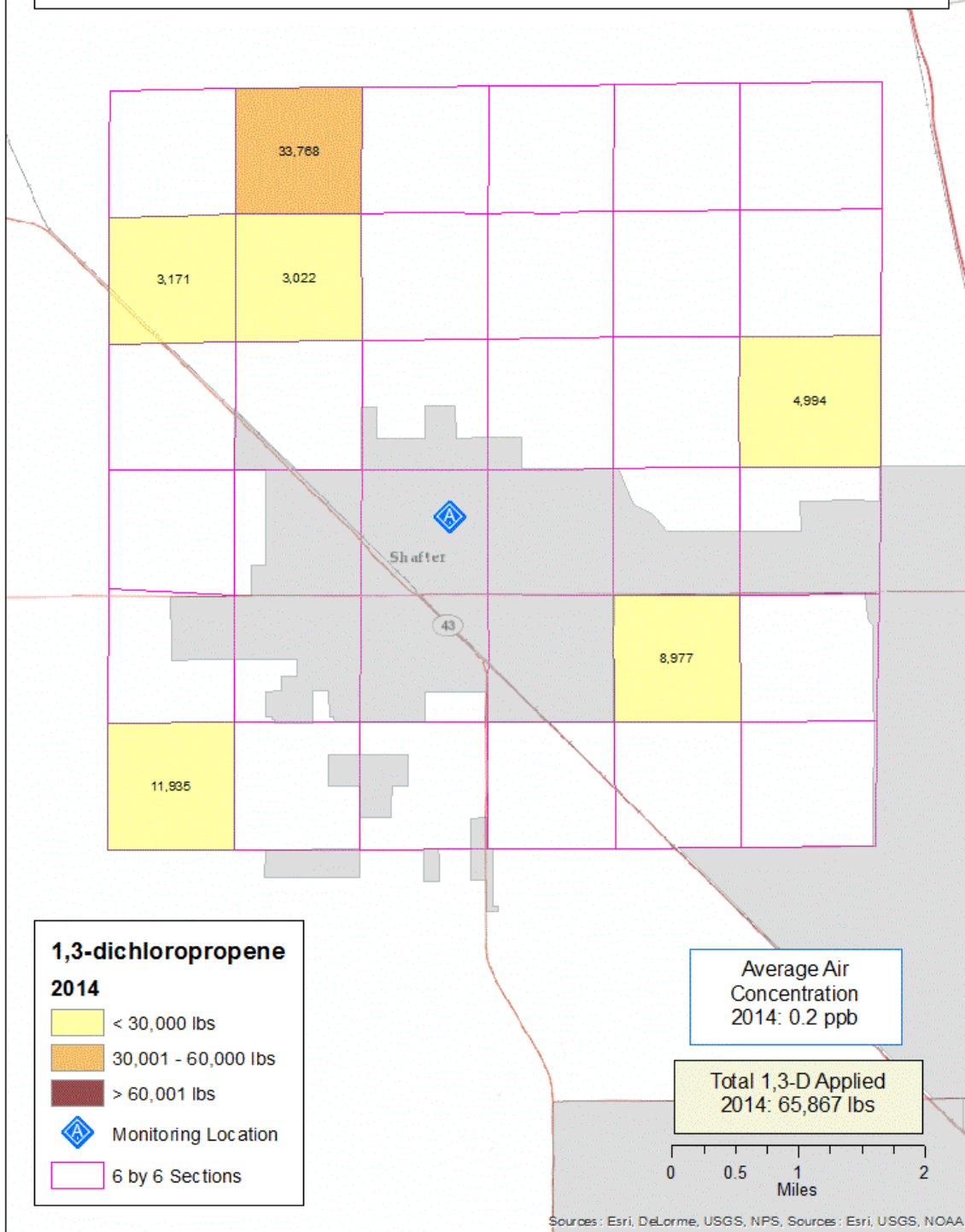


Total pounds of 1,3-dichloropropene applied in a six by six grid of sections around Shafter in 2013

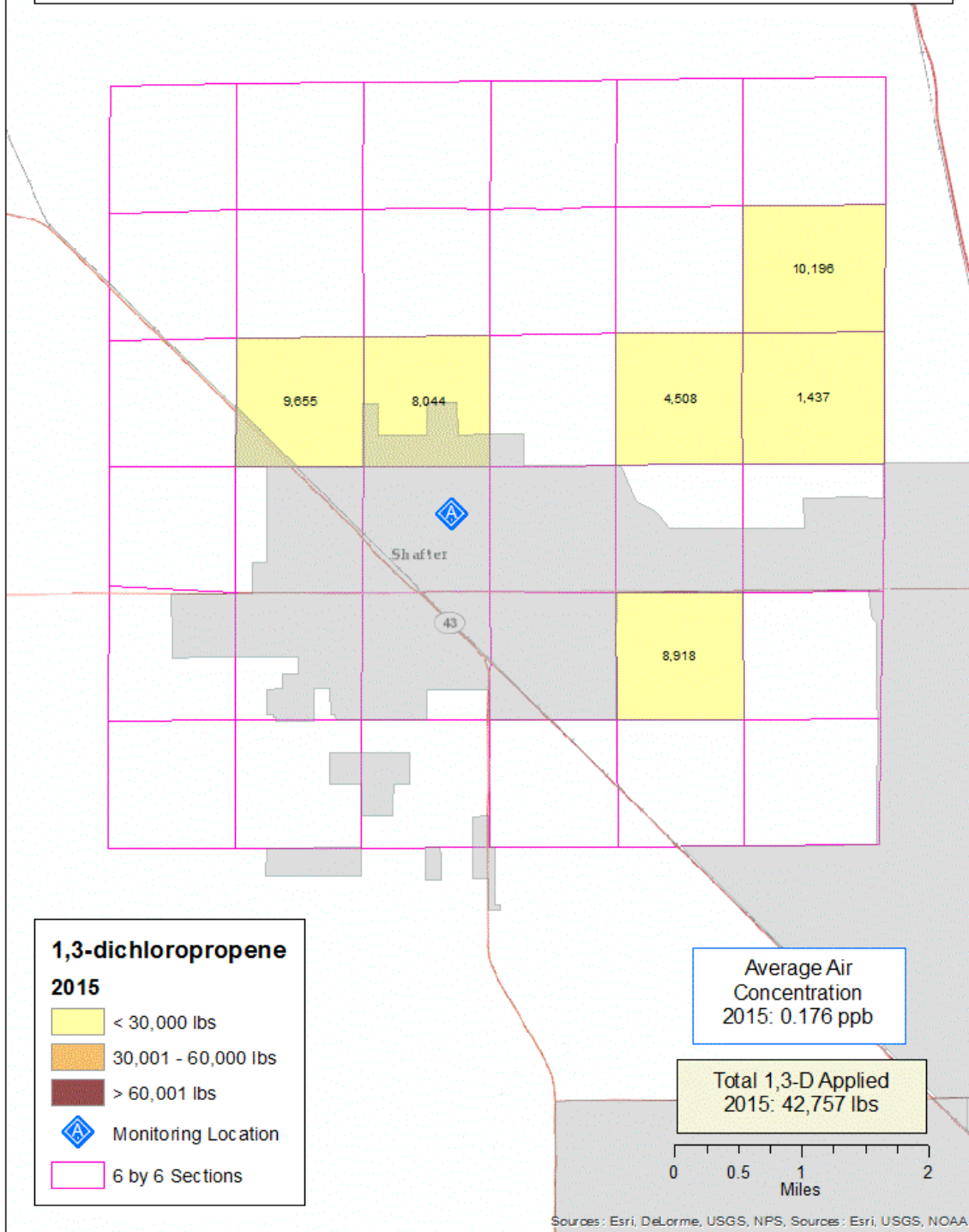




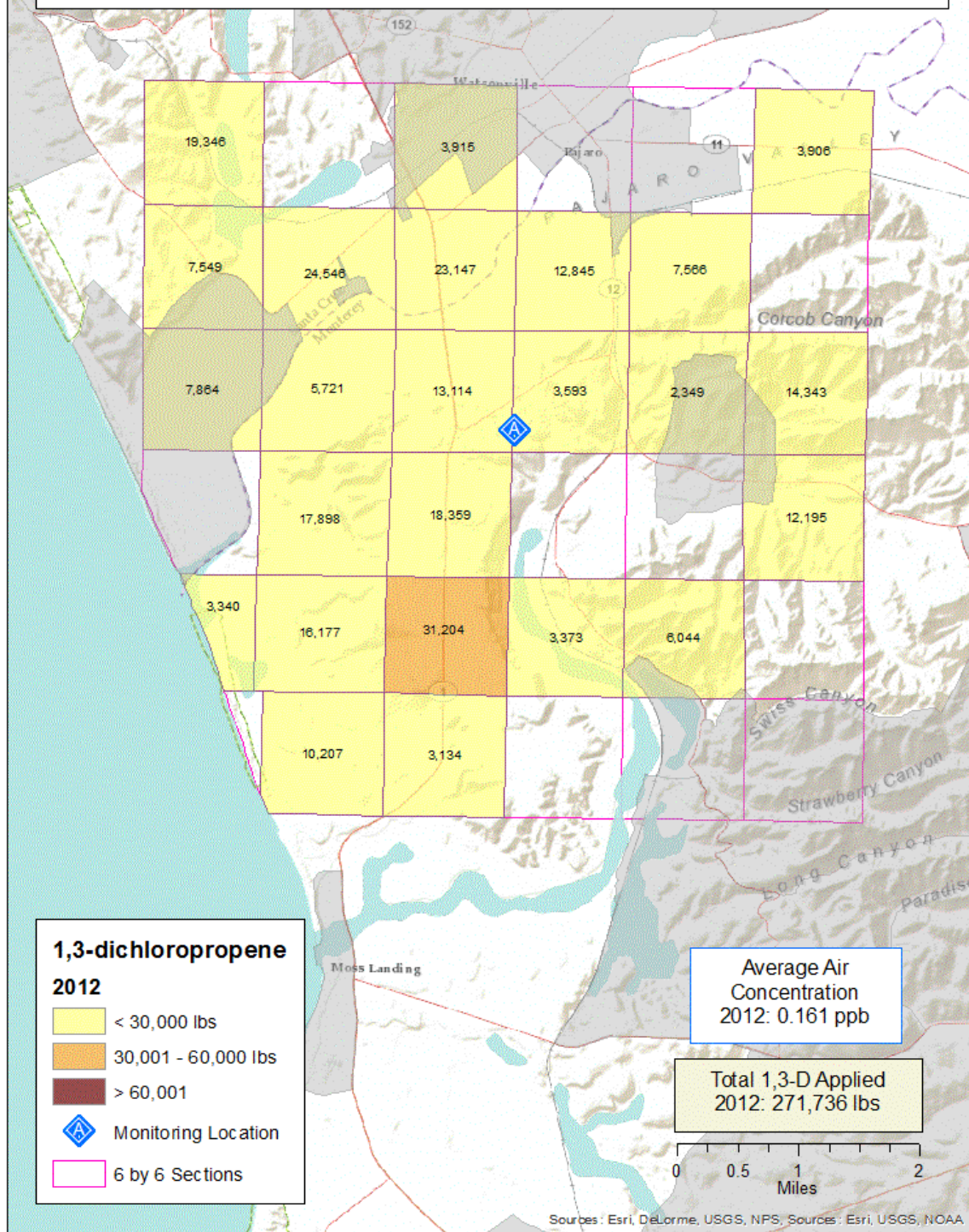
Total pounds of 1,3-dichloropropene applied in a six by six grid of sections around Shafter in 2014

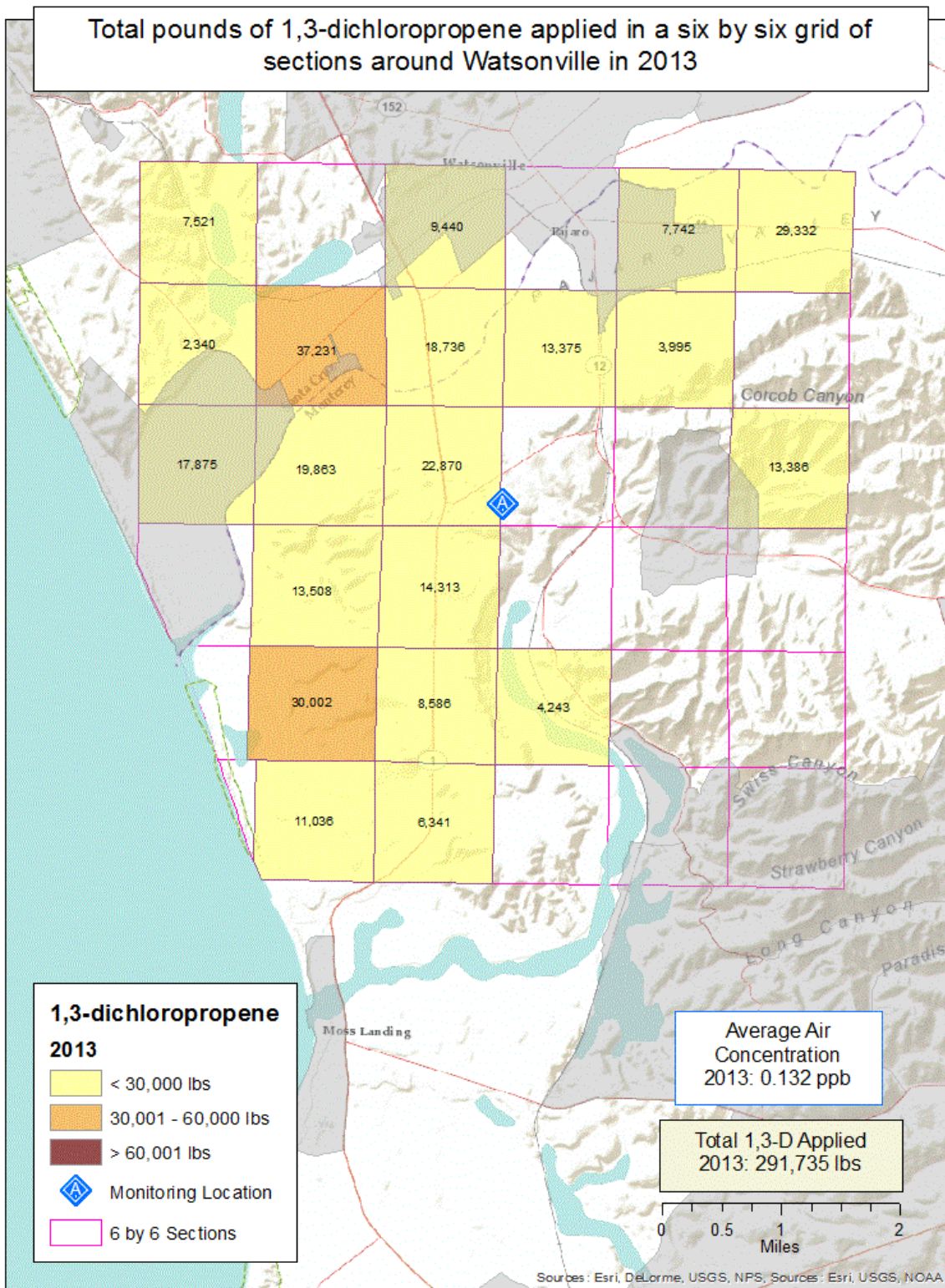


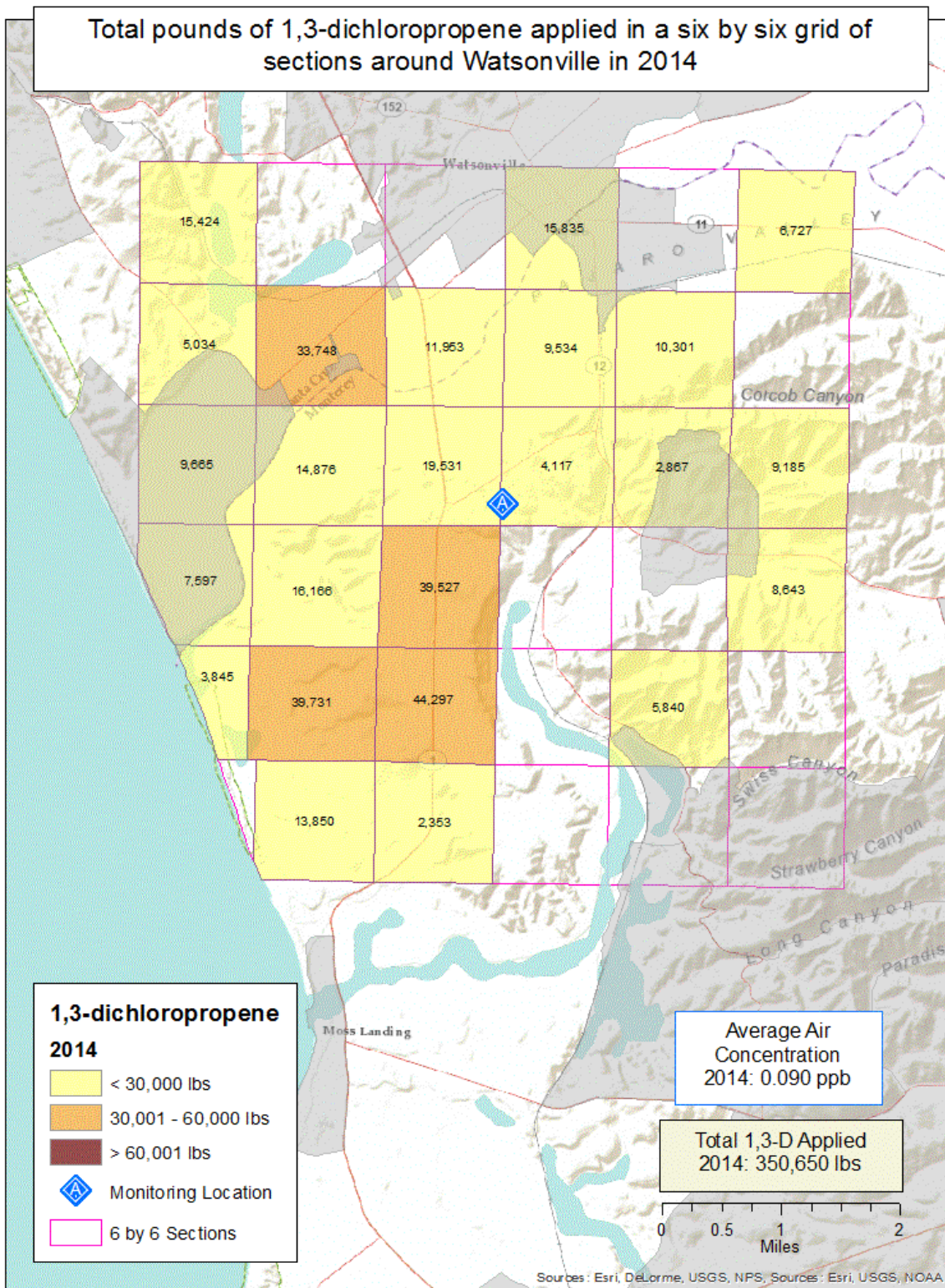
Total pounds of 1,3-dichloropropene applied in a six by six grid of sections around Shafter in 2015

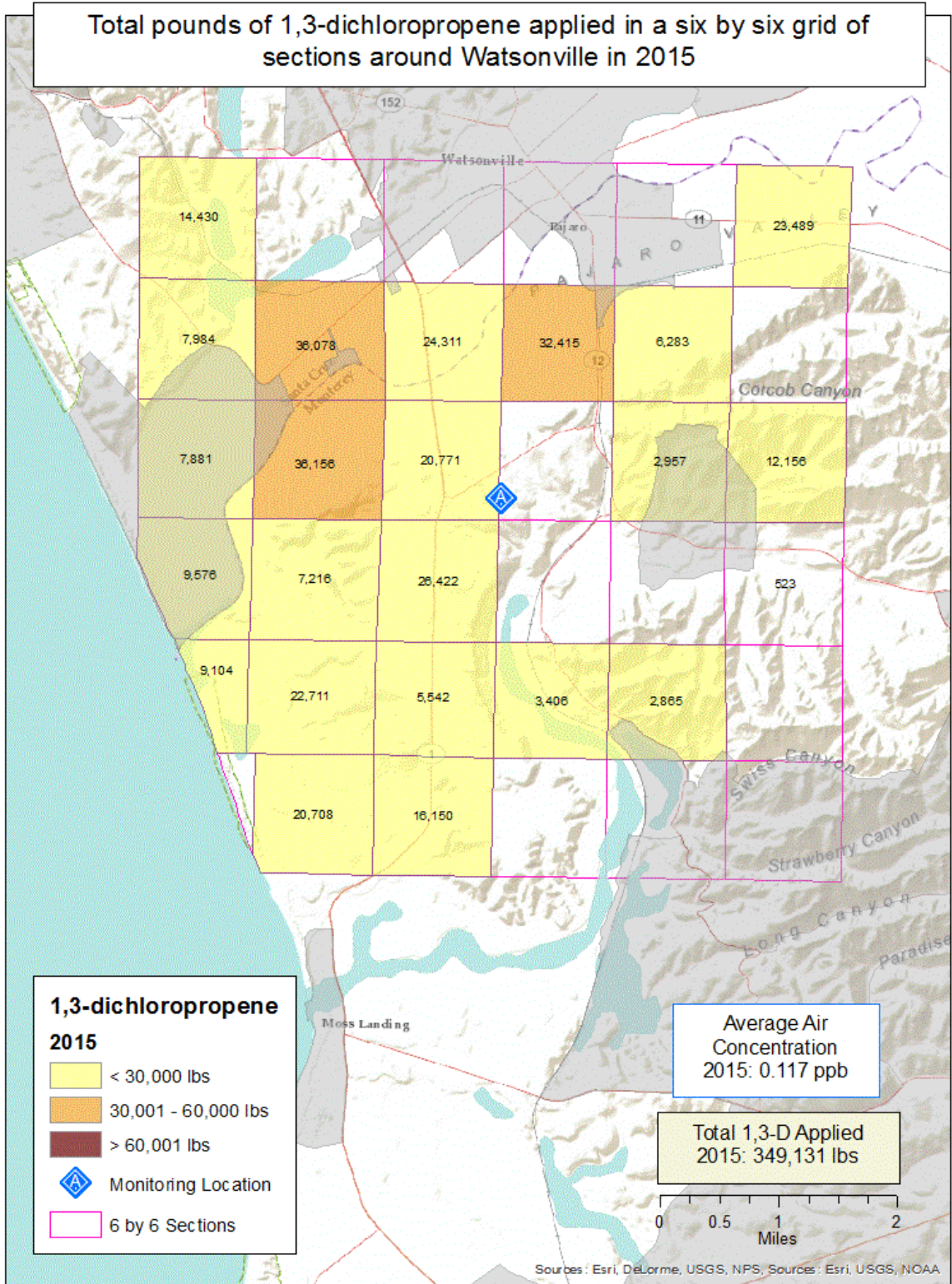


**Total pounds of 1,3-dichloropropene applied in a six by six grid of sections around Watsonville in 2012**







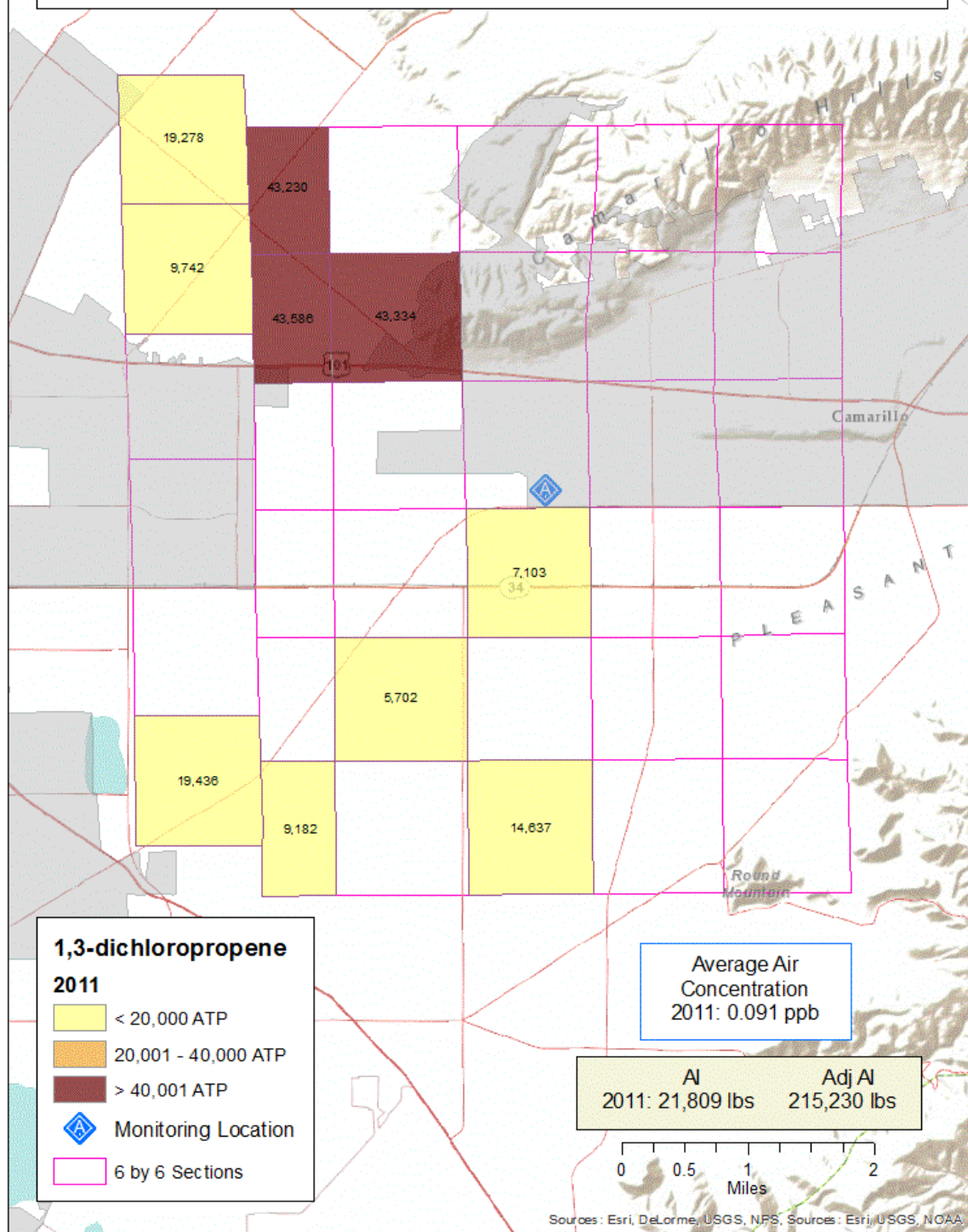


## **Appendix III**

### **DAS Use Map of 1,3-Dichloropropene in 6 × 6 Mile Area around Air Monitoring Stations in 2006 – 2015**

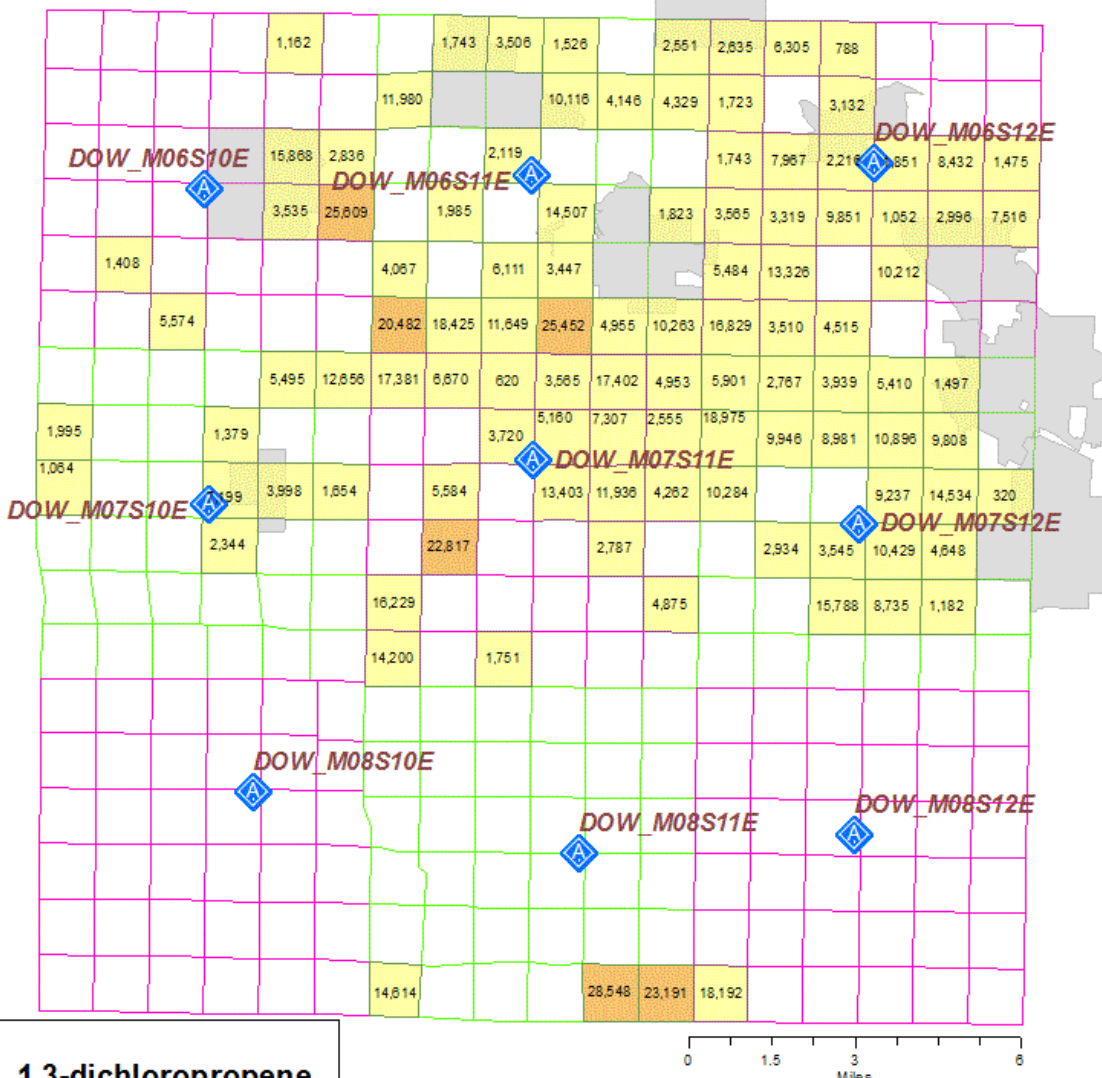
**(Source: Rosemary Neal, Senior Environmental Scientist, DPR)**

Adjusted pounds of 1,3-dichloropropene applied in a six by six grid of sections around Camarillo in 2011





Adjusted pounds of 1,3-dichloropropene applied in sections around Merced air monitoring locations in 2011



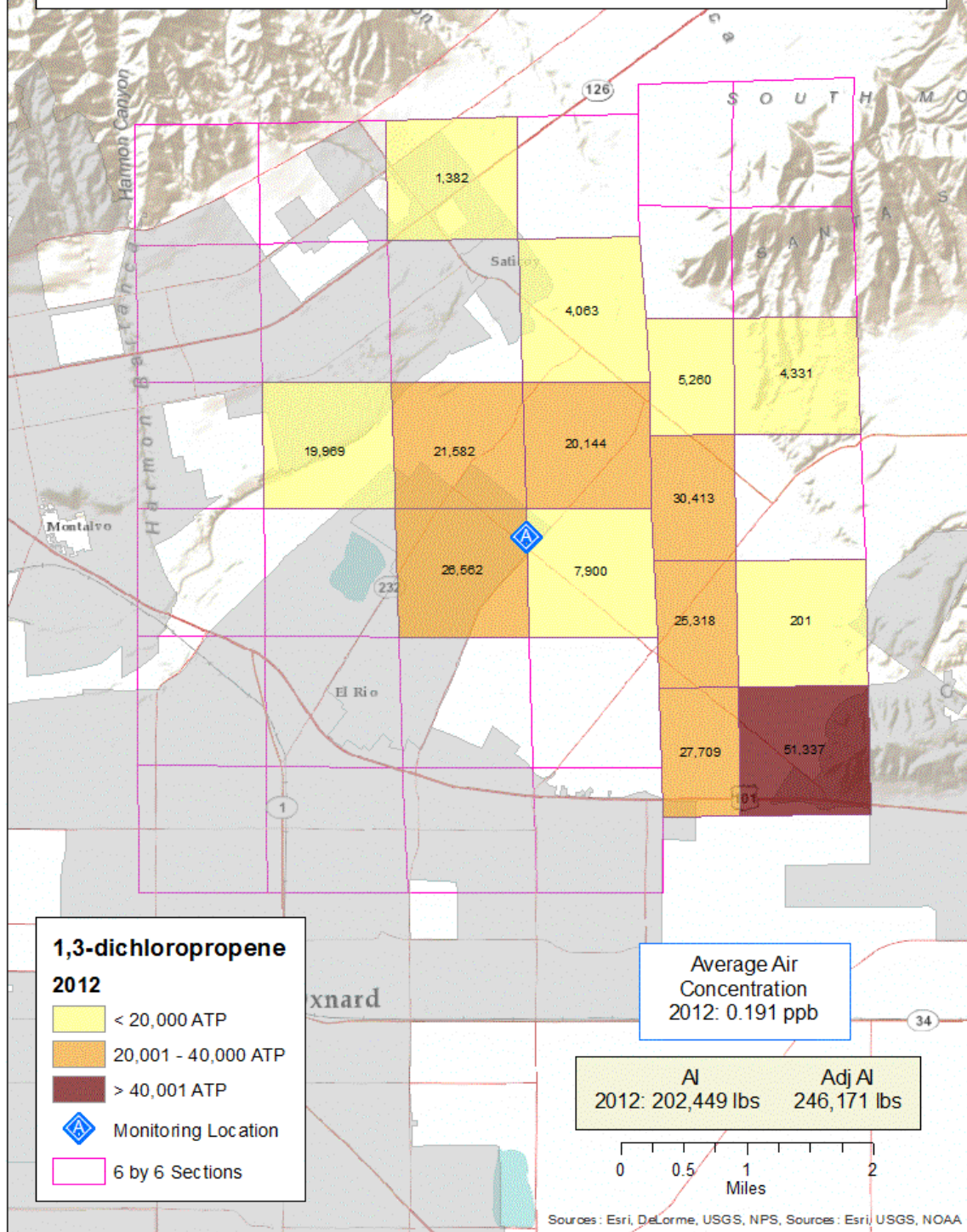
**1,3-dichloropropene 2011**

- < 20,000 ATP
- 20,001 - 40,000 ATP
- > 40,001 ATP
- Monitoring Location
- 6 by 6 Sections

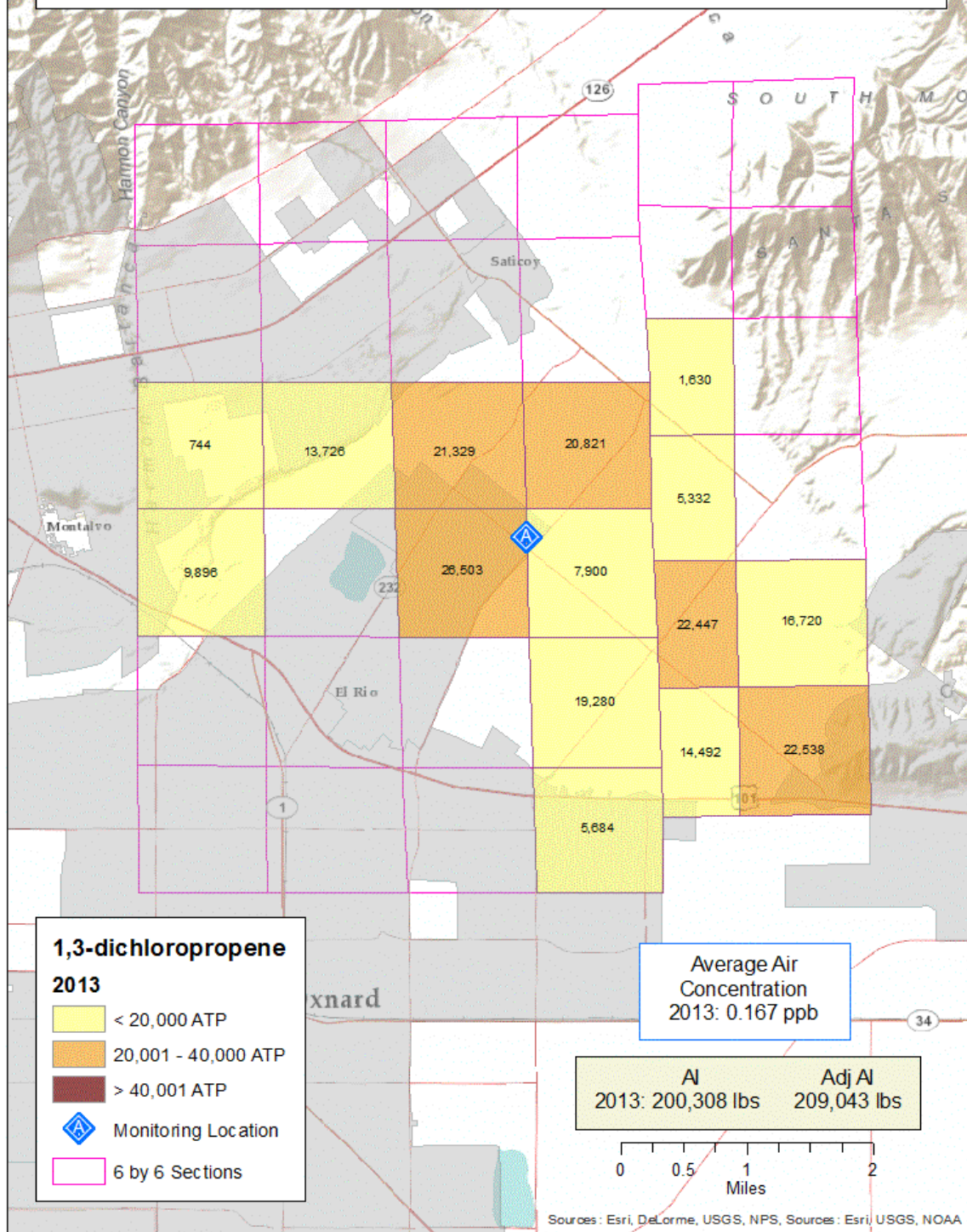
	AI	Adj AI
06S10E:	48,811 lbs	55,992 lbs
06S11E:	164,013 lbs	165,182 lbs
06S12E:	107,161 lbs	120,441 lbs
07S10E:	37,783 lbs	37,783 lbs
07S11E:	157,676 lbs	167,175 lbs
07S12E:	149,807 lbs	159,756 lbs
08S10E:	-	-
08S11E:	66,353 lbs	66,353 lbs
08S12E:	18,192 lbs	18,192 lbs

Average Air Concentration	
06S10E:	0.179 ppb
06S11E:	1.072 ppb
06S12E:	0.203 ppb
07S10E:	0.297 ppb
07S11E:	1.925 ppb
07S12E:	0.693 ppb
08S10E:	0.097 ppb
08S11E:	0.234 ppb
08S12E:	0.116 ppb

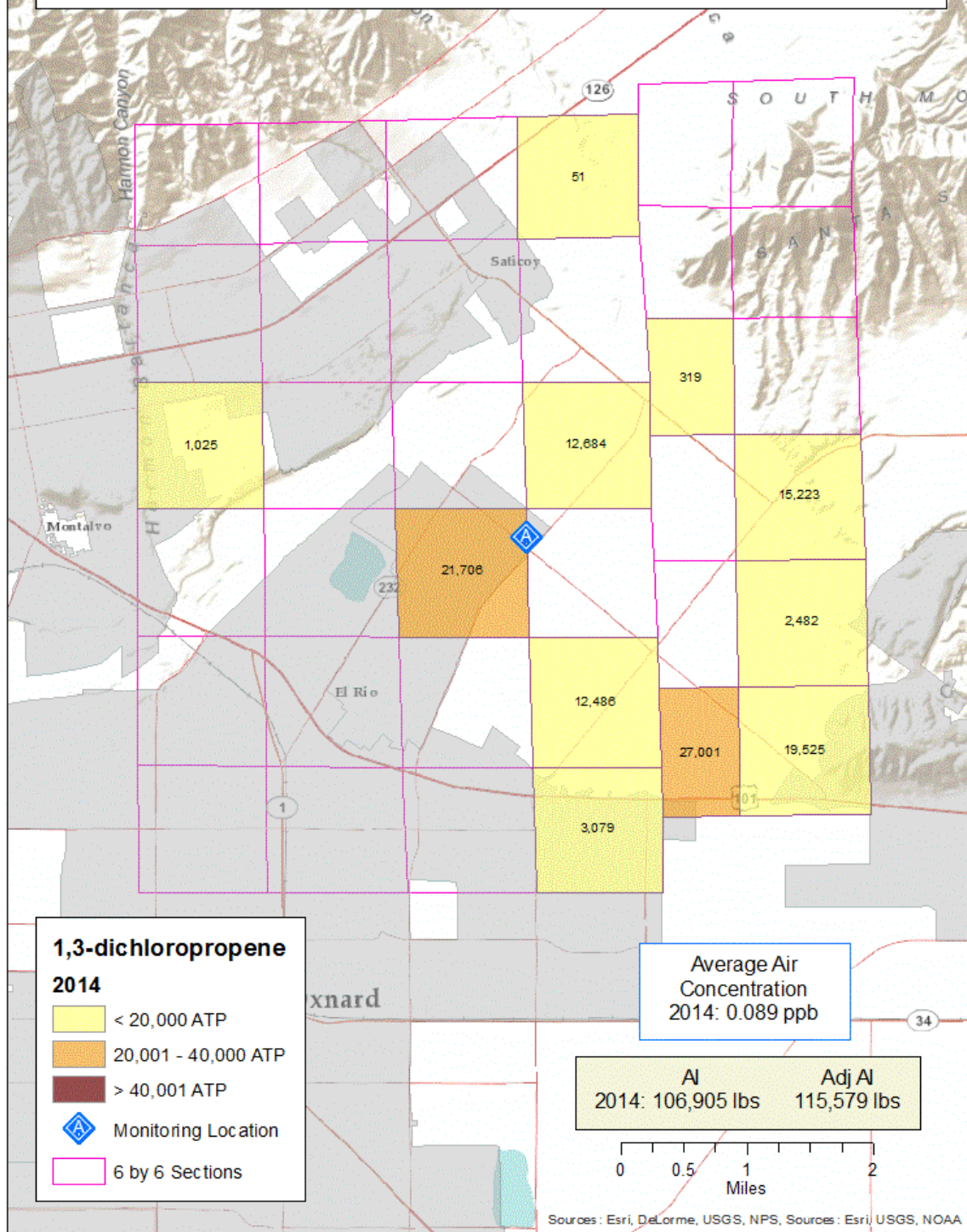
Adjusted pounds of 1,3-dichloropropene applied in a six by six grid of sections around Oxnard in 2012



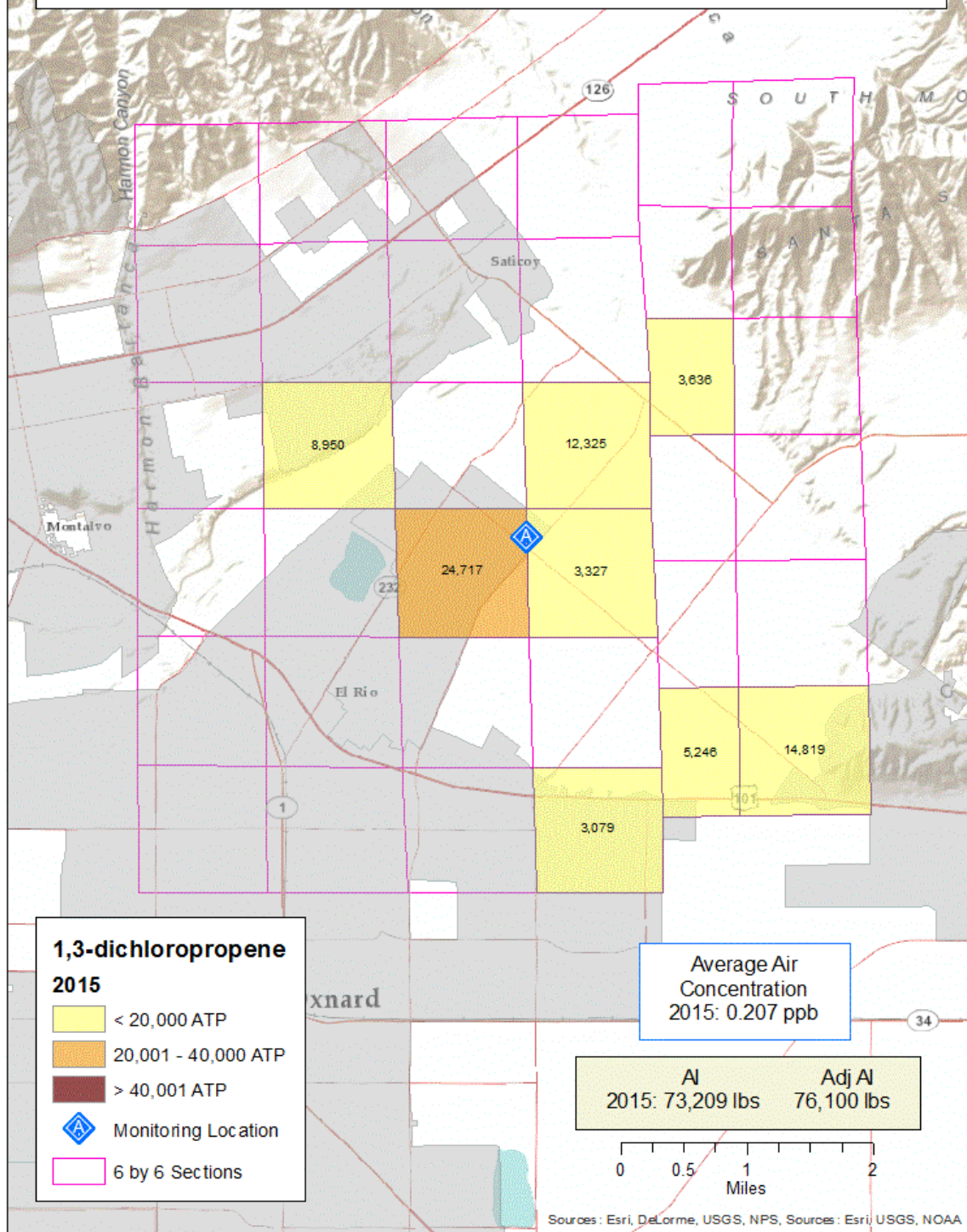
Adjusted pounds of 1,3-dichloropropene applied in a six by six grid of sections around Oxnard in 2013



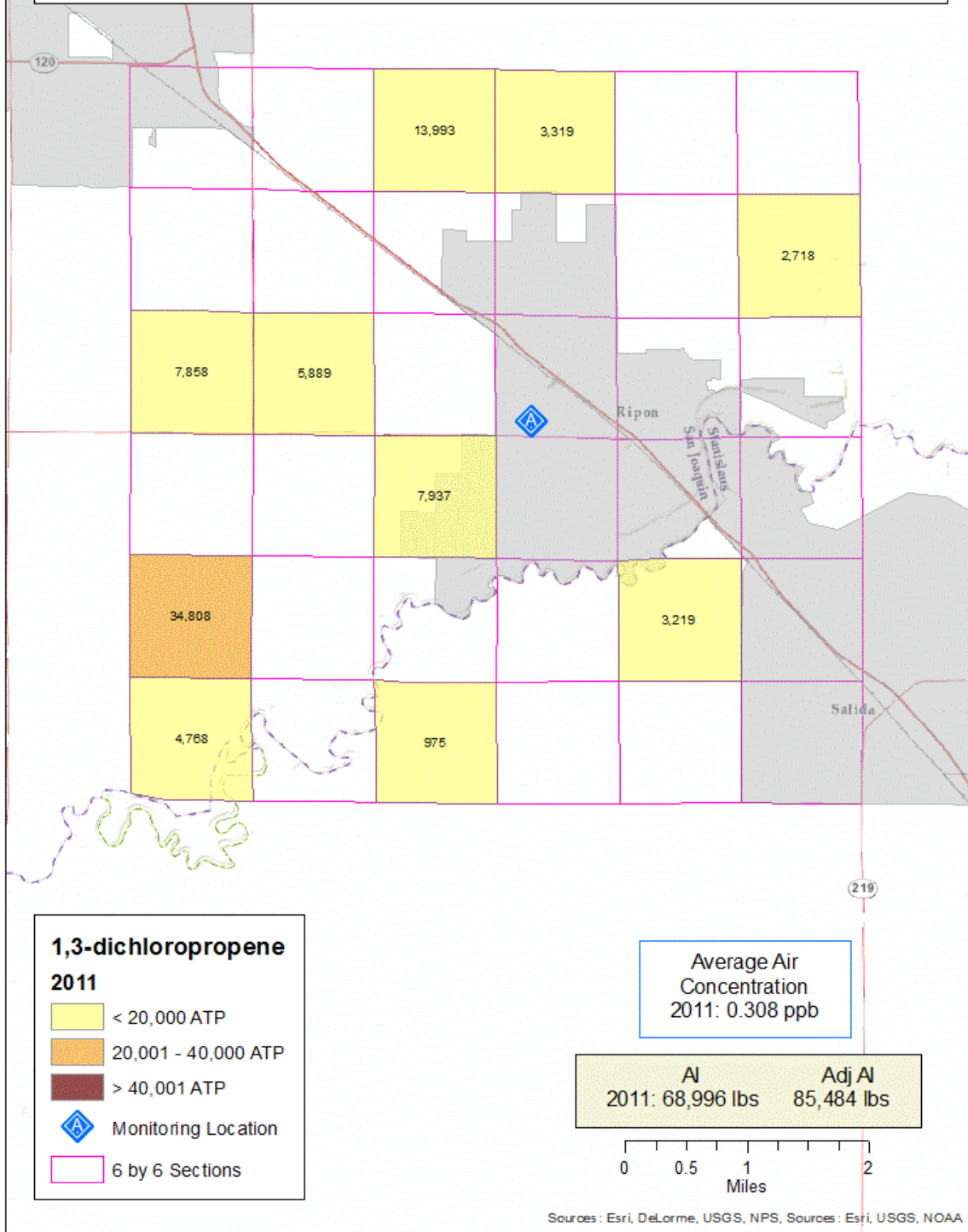
Adjusted pounds of 1,3-dichloropropene applied in a six by six grid of sections around Oxnard in 2014



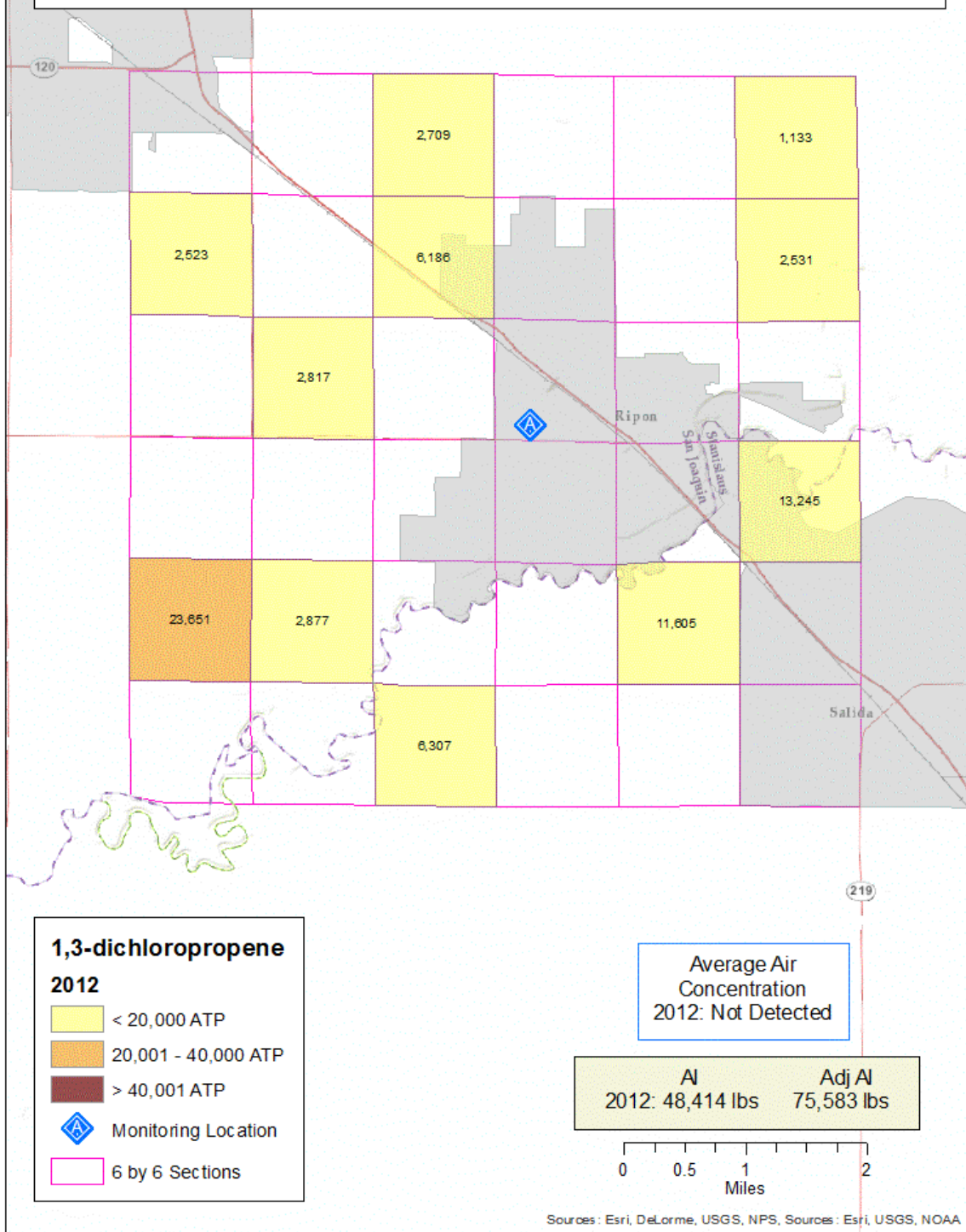
Adjusted pounds of 1,3-dichloropropene applied in a six by six grid of sections around Oxnard in 2015



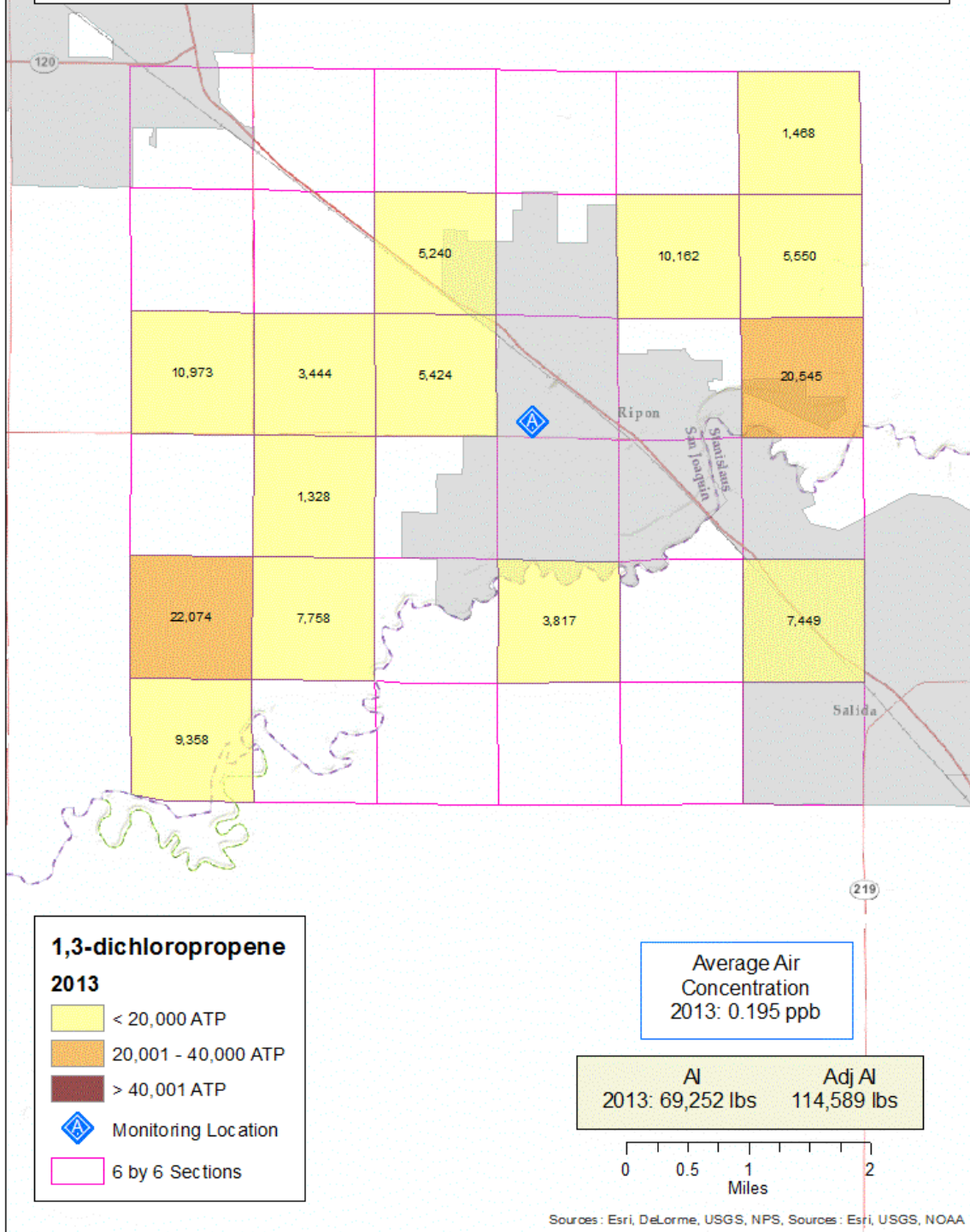
Adjusted pounds of 1,3-dichloropropene applied in a six by six grid of sections around Ripon in 2011



Adjusted pounds of 1,3-dichloropropene applied in a six by six grid of sections around Ripon in 2012

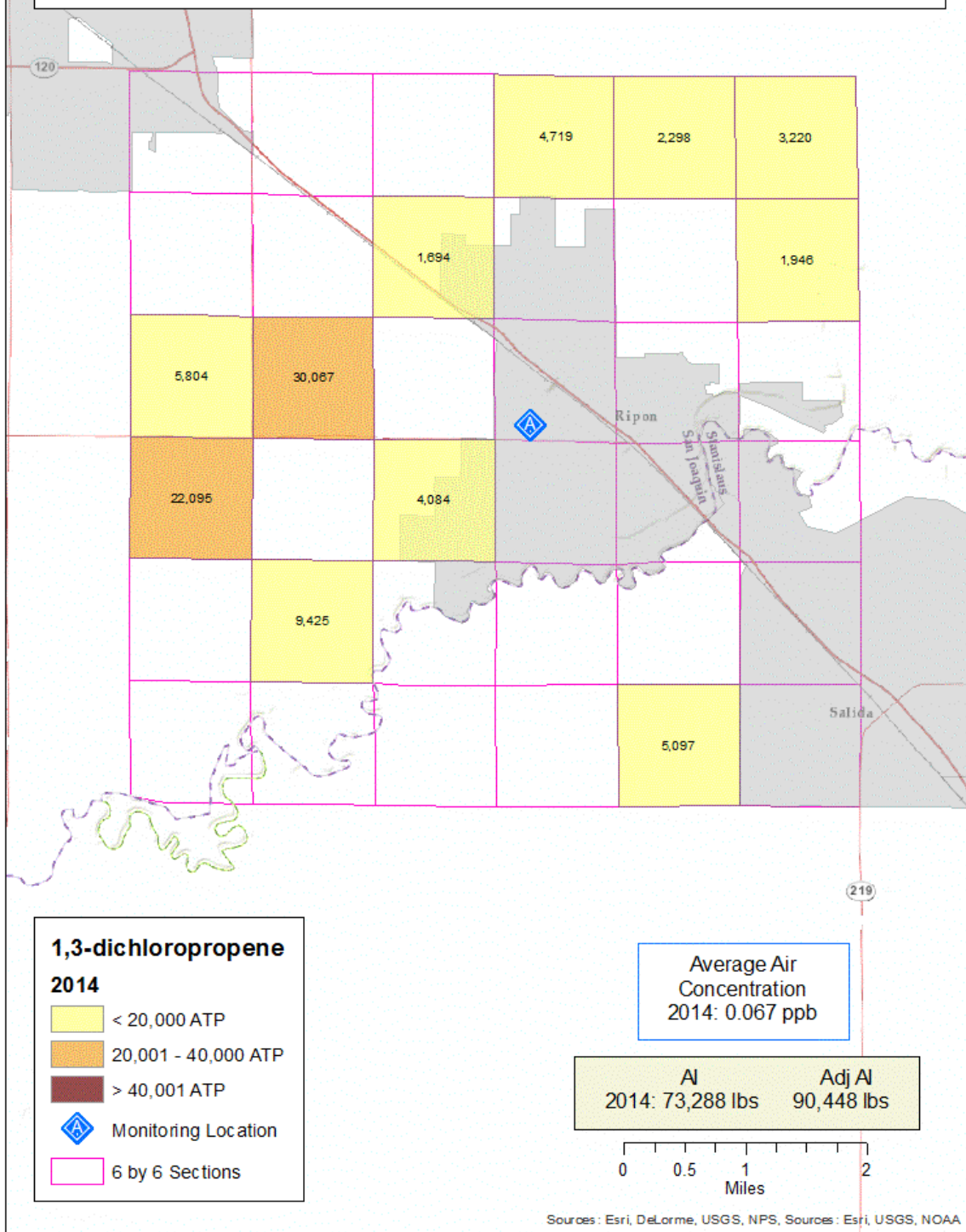


Adjusted pounds of 1,3-dichloropropene applied in a six by six grid of sections around Ripon in 2013

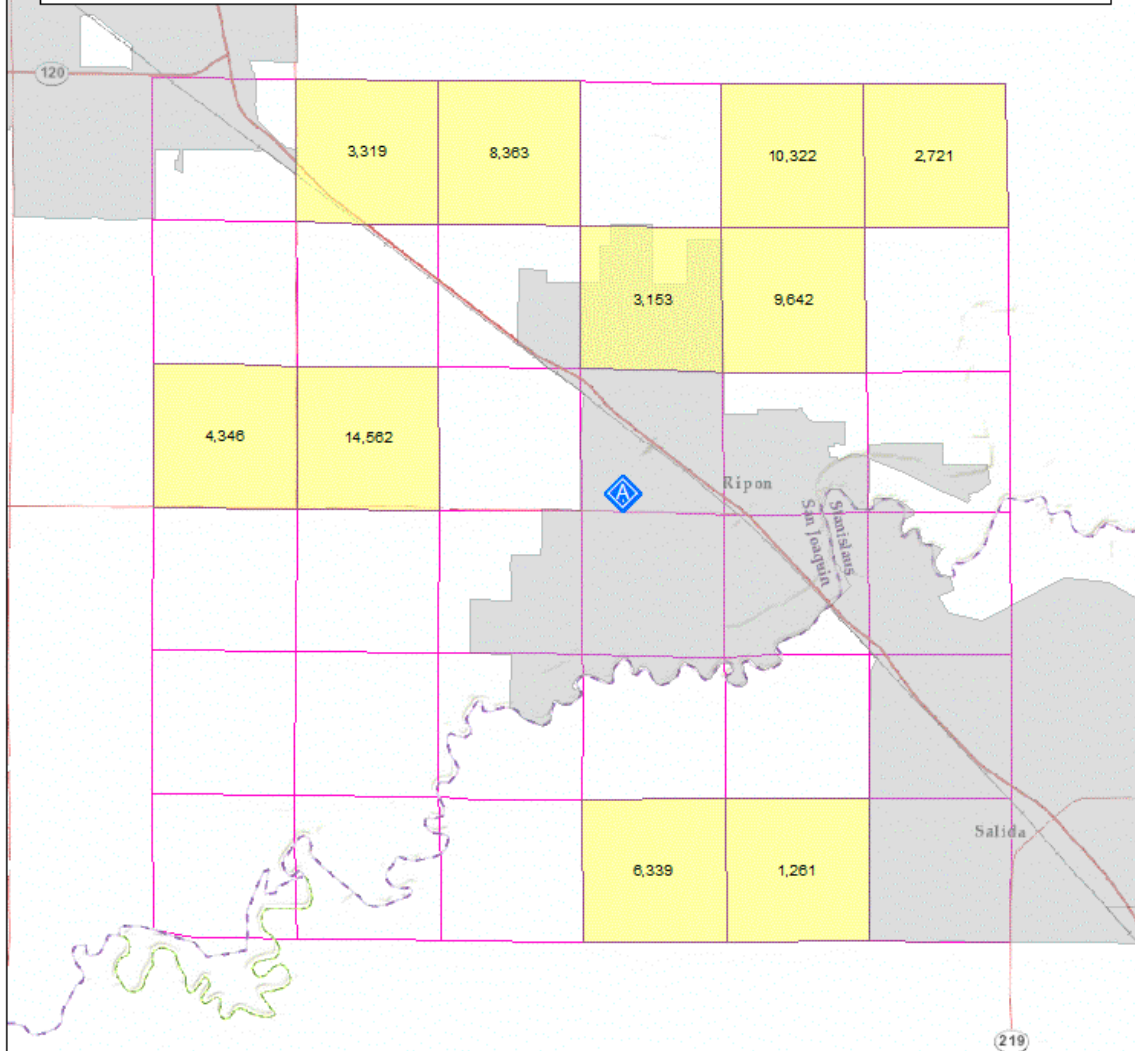




Adjusted pounds of 1,3-dichloropropene applied in a six by six grid of sections around Ripon in 2014



Adjusted pounds of 1,3-dichloropropene applied in a six by six grid of sections around Ripon in 2015

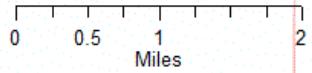


**1,3-dichloropropene  
2015**

- < 20,000 ATP
- 20,001 - 40,000 ATP
- > 40,001 ATP
- M Monitoring Location
- 6 by 6 Sections

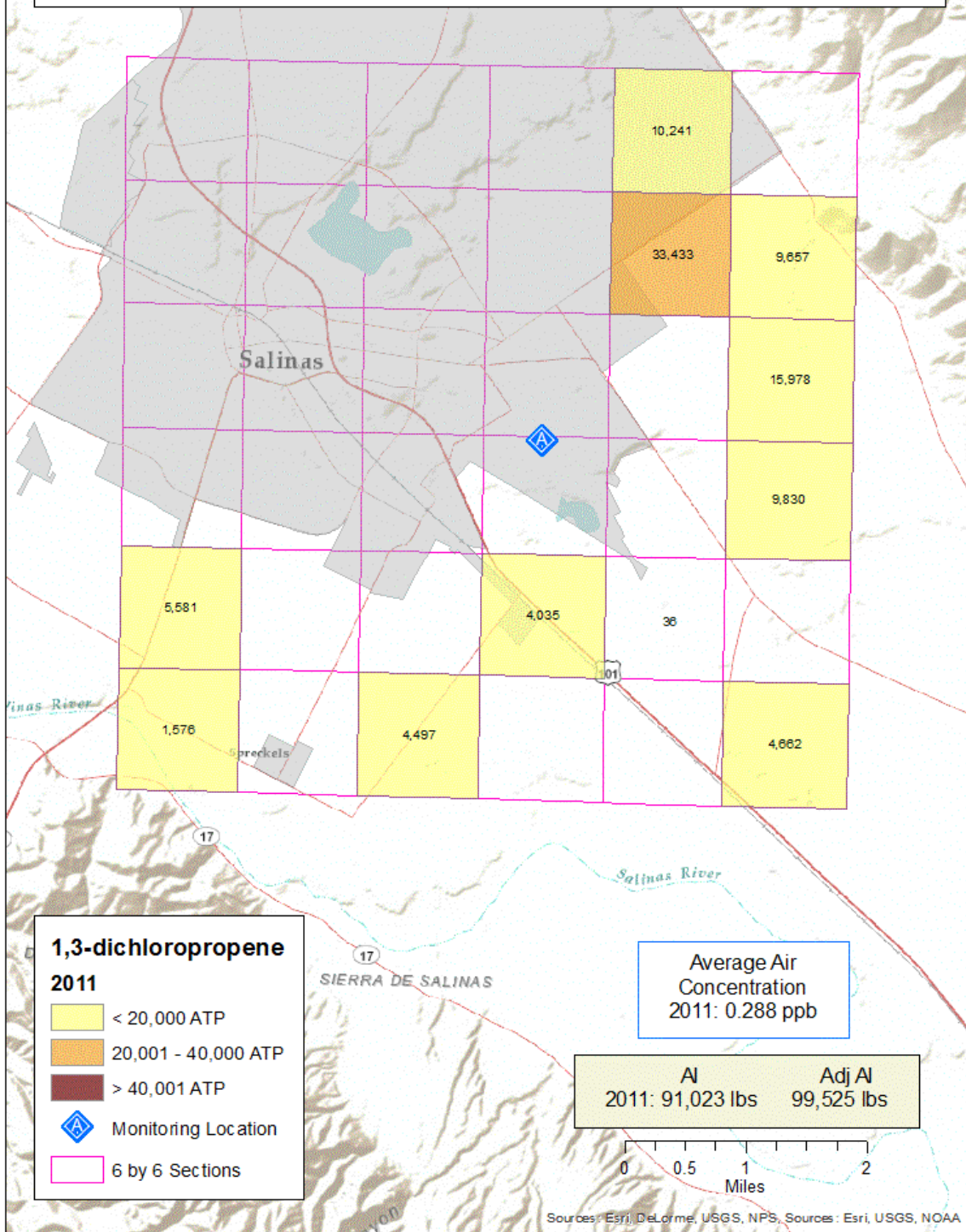
Average Air  
Concentration  
2015: 0.084 ppb

AI	Adj AI
2015: 51,756 lbs	64,028 lbs

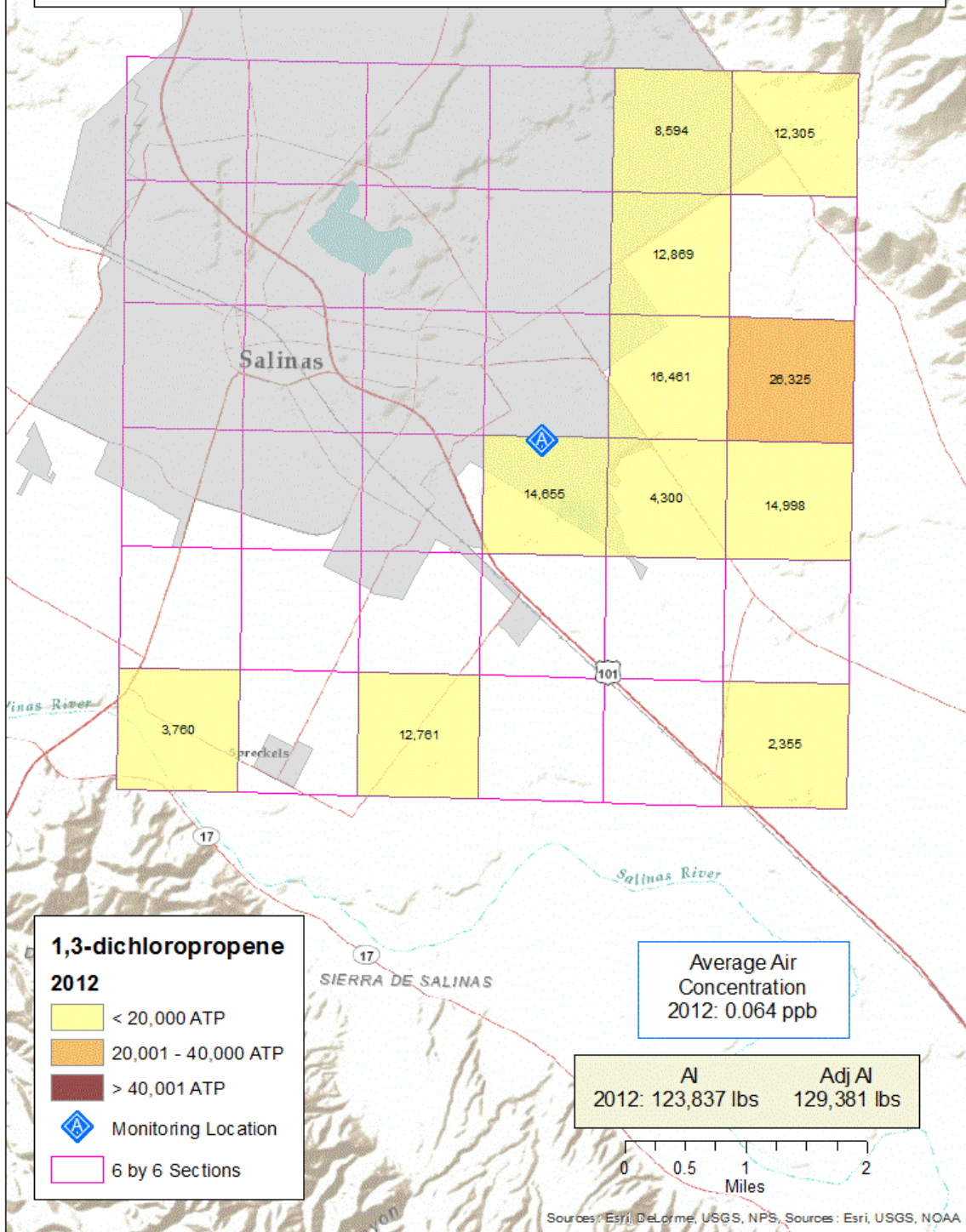


Sources: Esri, DeLorme, USGS, NPS, Sources: Esri, USGS, NOAA

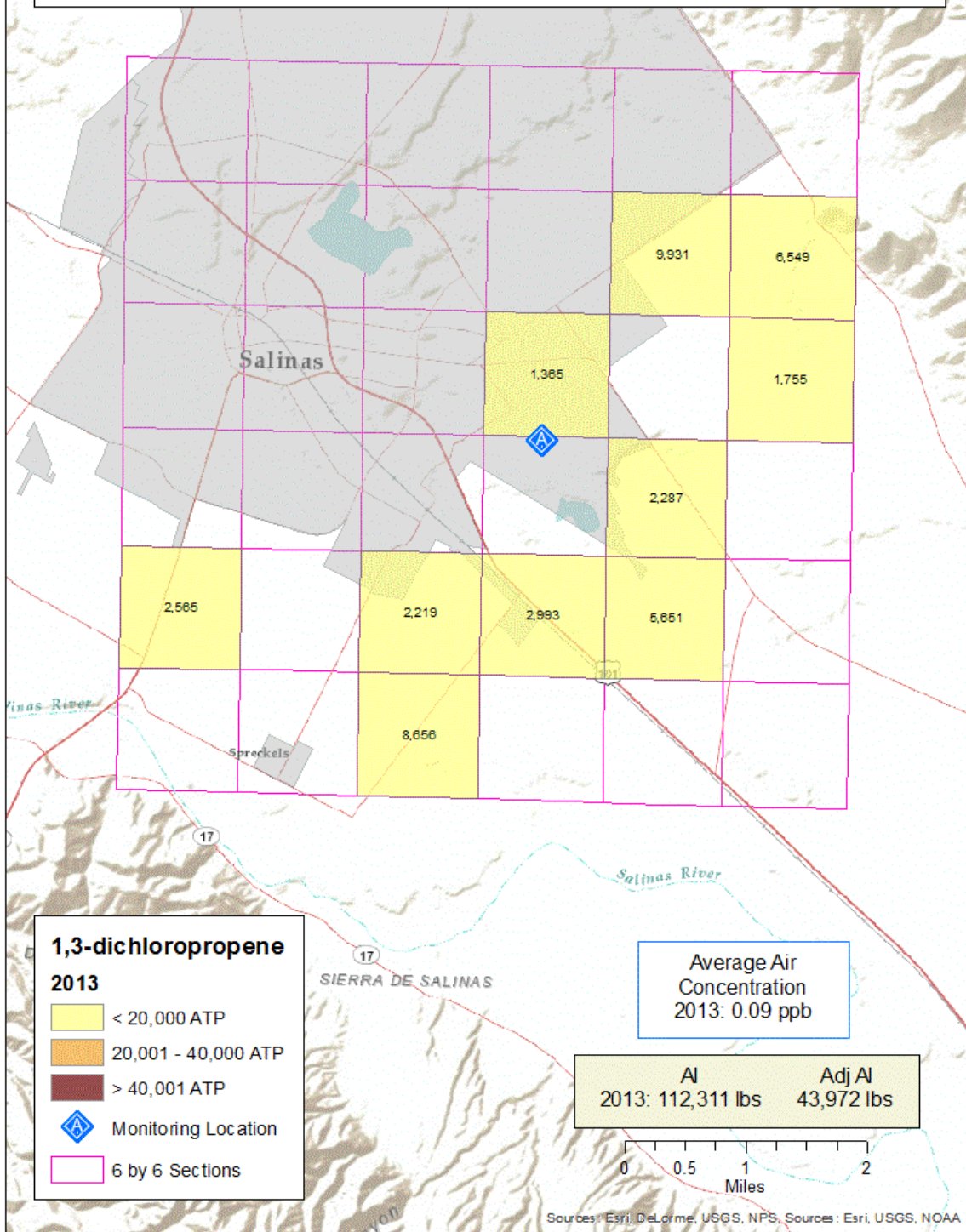
Adjusted pounds of 1,3-dichloropropene applied in a six by six grid of sections around Salinas in 2011



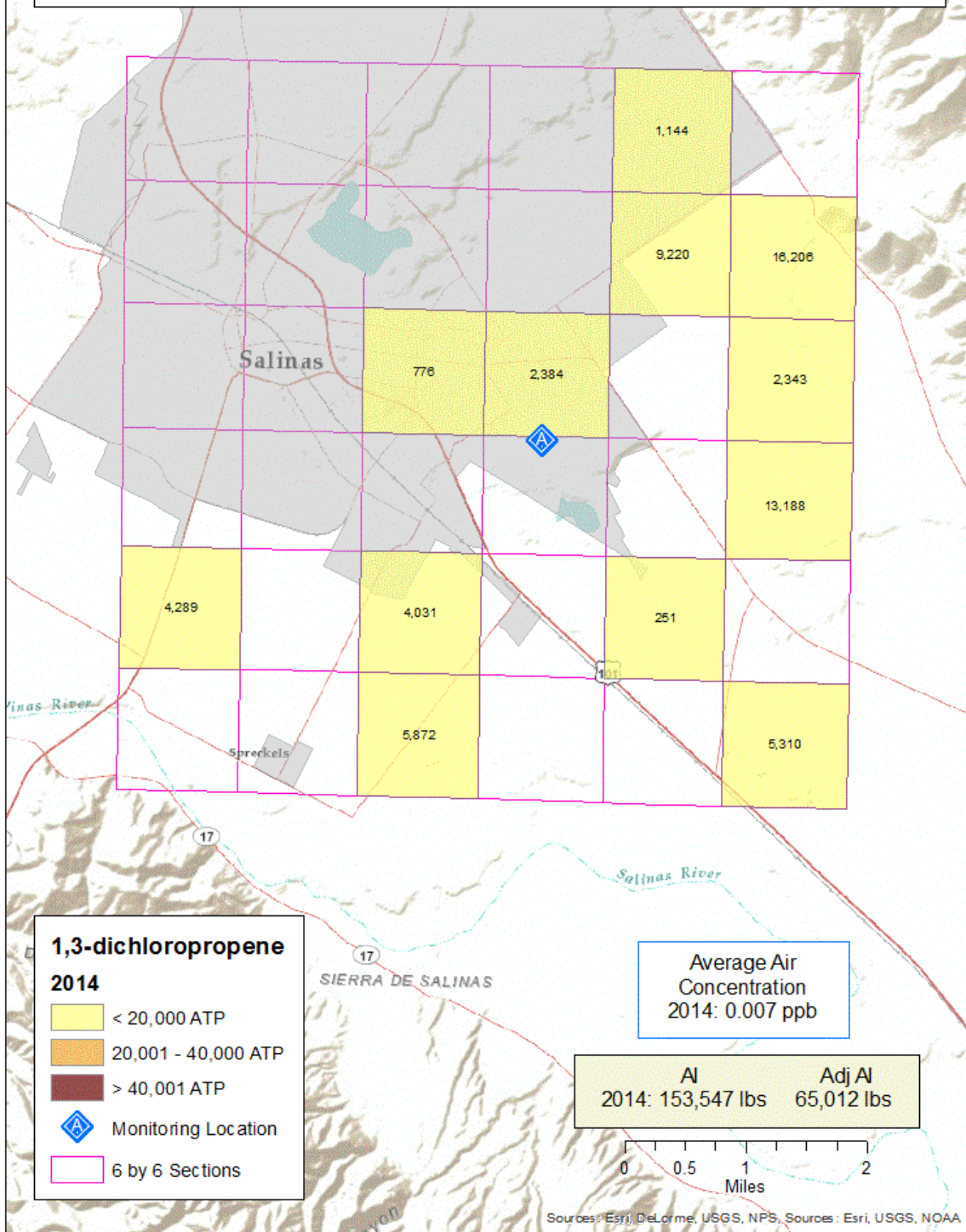
Adjusted pounds of 1,3-dichloropropene applied in a six by six grid of sections around Salinas in 2012



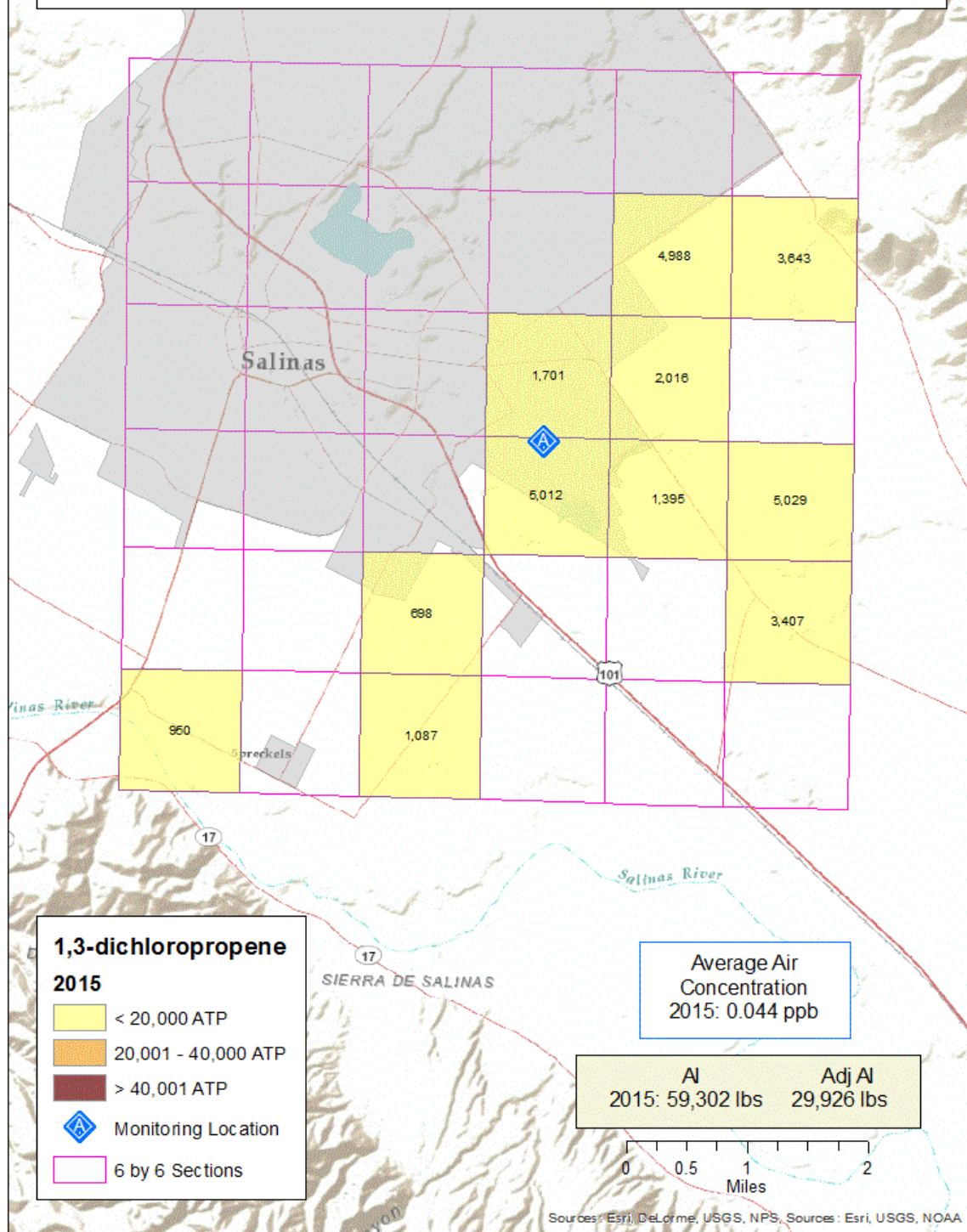
Adjusted pounds of 1,3-dichloropropene applied in a six by six grid of sections around Salinas in 2013



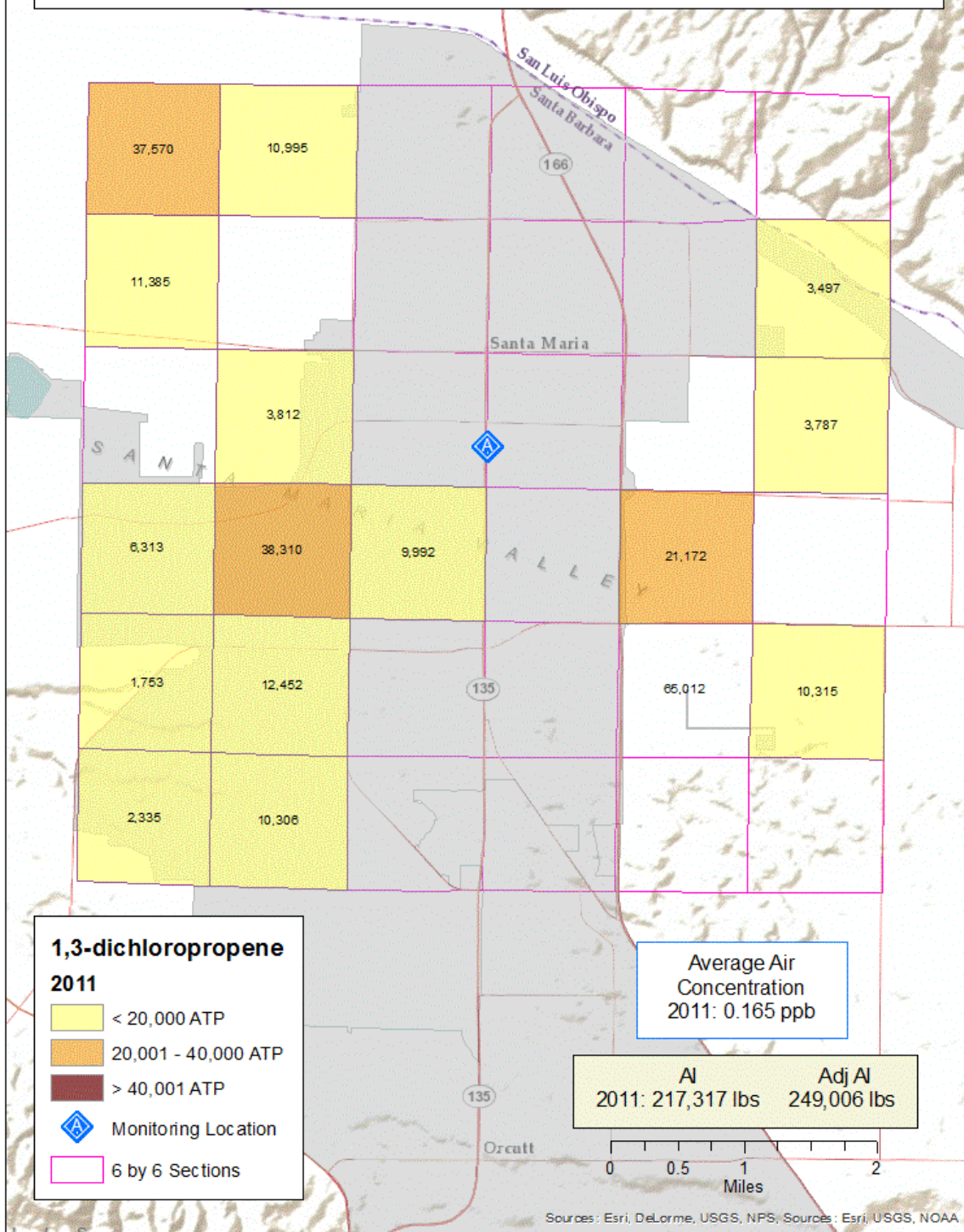
Adjusted pounds of 1,3-dichloropropene applied in a six by six grid of sections around Salinas in 2014



Adjusted pounds of 1,3-dichloropropene applied in a six by six grid of sections around Salinas in 2015

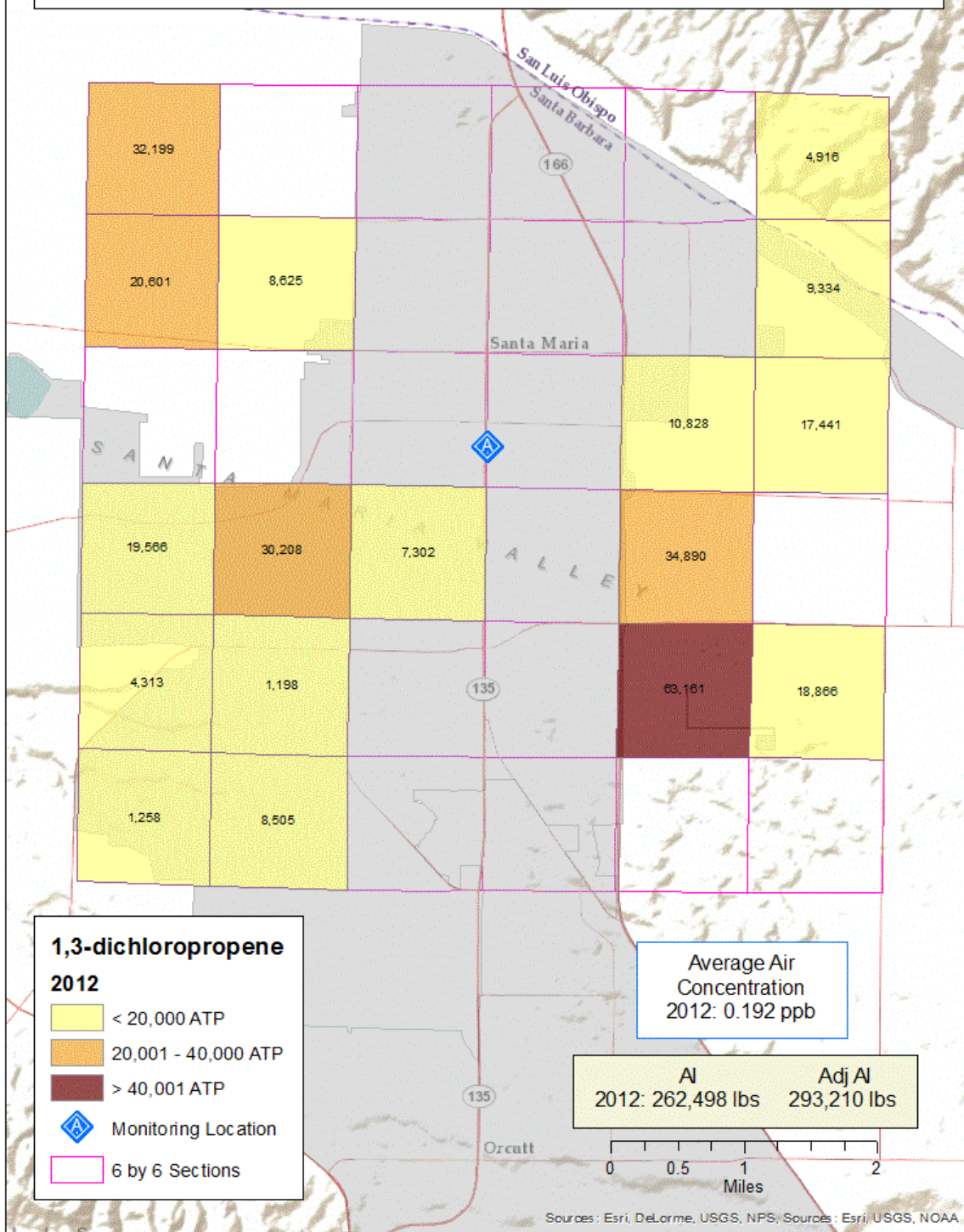


Adjusted pounds of 1,3-dichloropropene applied in a six by six grid of sections around Santa Maria in 2011

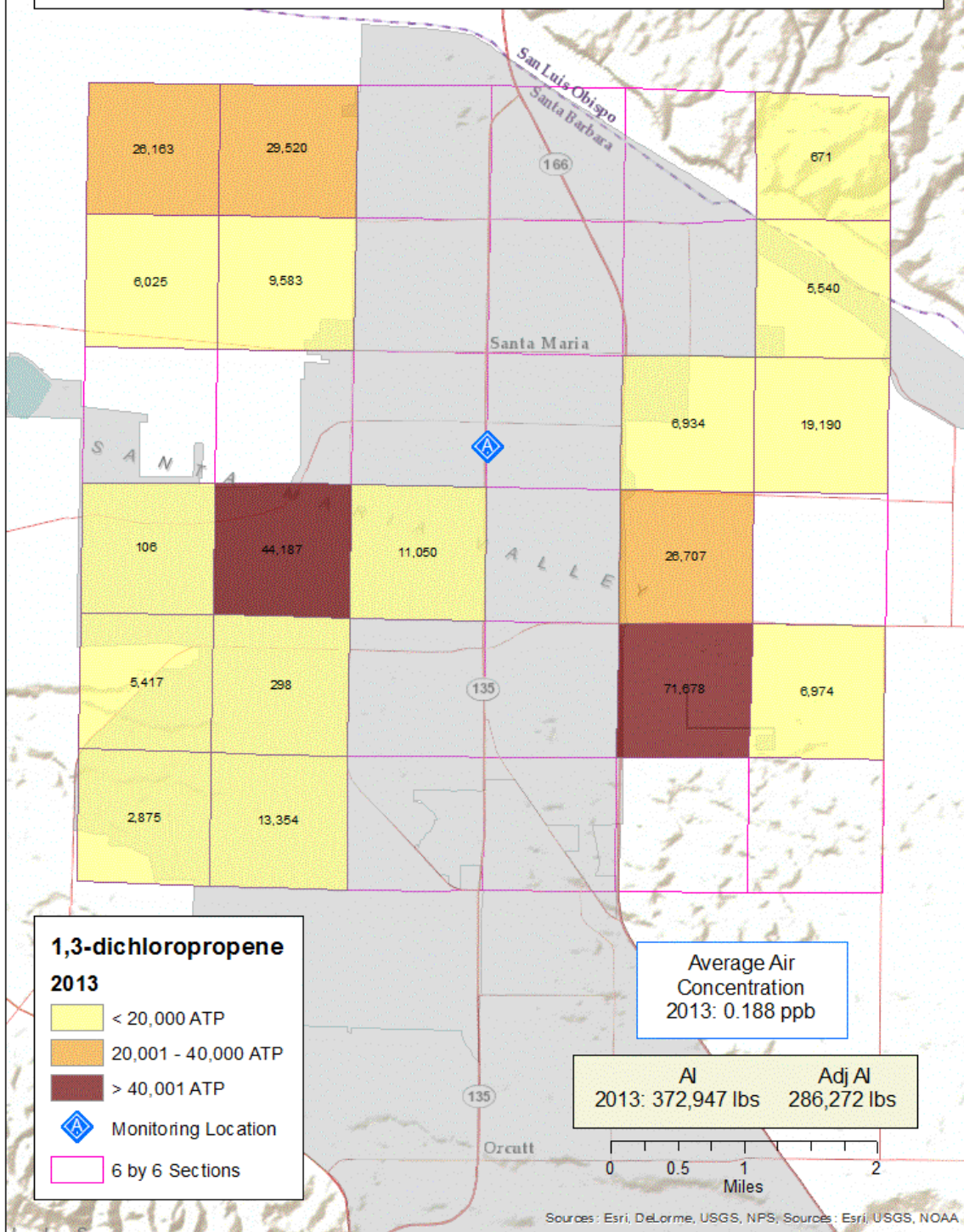




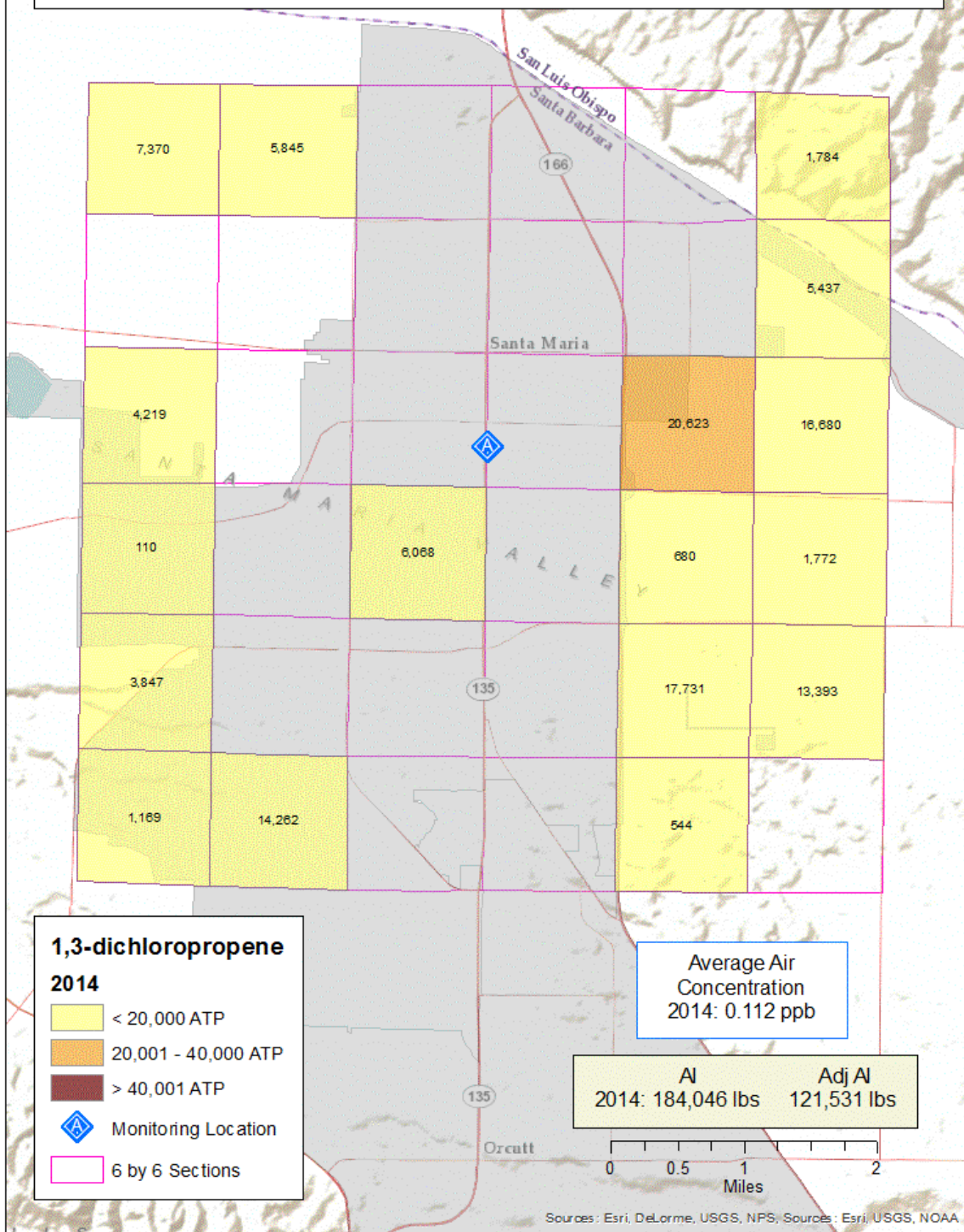
Adjusted pounds of 1,3-dichloropropene applied in a six by six grid of sections around Santa Maria in 2012



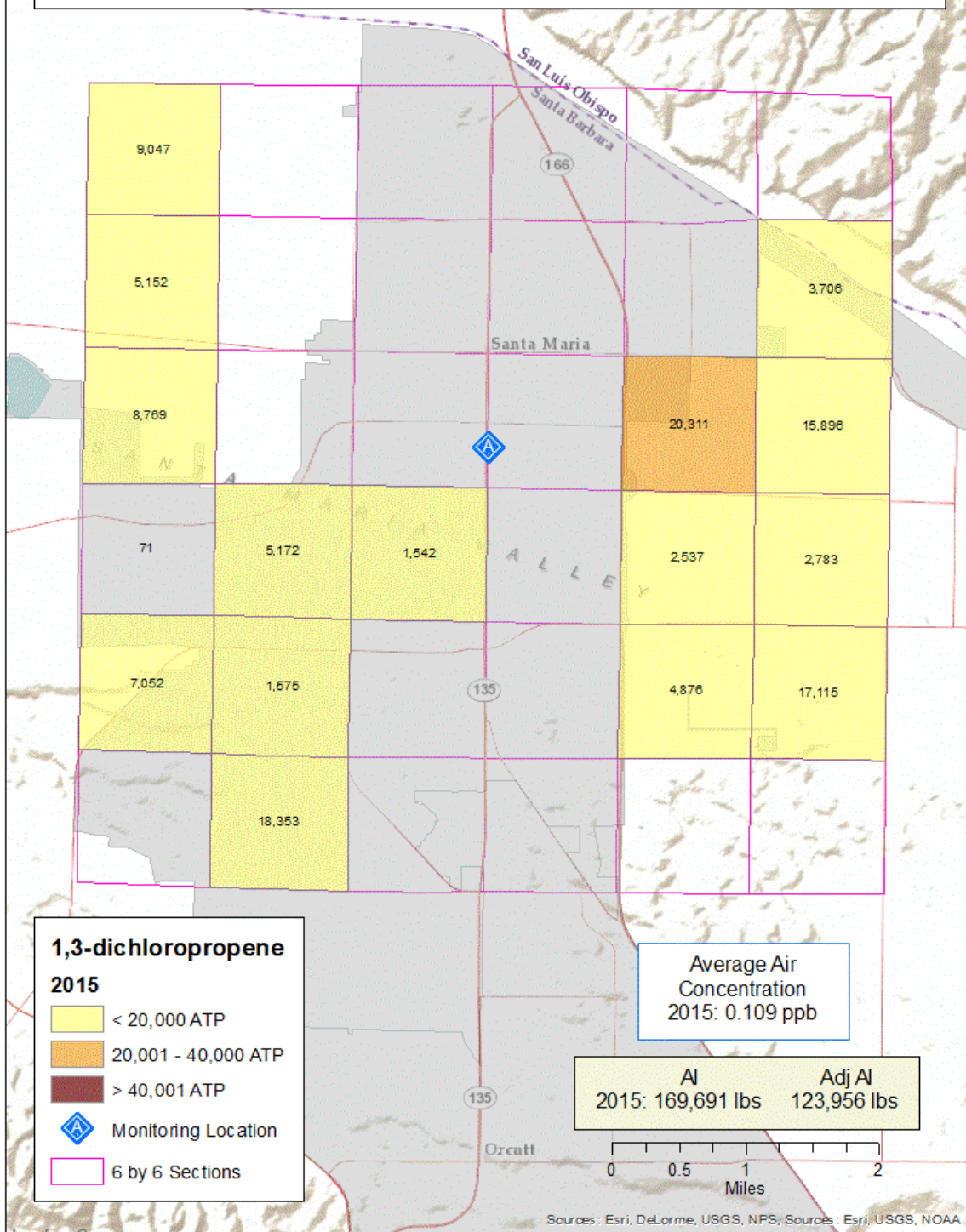
Adjusted pounds of 1,3-dichloropropene applied in a six by six grid of sections around Santa Maria in 2013



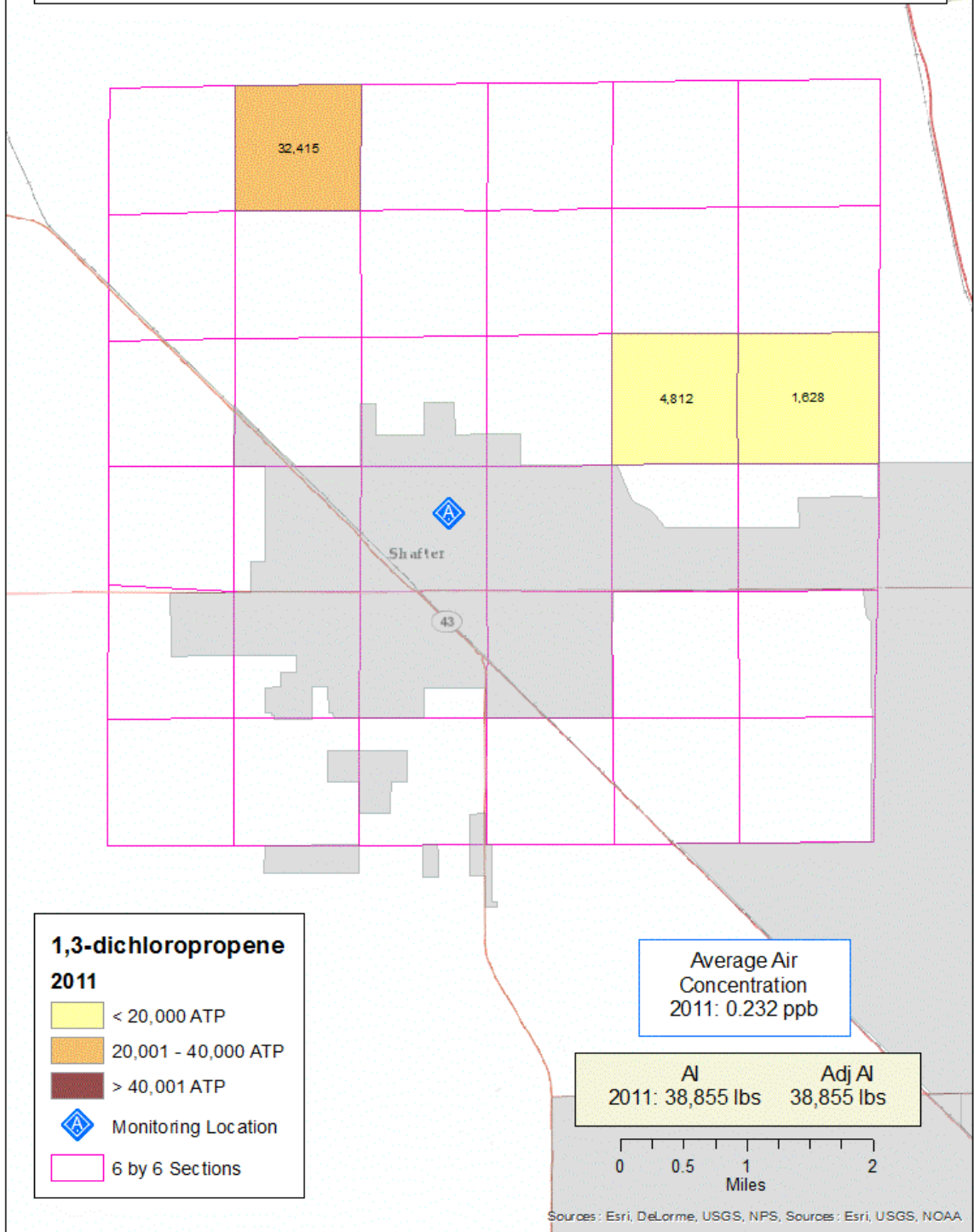
Adjusted pounds of 1,3-dichloropropene applied in a six by six grid of sections around Santa Maria in 2014



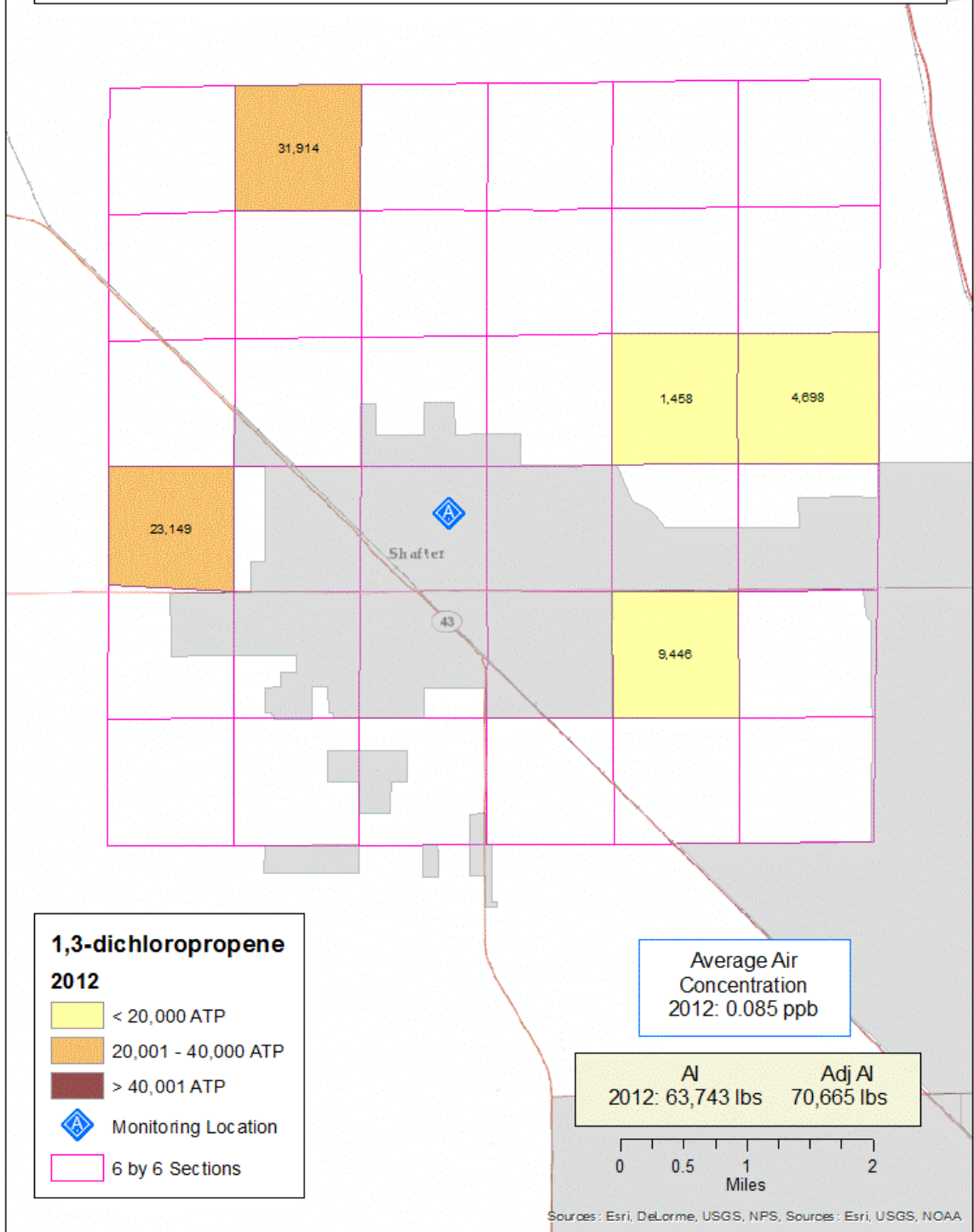
Adjusted pounds of 1,3-dichloropropene applied in a six by six grid of sections around Santa Maria in 2015



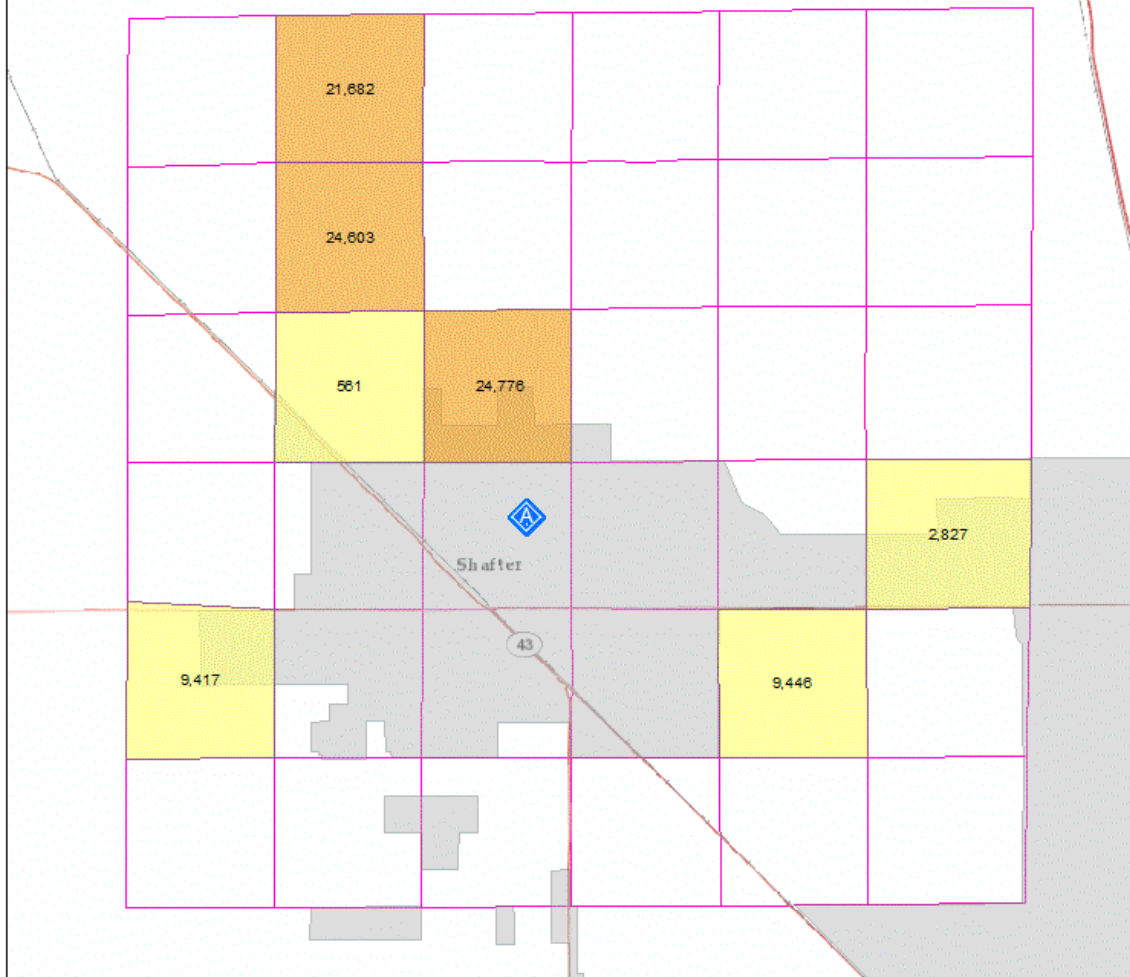
Adjusted pounds of 1,3-dichloropropene applied in a six by six grid of sections around Shafter in 2011



Adjusted pounds of 1,3-dichloropropene applied in a six by six grid of sections around Shafter in 2012



Adjusted pounds of 1,3-dichloropropene applied in a six by six grid of sections around Shafter in 2013

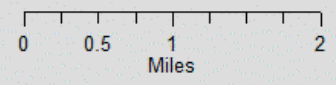


**1,3-dichloropropene  
2013**

- < 20,000 ATP
- 20,001 - 40,000 ATP
- > 40,001 ATP
- Monitoring Location
- 6 by 6 Sections

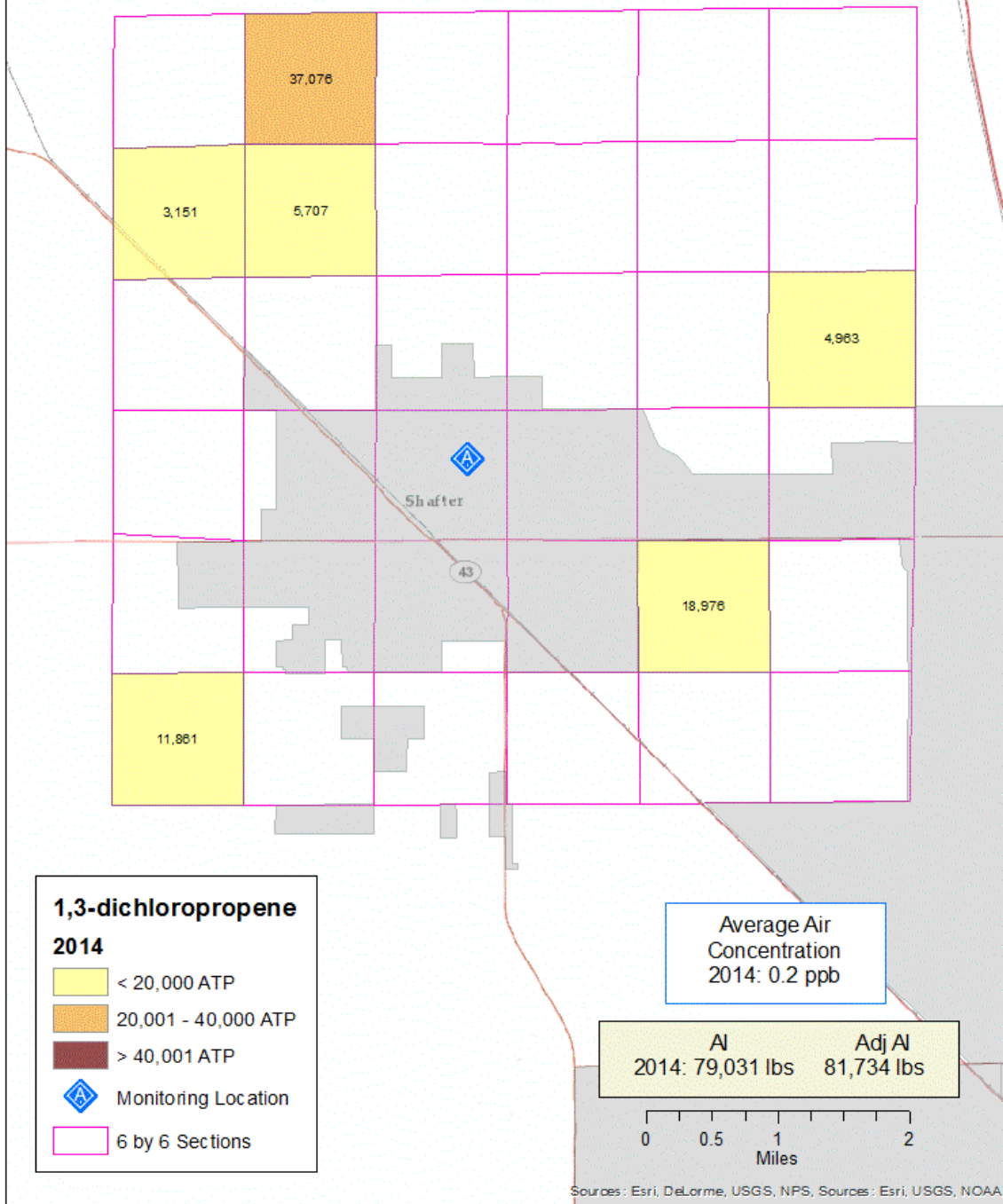
Average Air Concentration  
2013: 0.57 ppb

AI	Adj AI
2013: 72,415 lbs	93,312 lbs



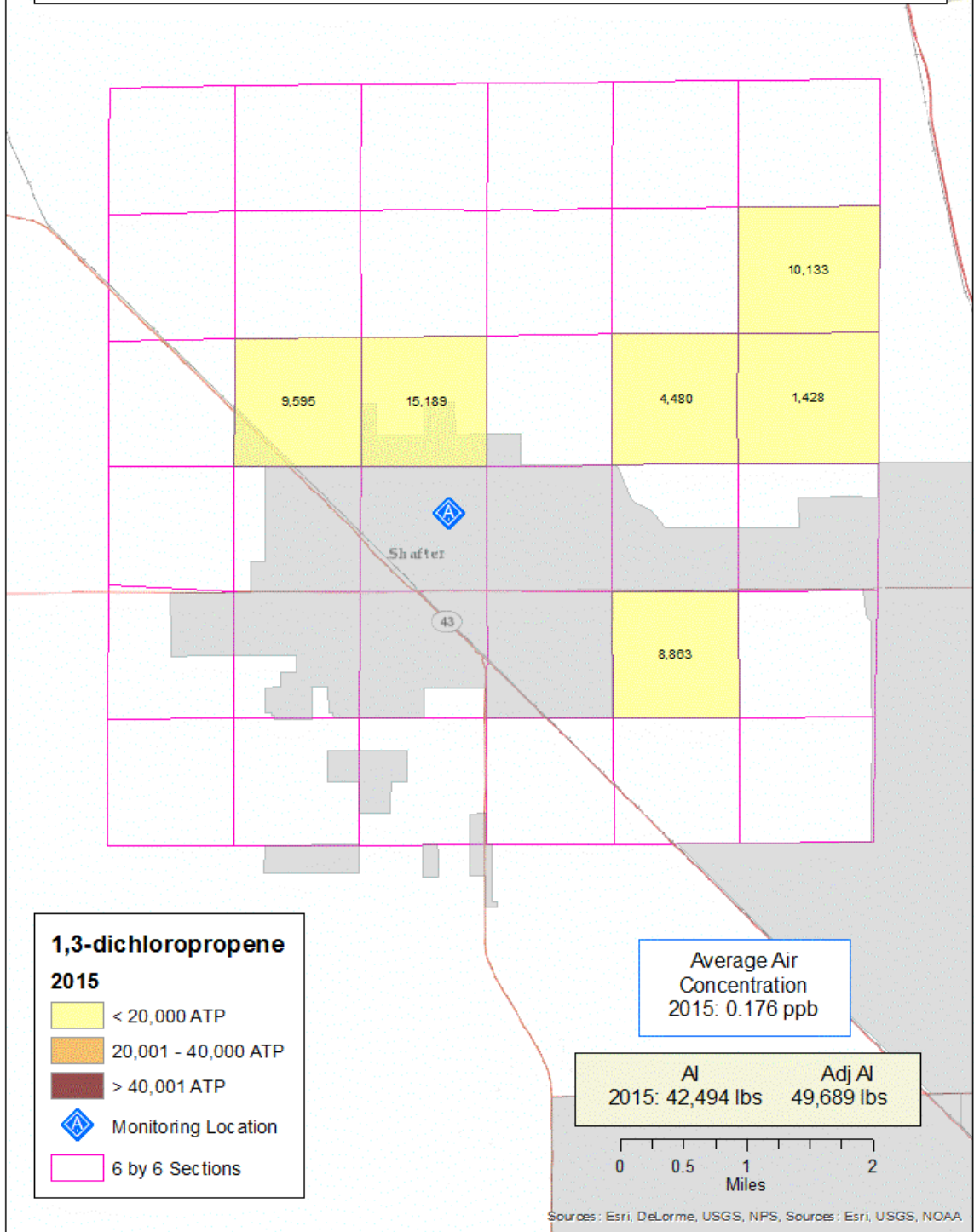
Sources: Esri, DeLorme, USGS, NPS, Sources: Esri, USGS, NOAA

Adjusted pounds of 1,3-dichloropropene applied in a six by six grid of sections around Shafter in 2014

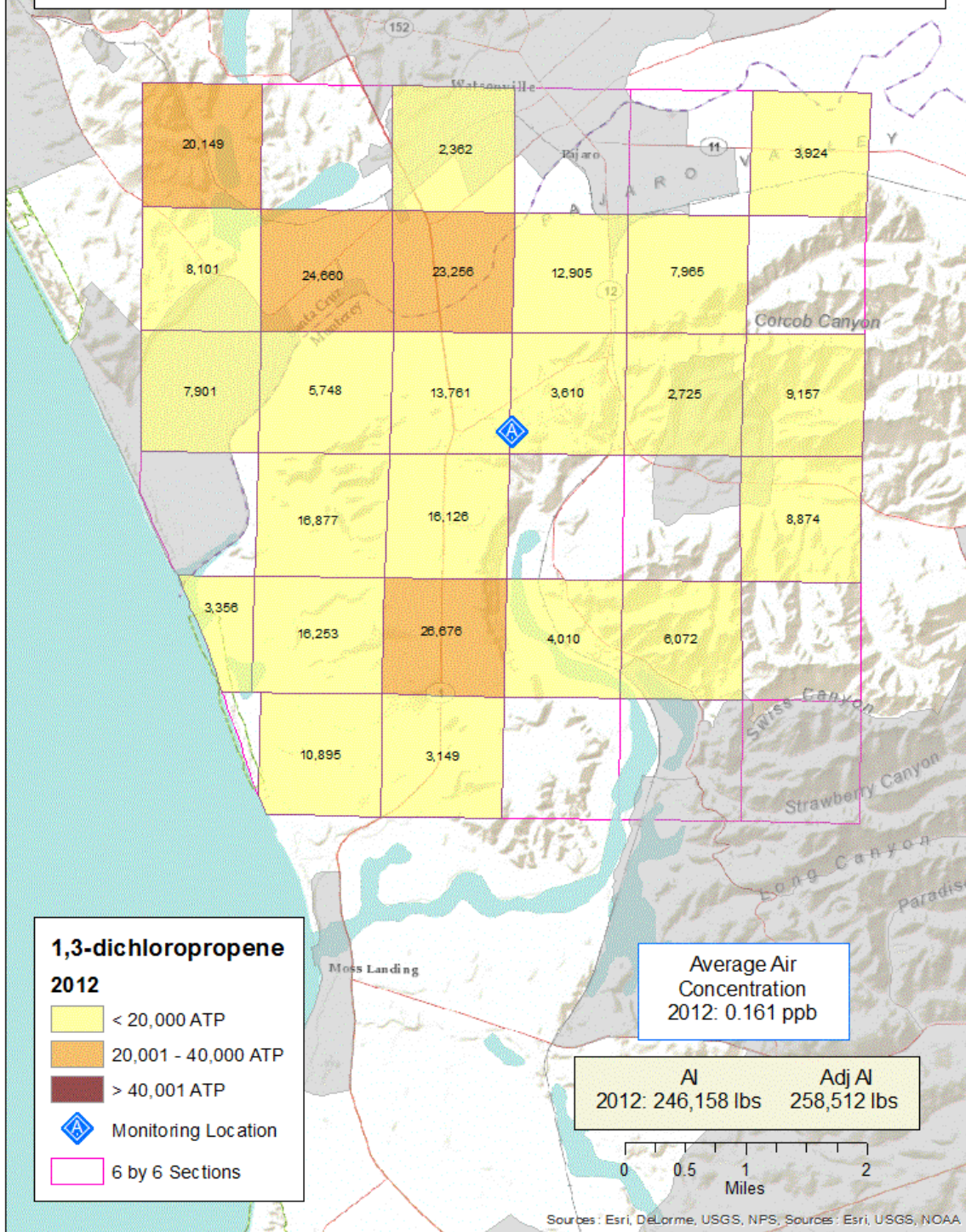




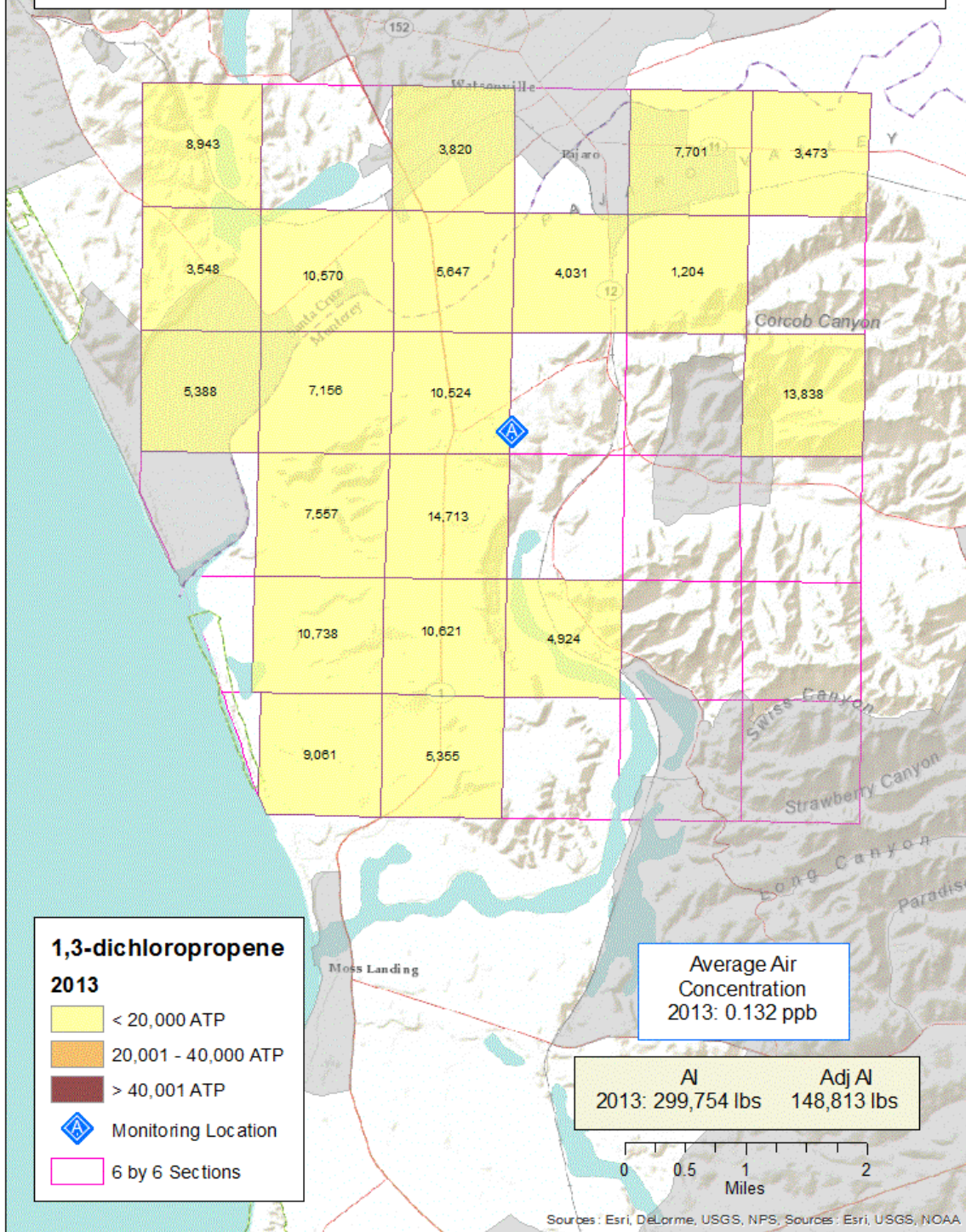
Adjusted pounds of 1,3-dichloropropene applied in a six by six grid of sections around Shafter in 2015



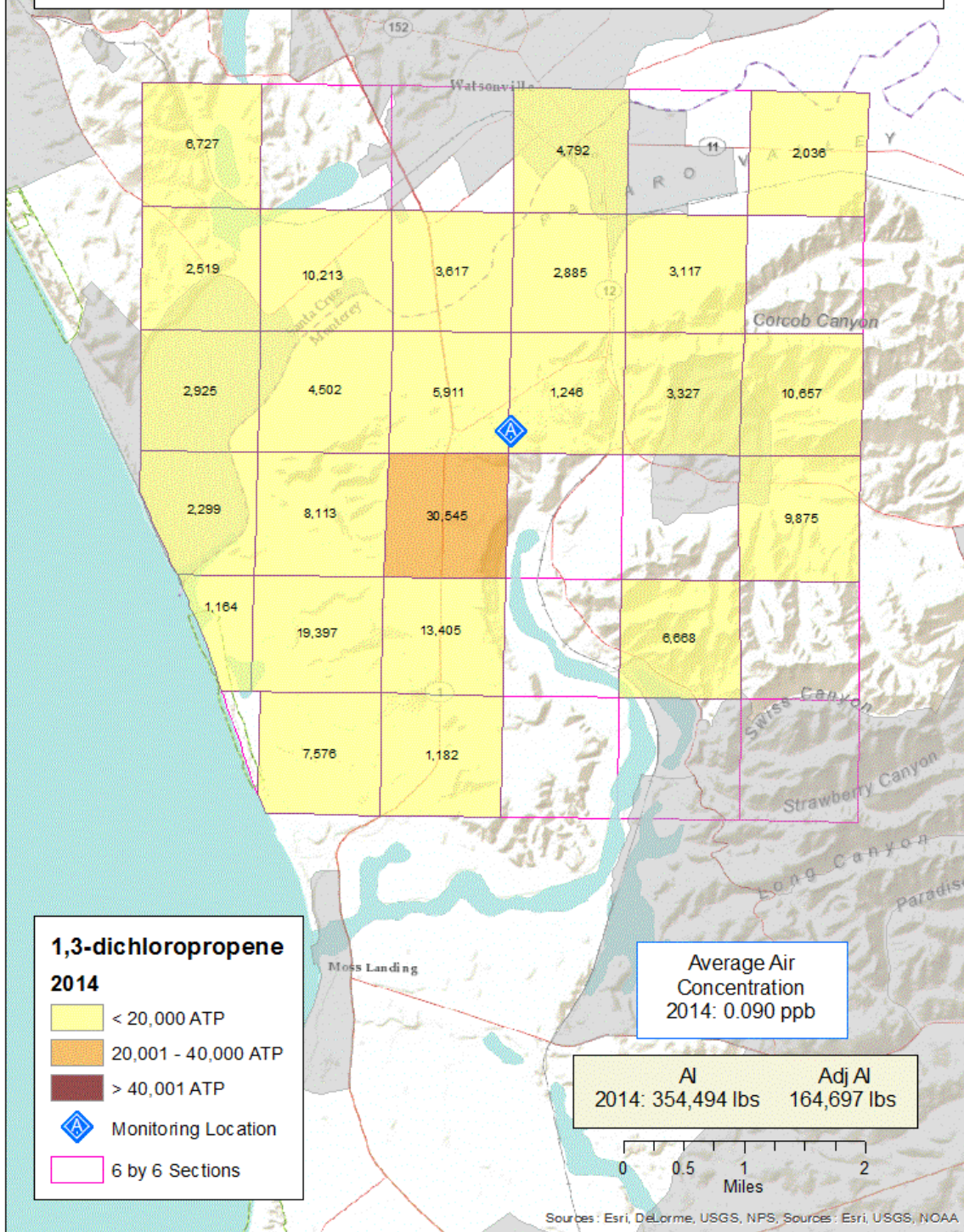
Adjusted pounds of 1,3-dichloropropene applied in a six by six grid of sections around Watsonville in 2012



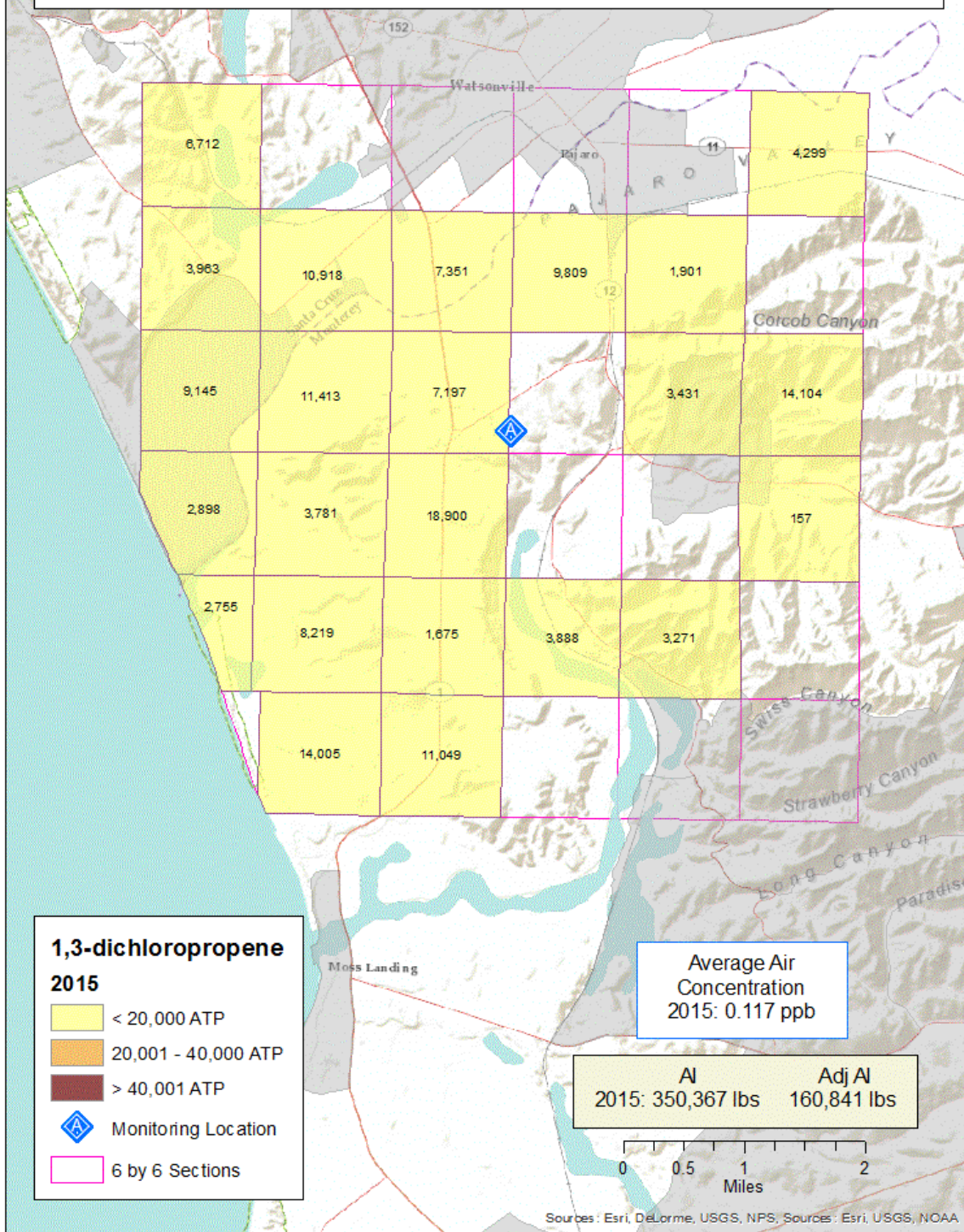
Adjusted pounds of 1,3-dichloropropene applied in a six by six grid of sections around Watsonville in 2013



Adjusted pounds of 1,3-dichloropropene applied in a six by six grid of sections around Watsonville in 2014



Adjusted pounds of 1,3-dichloropropene applied in a six by six grid of sections around Watsonville in 2015



## Appendix IV

### Ratios of Yearly Average Concentration and Annual Adjusted Total Pounds by Year and Sampling Site

Scenario I: 12-month Use						
Sampling Site	2006	2011	2012	2013	2014	2015
<b>Camarillo</b>		4.23E-07				
<b>Merced</b>		6.09E-06				
<b>Oxnard</b>			7.77E-07	7.99E-07	7.68E-07	2.72E-06
<b>Parlier</b>	5.73E-06					
<b>Ripon</b>		3.60E-06	6.62E-07	1.70E-06	7.36E-07	1.31E-06
<b>Salinas</b>		2.90E-06	4.92E-07	2.04E-06	1.13E-07	1.48E-06
<b>Santa Maria</b>		6.61E-07	6.55E-07	6.59E-07	9.19E-07	8.81E-07
<b>Shafter</b>		5.97E-06	1.20E-06	6.12E-06	2.45E-06	3.55E-06
<b>Watsonville</b>			6.24E-07	8.85E-07	5.44E-07	7.28E-07

Scenario II: 11-month Use						
Sampling Site	2006	2011	2012	2013	2014	2015
<b>Camarillo</b>		4.23E-07				
<b>Merced</b>		2.30E-06				
<b>Oxnard</b>			7.77E-07	7.99E-07	7.68E-07	2.72E-06
<b>Parlier</b>	4.69E-06					
<b>Ripon</b>		3.56E-06	2.55E-06	1.45E-06	1.14E-06	9.73E-07
<b>Salinas</b>		2.85E-06	4.65E-07	2.04E-06	1.13E-07	1.48E-06
<b>Santa Maria</b>		6.61E-07	6.55E-07	6.59E-07	9.19E-07	8.84E-07
<b>Shafter</b>		5.87E-06	1.45E-06	2.00E-06	2.20E-06	2.91E-06
<b>Watsonville</b>			6.24E-07	8.85E-07	5.44E-07	7.28E-07