LEGAL AGRICULTURAL USE DETERMINATION FOR DCPA DEGRADATE DETECTIONS IN CALIFORNIA

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ABSTRACT

Chlorthal-dimethyl (DCPA) is the active ingredient of a pre-emergent herbicide commonly known by the trade name Dacthal®. It is primarily used for control of annual grasses and certain broadleaved weeds in various fruit and vegetable crops and ornamental turf. DCPA was originally registered with the United States Environmental Protection Agency (US EPA) in 1958 and has been used in California since the late 1960s. DCPA has two major degradation products: monomethyl tetrachloroterephthalate (MTP) and 2,3,5,6-tetrachloroterephthalic acid (TPA). The California Department of Pesticide Regulation (DPR) conducted groundwater monitoring between 1990 and 1997 in different areas of the state where DCPA had been used, looking specifically for DCPA, MTP, and TPA. None of the laboratory analyses of the collected samples yielded a confirmed detection of DCPA or MTP. However, the analyses did confirm detections of TPA in samples collected in several counties, including five detections in the Salinas Valley of Monterey County and six detections in a region that spans Arroyo Grande in San Luis Obispo County to Lompoc in Santa Barbara County. To assess current levels of these chemicals, sampling was conducted during 2017 in the same general areas of Monterey, San Luis Obispo, and Santa Barbara counties where the previous TPA detections were found. During the winter and spring of 2017, thirteen unique wells were sampled in the Salinas Valley for DCPA, MTP, and TPA. No detections of DCPA were found in any of the wells above DPR's reporting level of 0.05 parts per billion (ppb). However, two wells contained MTP concentrations of 0.056 and 0.13 ppb and five wells contained TPA concentrations in the range of 0.916 to 101 ppb. The 101 ppb concentration exceeded the lifetime Health Advisory Level (HAL) of 70 ppb set for DCPA by the US EPA and adopted by DPR as a Reference Health Level for TPA. During the fall of 2017, twenty-three wells were sampled in areas located in southern San Luis Obispo County and Santa Barbara County. Again, no detections of DCPA were found. However, three wells contained MTP concentrations in the range of 0.063 to 0.101 ppb and thirteen wells contained TPA concentrations in the range of 0.121 to 159 ppb. Two wells, in particular, contained TPA concentrations (133 and 159 ppb) that exceeded the lifetime HAL of 70 ppb. The wells with the three highest detections (66.5, 133, and 159 ppb) were located individually in three consecutively adjacent sections in the east to west direction.

From review of data describing the environmental fate properties of DCPA and its degradation products, DCPA was found to be neither mobile nor persistent in soil. MTP is considered highly mobile in soil but not very persistent. However, TPA was determined to be both mobile and persistent in soil and considered to have a high potential to contaminate groundwater. As such, TPA has been detected in groundwater in eight counties in California and in groundwater in several other states, including Washington, Oregon, Idaho, New York, and Michigan. Given the historical use of DCPA in California and the locations of TPA detections in groundwater relative to those use patterns, it is the conclusion of this report that these data satisfy the criteria to make a Legal Agricultural Use determination that the detections of TPA found in wells between 1991 and 2017 are due to legal agricultural use of the parent active ingredient DCPA in those regions.

INTRODUCTION

The Pesticide Contamination Prevention Act (PCPA) is defined in Sections 13141-13152 of the California Food and Agricultural Code (FAC). Section 13149 mandates that when a laboratory-confirmed detection[1] of a pesticide active ingredient or other specified ingredient or degradation product of a pesticide is found in groundwater and the detection is determined to be due to legal agricultural use of the pesticide, then the California Department of Pesticide Regulation (DPR) is required to conduct a formal review (Detection Response Process) to determine if use of the pesticide should continue and, if so, under what conditions. The PCPA was originally enacted in 1985 under Assembly Bill 2021 (AB 2021) and was significantly revised in 2014 under Senate Bill 1117 (SB 1117). Under the AB 2021 version of the PCPA, an active ingredient would be entered into the Detection Response Process if one of its degradation products was found in groundwater and if the measured levels of that degradation product were determined to be high enough to pose a threat to public health (i.e., if the measured concentration exceeded an established health level). The revision of the PCPA in 2014 under SB 1117 lifted the requirement to demonstrate a threat to public health of degradation products found in groundwater. Consequently, a pesticide active ingredient can now be entered into the Detection Response Process when its degradation product is simply found in groundwater and determined to have originated from the legal agricultural use of its parent active ingredient.

Chlorthal-dimethyl (DCPA) is the active ingredient of a pre-emergent herbicide commonly known by its tradename Dacthal. DCPA has two major degradation products: monomethyl tetrachloroterephthalate (MTP) and 2,3,5,6-tetrachloroterephthalic acid (TPA). In general, DCPA is rarely, if ever, detected in groundwater. However, numerous detections of the combined analysis for MTP/TPA in groundwater have been documented over the years in several states, including Washington (Cook, 2014), Oregon (ODEQ, 2003), Idaho (ISDA, 2007), New York (NYSDEC, 2014), and Michigan (ATSDR, 2009). In California, DPR conducted groundwater monitoring between 1990 and 1997 in ten counties where DCPA had been used, looking specifically for individual detections of DCPA, MTP, and TPA in groundwater. None of the laboratory analyses of the collected samples from that monitoring yielded a confirmed detection of DCPA or MTP. However, the laboratory analysis did confirm detections of TPA in eight counties (CDPR, 2015). None of the TPA detections at the time, however, exceeded the lifetime Health Advisory Level of 70 ppb set by the United States Environmental Protection Agency (US EPA) (US EPA, 2008). The TPA detections also did not exceed the advisory level of 3,500 ppb established by the Drinking Water Program of the California Department of Health Services (now the Division of Drinking Water in the State Water Resources Control Board) in 1990 (CDHS, 1990).

[1] A chemical detection by laboratory analysis is considered "confirmed" by either (a) an analytical chemical method approved by DPR that provides unequivocal identification of the chemical, or (b) verification, within 30 days, by a second analytical method or second analytical laboratory approved by DPR (Aggarwal, 2012; 2017).

In order to enter DCPA into the Detection Response Process, detections of TPA must satisfy DPR's Legal Agricultural Use criteria. In general, a Legal Agricultural Use determination is made when the detections of the active ingredient or its degradation product satisfy the following three criteria:

1. The active ingredient or its degradation product is detected in two or more wells in the same one-square mile section of land or in adjacent sections (Goh, 1992).

2. The active ingredient is formulated in product(s) labeled for agricultural use (Oshima, 1987).

3. The active ingredient has reported agricultural use in the vicinity of the detections or there are sites within the section where the active ingredient might be used (Oshima, 1987).

Situations may occur, however, in which detections are found in wells that are located in different, non-adjacent sections but within a region in which the active ingredient has been applied as a pesticide labeled for agricultural use. In those instances, a Legal Agricultural Use determination can still be made when the following criterion is satisfied:

4. There is a **preponderance of evidence** presented that the detections of the active ingredient or its degradation product are the result of legal agricultural use of the active ingredient in the region in which the detections were found.

The purpose of this report is to make a Legal Agricultural Use determination for the detections of the degradation product TPA of DCPA in California. The report will focus on detections of TPA and associated DCPA use in the Salinas Valley of Monterey County and in a region extending from Arroyo Grande in San Luis Obispo County to Lompoc in Santa Barbara County. To provide current evidence for the Legal Agricultural Use determination, additional groundwater monitoring for DCPA, MTP, and TPA was conducted in those two regions during 2017.

REPORTED AGRICULTURAL USE

DCPA is a pre-emergent herbicide used for control of annual grasses and certain broadleaved weeds in various fruit and vegetable crops and ornamental turf. It was originally registered with the US EPA in 1958 by the Diamond Alkali Company and has been used in California since the late 1960s. Use of DCPA continued in California until 1998 when ISK Biosciences, the prevailing registrant of DCPA at the time, discontinued its production. Dacthal herbicide products were reintroduced to the market in 2001 when the rights were acquired by the Amvac Chemical Corporation (AMVAC).

Beginning in 1990, information describing each application of a pesticide labeled for agricultural use was required to be reported to DPR. As such, the DPR Pesticide Use Report (PUR) database contains reported agricultural use of DCPA (in pounds) at the section scale (i.e., 1 square mile) from 1990 to present (CDPR, 2017a). Total annual use of DCPA in California from 1990 to 2016 is shown on Figure 1. Annual use declined steadily during the 1990s from a high of

849,074 pounds (lbs) in 1992 to a low of 133,688 lbs in 2000 (Figure 1). A significant drop in annual use occurred around 1998 and coincides with the approximate removal of Dacthal products from the market by ISK Biosciences. Use continued to decline for the next few years with the selling of existing stocks of Dacthal products. After reintroduction of Dacthal products to the market by AMVAC around 2001, annual use of DCPA increased again. From 2001 to 2016 annual use statewide leveled off somewhat with an average rate of 192,067 lbs per year. Total reported use of DCPA during 2016 was 190,990 lbs.

The median time between pesticide application at the ground surface and subsequent detection in shallow domestic water wells (i.e., travel time) has been estimated to be about 7 to 9 years based on vadose zone transport modeling and an analysis of chlorofluorocarbon (CFC) groundwater age dating data (Spurlock et al., 2000). Using the 7- to 9-year travel time range as a basis for planning, an 11-year period from 2000 and 2010 was conservatively chosen as a "recent" period of DCPA use to plan additional sampling in regions where DCPA has had high recent use and where historic detections of TPA (i.e., from 1990 to 1997) have also been found (CDPR, 2017b).

Annual DCPA use by county from 2000 to 2010 is presented in Table 1. The top users of DCPA were Monterey and Imperial counties with average annual usages of 75,526 and 45,731 lbs per year, respectively. Lesser amounts of DCPA (< 13,000 lbs per year) were used in Ventura, Fresno, Riverside, and Santa Barbara counties (Table 1). Total annual use of DCPA in Monterey, San Luis Obispo, and Santa Barbara counties from 1990 to 2016 are shown on Figures 2, 3, and 4, respectively. The trends in annual use of DCPA in these three counties from 1990 to 2016 are similar to the statewide trend (Figure 1). Although not graphically displayed, trends in annual use of DCPA for Imperial, Ventura, Fresno, and Riverside counties are also similar to that of the state (Figure 1).

Maps displaying total DCPA use from 2000 to 2010 at the section scale for Monterey, Imperial, Ventura, Fresno, Riverside, and San Luis Obispo/Santa Barbara counties are shown on Figures 5 through 10, respectively. Sections with the highest total use were generally located in the Salinas Valley of Monterey County (Figure 5). The individual section with the overall highest total use from 2000 to 2010 in the state (25,540 lbs) was located in Ventura County (Figure 7). Total DCPA use by crop statewide from 2000 to 2010 is presented in Table 2. Broccoli, onion, cauliflower, and cabbage crops combine to account for nearly 88% of the DCPA applied for agricultural use in the state over this period, with broccoli alone accounting for nearly half the total use at 46% (Table 2).

DETECTIONS IN GROUNDWATER

The DPR Well Inventory Database contains measured concentrations of pesticides or their degradation products in wells sampled by various local, state, and federal agencies (CDPR, 2015). DPR conducted its own groundwater sampling between 1990 and 1997 in ten counties where DCPA had been legally used, looking specifically for DCPA, MTP, and TPA. None of the laboratory analyses of the collected samples yielded a confirmed detection of DCPA or MTP. However, the laboratory analysis did confirm 32 detections of TPA in samples collected in eight counties and those findings are summarized in Table 3. The approximate locations of wells with

TPA detections statewide are plotted on Figure 11 for central California and on Figure 12 for southern California. Locations of TPA detections at the section scale as defined by the Public Lands Survey System (PLSS) (i.e., Meridian & Baseline, Township, Range, and Section) are presented in Table 4. The approximate locations of confirmed TPA detections relative to the spatial distributions of DCPA use on a section basis in Monterey, Fresno, and San Luis Obispo/Santa Barbara counties are also displayed on Figures 5, 8, and 10, respectively. For the 1990 to 1997 sampling period, six detections were found in Santa Clara County; five detections were found in each of Kern and Monterey counties; four detections were found in Fresno County and in the Santa Maria Groundwater Basin area of San Luis Obispo and Santa Barbara counties; and three detections were found in each of Madera and Los Angeles counties (Tables 3 and 4).

Although confirmed TPA detections were found in Kern, Santa Clara, Los Angeles, and Madera counties, the total DCPA use from 2000 to 2010 in those counties is significantly smaller than the use in the top seven counties with the highest DCPA use (i.e., Monterey, Imperial, Ventura, Fresno, Riverside, Santa Barbara, and San Luis Obispo) (see Table 1). In Fresno County, two of the previous confirmed detections of TPA were found in wells located within the City of Fresno. The two other detections were in areas that did not have any appreciable DCPA use from 2000 to 2010. Because of these factors, this Legal Agricultural Determination focuses on the counties with both confirmed detections from 1990 to 1997 and significant DCPA use from 2000 to 2010: Monterey, San Luis Obispo, and Santa Barbara counties. Additional sampling was therefore conducted during 2017 in the Salinas Valley of Monterey County, the Santa Maria Groundwater Basin area in San Luis Obispo and Santa Barbara counties, and the Santa Ynez River Valley Groundwater Basin area in Santa Barbara County to assess current concentrations of DCPA, MTP, and TPA in those regions. Background and planning information for the additional sampling is documented in the DPR sampling protocol (CDPR, 2017b).

Groundwater monitoring for DCPA, MTP, and TPA was conducted in the Salinas Valley of Monterey County during the winter and spring of 2017. The results of the sampling are summarized in Tables 3 and 4. Between January and June, thirteen unique wells between the cities of Salinas and Greenfield were sampled and five of those wells contained detections of TPA ranging in concentration from 0.916 to 101 ppb (Table 3). The approximate locations of the five wells with detections are displayed on Figure 5 and listed in Table 4. A Maximum Contamination Level (MCL) is the maximum permissible level of a contaminant in water that is delivered to any user of a public water system. MCL values for different chemicals are established by the California Department of Public Health (DPH) and the US EPA. Currently, there is no MCL established for either DCPA or its degradation products (MTP and TPA). A lifetime Health Advisory Level (HAL) is the concentration of a chemical in drinking water that is not expected to cause any adverse non-carcinogenic effects for a lifetime of exposure. A lifetime HAL for DCPA of 70 ppb was established by the US EPA's Office of Water (US EPA, 2008). The lifetime HAL for DCPA has also been accepted as a health reference level (HRL) for

TPA by DPR (Lohstroh and Koshlukova, 2017). One well located in section M-19S/06E-01 sampled during January exceeded the HAL of 70 ppb with a TPA concentration of 101 ppb (Table 4). When that same well was re-sampled four months later in May the measured TPA concentration decreased to 57.2 ppb. The two wells with the highest concentrations of TPA (101 and 22.7 ppb) were also the only wells sampled in the Salinas Valley that contained measurable concentrations of MTP (0.073 and 0.13 ppb) above DPR's reporting level of 0.05 ppb (Table 4). These two wells were located in sections M-19S/06E-01 and M-19S/07E-05, just southwest and south of the City of Greenfield, respectively (Figure 5).

Groundwater monitoring for DCPA, MTP, and TPA was also conducted in a region extending from Arroyo Grande in San Luis Obispo County to Lompoc in Santa Barbara County during the fall of 2017. The results of the sampling are also summarized in Tables 3 and 4. During October and November, twenty-three unique wells were sampled and thirteen of those wells contained detections of TPA (Table 3). Three of the TPA detections were found in San Luis Obispo County and ranged in concentration from 0.121 to 0.383 ppb (Table 3). The other ten detections of TPA were found in Santa Barbara County and ranged in concentration from 0.435 to 159 ppb (Table 3). Eleven of the thirteen TPA detections were from wells considered to be located within the Santa Maria Groundwater Basin while the other two detections were located in the Santa Ynez River Valley Groundwater Basin (Figure 10). Two wells (S-10N/35W-10 and S- 10N/35W-09) in the Santa Maria Groundwater Basin area within Santa Barbara County, in particular, exceeded the lifetime HAL of 70 ppb with TPA concentrations of 133 and 159 ppb (see Figure 10 and Table 4). A third well (S-10N/35W-08) had a TPA concentration of 66.5 ppb, just below the lifetime HAL of 70 ppb (Table 4). These three wells with the highest detections (133, 159, and 66.5 ppb) were located individually in three consecutively adjacent sections in the east to west direction (Figure 10).

As mentioned previously, detections of DCPA and/or its degradation products in groundwater have been documented in several other states including Washington (Cook, 2014), Oregon (ODEQ, 2003), Idaho (ISDA, 2007), New York (NYSDEC, 2014), and Michigan (ATDSR, 2009).

ENVIRONMENTAL FATE PROPERTIES

As part of the registration evaluation process for a new active ingredient, DPR performs an initial evaluation to assess the potential for the active ingredient or its degradation products to migrate through the soil root and deep vadose zones into groundwater. Pesticides or their degradation products are considered to have a higher potential to reach groundwater if the pesticides are incorporated into the soil and the pesticides or their degradation products are highly mobile and persistent in the soil root zone. The physical-chemical properties that characterize mobility of the active ingredient or degradation product in soil are its solubility in water and its adsorption potential to the soil solid phase. The physical-chemical properties assessed by DPR that characterize the persistence of the active ingredient or degradation product in soil are its hydrolysis half-life, aerobic soil metabolism half-life, anaerobic soil metabolism half-life, and terrestrial field dissipation (TFD) half-life. DPR has established pesticide property threshold values for water solubility, soil adsorption coefficient adjusted for organic carbon (Koc), hydrolysis half-life, aerobic soil metabolism half-life, and anaerobic soil metabolism half-life. These threshold values are collectively referred to as Specific Numerical Values (SNVs) and are presented in Table 5. When a pesticide or its degradation product exceeds a SNV for either water solubility or Koc, then that chemical is considered to be mobile in soil. Similarly, when a pesticide or its degradation product exceeds a SNV for hydrolysis half-life, aerobic soil metabolism half-life, or anaerobic soil metabolism half-life, then that chemical is considered to be persistent in soil. DPR has not established a SNV for the TFD half-life. However, the TFD half-life is an important parameter input for the screening model that DPR uses in the registration evaluation process to quantitatively estimate the concentration in groundwater of the active ingredient or its degradation product at a hypothetical shallow domestic well.

The DPR Pesticide Chemistry Database contains information on the physical and chemical properties of pesticide active ingredients and certain degradation products (CDPR, 2017c). Known values of the physical-chemical properties of DCPA, MTP, and TPA are summarized in Table 5. To gauge their environmental fate, these properties are compared against the SNVs for mobility and persistence in soil set by DPR (Table 5). In general, DCPA is not considered very mobile in soil since it has low water solubility and a high soil adsorption coefficient. DCPA is also moderately persistent with an aerobic soil metabolism half-life in the range of 17.7 to 38.8 days and a TFD half-life ranging from 8 to 34.8 days. MTP is considered mobile in soil due to its high water solubility (3,000 mg/L) and low soil adsorption coefficient (30 cm^3/g). However, MTP has been found to be not very persistent with an aerobic soil metabolism half-live of 2.8 days (Wettasinghe and Tinsley, 1993). By comparison to the SNVs, TPA is considered both mobile in soil, with high water solubility (5,780 mg/L) and negligible soil adsorption potential, and persistent in soil, with an aerobic soil metabolism half-life of more than 300 days (Wettasinghe and Tinsley, 1993).

The numerous detections of TPA in groundwater in California are consistent with its physical-chemical properties which indicate that it is both highly mobile and persistent in soil, suggesting a theoretical high potential for migrating to groundwater. MTP is considered highly mobile in soil but not very persistent. Although it may possess comparable mobility in soil with TPA, the tendency of MTP to be less persistent in soil than TPA is reflected in far fewer detections of MTP in groundwater than TPA in California (Tables 3 and 4). DCPA is not considered to be either mobile or persistent in soil. Its relatively short half-life in soil and high sorption to the soil solid phase suggests that DCPA has a low theoretical potential to migrate to groundwater, a conclusion corroborated by the lack of any confirmed detections of DCPA in California from any historic or recent sampling (Table 3).

LEGAL AGRICULTURAL USE DETERMINATION

In this section, a Legal Agricultural Use determination is made for detections of TPA, the degradation product of the pesticide active ingredient DCPA. The determination is made by satisfying DPR's Legal Agricultural Use criteria with respect to TPA detections found most notably in the Salinas Valley of Monterey County and in the Santa Maria Groundwater Basin area of San Luis Obispo and Santa Barbara counties. The Legal Agricultural Use criteria were described earlier in this report and are listed again below with associated arguments for how they are satisfied by groundwater monitoring data, reported DCPA use data, and other supporting information.

1. The active ingredient or its degradation product is detected in two or more wells in the same one-square mile section of land or in adjacent sections (Goh, 1992).

   Seven of the TPA detections found in the Santa Maria Groundwater Basin during 2017 satisfy the above criterion. Adjacent sections S-10N/35W-08 and S-10N/35W-09 contained the TPA detections of 66.5 and 159 ppb, respectively (Table 4). Also, adjacent sections S-10N/35W-09 and S-10N/35W-10 contained the TPA detections of 159 and 133 ppb, respectively. In fact, the three highest TPA detections (133, 159, and 66.5 ppb) were each located (from east to west) in three consecutively adjacent sections in the Santa Maria Groundwater Basin (Figure 10). Also, in the northern part of the Santa Maria Groundwater Basin near Arroyo Grande, adjacent sections M-32S/13E-28 and M- 32S/13E-32 contained the detections of 0.383 and 0.121 ppb, respectively. Finally, in the Santa Ynez River Valley Groundwater Basin near Lompoc, the adjacent sections S- 07N/35W-24 and S-07N/35W-25 contained the TPA detections of 0.435 and 0.867 ppb, respectively (Figure 10 and Table 4).

2. The active ingredient is formulated in product(s) labeled for agricultural use (Oshima, 1987).

   DCPA is the active ingredient of a pre-emergent herbicide commonly known by the tradename Dacthal. Currently, DCPA is manufactured and marketed by AMVAC in the pesticide product Dacthal® Flowable Herbicide (AMVAC, 2015). The Dacthal® Flowable Herbicide formulation contains 54.9% of DCPA by weight. It is an agricultural herbicide that controls annual grasses and certain broadleaved weeds and is labeled for use on ornamental turf, a wide range of nursery stock, strawberries, seeded melons, and numerous vegetable crops (e.g., broccoli, cauliflower, onions, and kale).

3. The active ingredient has reported agricultural use in the vicinity of the detections or there are sites within the section where the active ingredient might be used (Oshima, 1987).

   DCPA has been used in California since the late 1960s. Reported agricultural use (i.e., individual applications) of DCPA has been required by DPR since 1990. Figure 1 shows the continuing use of DCPA in California from 1990 through 2016. Total DCPA use on a section basis from 2000 to 2010 for Monterey and San Luis Obispo/Santa Barbara counties is shown on Figures 5 and 10, respectively. Also included on those maps were the locations of confirmed detections of TPA relative to the distribution of DCPA use. Reported use of DCPA occurred in each section where a well that possessed a confirmed detection of TPA was also located (Figures 5 and 10). For all recent TPA detections in the Salinas Valley, Santa Maria, and Santa Ynez River Valley groundwater basins, DCPA use occurred in most of the sections that surrounded the sections where those TPA detections were found (Figures 5 and 10).

In the Salinas Valley, TPA detections were found in wells that were located in different, non-adjacent sections but in a region in which DCPA had significant reported agricultural use. These detections do not strictly meet the first criterion listed above but a Legal Agricultural Use determination can still be made for the TPA detections found in the Salinas Valley by satisfying the following:

4. There is a **preponderance of evidence** presented that the detections of the active ingredient or its degradation product are the result of legal agricultural use of the active ingredient in the region in which the detections were found.

   Historically it has been difficult for DPR to gain access and collect groundwater samples in the Salinas Valley from multiple wells within a single section or wells in adjacent sections. Despite significant agricultural use of DCPA there, this difficulty prevents DPR from satisfying the first Legal Agricultural Use criterion (i.e., detections in two or more wells in the same one-square mile section of land or in adjacent sections) using the given historic and recent dataset of TPA detections in the Salinas Valley. Nevertheless, five TPA detections were found between 1990 and 1997 and five more detections were found recently during 2017. No DCPA use data is available prior to 1990 to strictly corroborate the five TPA detections found between 1990 and 1997. However, the trend in annual use in Monterey County between 1990 to 2016 (Figure 2), coupled with long-term production of crops in the Salinas Valley for which DCPA is used for weed control (e.g., broccoli, cauliflower, onions), clearly suggests that DCPA use in the Salinas Valley was likely significant in at least several years prior to 1990. DCPA use in the Salinas Valley from 2000 to 2010 on a section basis and the approximate locations of the five wells in which TPA was detected during 2017 are both shown on Figure 5. All five wells with TPA detections in 2017 were located in sections with DCPA use that occurred between 2000 and 2010. Four of the five wells found with TPA detections in 2017 contained concentrations that ranged from 8.2 to 101 ppb. No evidence was found at each well location to indicate that the TPA concentrations found were the result of point source contamination. Consequently, historic and recent TPA detections in the Salinas Valley and significant DCPA use there between 1990 and 2016 provide a preponderance of evidence that those detections originated as a result of legal agricultural use of DCPA in the general areas of the Salinas Valley in which the detections were found.

CONCLUSION

Historic and recent groundwater monitoring data were evaluated for agricultural areas where DCPA has reported use in the Salinas Valley in Monterey County, the Santa Maria Groundwater Basin in San Luis Obispo/Santa Barbara counties, and the Santa Ynez River Valley Groundwater Basin in Santa Barbara County. It is the conclusion of this report that these data satisfy the criteria to make a Legal Agricultural Use determination that the detections of TPA found in wells between 1991 and 2017 are due to legal agricultural use of the parent active ingredient DCPA in those regions. This conclusion is generally supported by historic confirmed detections of TPA in other counties of the state where DCPA had likely been used and documented detections of TPA in groundwater in other states.

REFERENCES

Contact GWPP@cdpr.ca.gov for references not currently available on the web.

Aggarwal, V. 2012. Memorandum to Lisa Ross. Evaluating analytical methods for compliance with the Pesticide Contamination Prevention Act requirements. Previously available at: <cdpr.ca.gov/docs/emon/pubs/ehapreps/analysis_memos/2391_ross.pdf> (verified January 16, 2018). California Department of Pesticide Regulation, Sacramento, California.

Aggarwal, V. 2017. Memorandum to Joy Dias. The Qualification of Method EMON-SM-05-040 as Unequivocal According to Criteria in the Pesticide Contamination Prevention Act. Available at: <http://www.cdpr.ca.gov/docs/emon/pubs/anl_methds/2588-dacthal_in_ground_water_unequivocal_memo.pdf> (verified January 16, 2018). California Department of Pesticide Regulation, Sacramento, California.

AMVAC. 2015. Dacthal® Flowable Herbicide (label). Amvac Chemical Corporation.

ATSDR 2009. Agency for Toxic Substances & Disease Registry: Health Consultation; Dacthal Groundwater Contamination; Coloma Township, Berrien County, Michigan. Available at: https://www.atsdr.cdc.gov/HAC/pha/pha.asp?docid=379&pg=1 (verified January 16, 2018).

California Department of Health Services (CDHS). 1990. Memorandum from J. Brown, Pesticide and Environmental Toxicology Section, DHS, to A. Milea, Office of Drinking Water, DHS, "TPA Interim Action Level", December 10, 1990. Note: archived advisory levels for drinking water available at: <https://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/documents/notificationlevels/archivedadvisorylevels.pdf> (verified January 16, 2018).

California Department of Pesticide Regulation (CDPR). 2015. Well Inventory Database. Available at: <http://www.cdpr.ca.gov/docs/emon/grndwtr/wellinv/wirmain.htm> (verified January 16, 2018). California Department of Pesticide Regulation, Sacramento, California.

CDPR. 2017a. Pesticide Use Reports. Available at: <http://www.cdpr.ca.gov/docs/pur/purmain.htm> (verified January 16, 2018). California Department of Pesticide Regulation, Sacramento, California.

CDPR. 2017b. Study #300: Protocol for Groundwater Monitoring of DCPA and its Degradates (MTP and TPA). Available previously at: <cdpr.ca.gov/docs/emon/pubs/protocol/study300_dcpa_protocol_final.pdf> (verified January 16, 2018). California Department of Pesticide Regulation, Sacramento, California.

CDPR. 2017c. Pesticide Chemistry Database. California Department of Pesticide Regulation, Sacramento, California.

CDPR. 2018. Unpublished concentrations of DCPA, MTP, and TPA in groundwater from laboratory analyses of samples collected under Ground Water Study #300. California Department of Pesticide Regulation, Sacramento, California.

Cook, K. V. 2014. Monomethyl tetrachloroterephthalic acid (MTP) and Tetrachloroterephthalic acid (TPA) Groundwater Occurrence in Washington State. Washington State Department of Agriculture, Natural Resource Assessment Section, Olympia, WA.

Goh, K.S. 1992. Memorandum to John S. Sanders, Ph.D. Identification of Pesticide Management Zones. California Department of Pesticide Regulation, Sacramento, California.

Idaho State Department of Agriculture (ISDA). 2007. Dimethyl Tetrachloroterephthalate (DCPA) Pesticide Management Plan. June 2007.

Lohstroh, P. and S. Koshlukova. 2017. Memorandum to Shelley DuTeaux. Evaluation of the Potential Human Health Effects from Drinking Ground Water Containing Dacthal (DCPA) Degradates. Available at: <http://www.cdpr.ca.gov/docs/hha/memos/tpa%20in%20ground%20water%20reply%20final%2002232017%20complete%20executed.pdf> (verified January 16, 2018). California Department of Pesticide Regulation, Sacramento, California.

New York State Department of Environmental Conservation (NYSDEC). 2014. Water Quality Monitoring Data for Pesticides on Long Island, NY (referenced in the NYSDEC Long Island Pesticide Pollution Prevention Strategy). July 11, 2014.

Oregon State Department of Environmental Quality (ODEQ). 2003. Northern Malheur County Groundwater Management Area BMP Implementation Report. DEQ Water Quality Division. December, 29, 2003.

Oshima, R. 1987. Memorandum to EM and PM employees. Legal Agricultural Use Criteria. Available at: <http://www.cdpr.ca.gov/docs/emon/grndwtr/polprocd/policy26.pdf> (verified January 16, 2018). California Department of Pesticide Regulation, Sacramento, California.

Spurlock, F, Burow, K., and N. Dubrovsky. 2000. Chlorofluorocarbon dating of herbicide containing well waters in Fresno and Tulare Counties, California. Journal of Environmental Quality, 29, 474–483.

United States Environmental Protection Agency (US EPA). 2008. Drinking Water Health Advisory for Dacthal and Dacthal Degradates: Tetrachloroterephthalic Acid (TPA) and

Monomethyl Tetrachloroterephthalic Acid (MTP). Prepared by Health and Ecological Criteria Division (HECD), Office of Science and Technology (OST), Office of Water (OW) for Office of Groundwater/Drinking Water (OGWDW), OW, U.S. EPA.

University of Hertfordshire. 2018. Pesticide Properties Database (PPDB). Available at: <https://sitem.herts.ac.uk/aeru/ppdb/en/index.htm> (verified January 16, 2018). Hertfordshire, United Kingdom.

Wettasinghe, A. and I.J. Tinsley. 1993. Degradation of Dacthal and its Metabolites in Soil. Bulletin of Environmental Contamination and Toxicology. 50:226-231.

Tables

Table 1. Annual DCPA use (pounds) by county from 2000 to 2010 (CDPR, 2017a).

County	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	Total	Average
Monterey	77,704	78,985	74,270	77,743	94,815	73,347	75,683	77,692	74,900	66,731	58,921	830,790	75,526
Imperial	17,056	38,811	48,616	60,166	53,111	64,055	58,885	54,303	36,743	27,709	43,584	503,039	45,731
Ventura	8,267	12,358	22,475	27,094	16,828	15,139	9,185	5,000	6,294	6,629	8,578	137,847	12,532
Fresno	2,820	1,660	7,763	2,072	2,154	23,328	29,252	7,000	3,731	20,999	10,978	111,757	10,160
Riverside	9,610	9,160	8,225	11,586	9,852	9,308	24,279	19,433	16,039	5,523	2,225	125,239	11,385
Santa Barbara	4,888	11,658	11,132	10,312	16,013	12,396	10,464	7,401	8,607	4,799	4,497	102,167	9,288
San Luis Obispo	1,187	6,424	6,510	10,273	7,154	6,977	8,173	5,958	3,902	4,255	5,092	65,904	5,991
San Benito	5,540	5,254	7,011	7,890	7,341	6,794	8,298	5,046	5,059	3,463	5,699	67,394	6,127
San Bernardino	824	3,325	8,259	9,704	3,774	3,920	4,984	6,120	5,704	8,151	5,036	59,802	5,437
Kern	2,400	1,920	732	756	324	1,853	4,612	7,871	7,084	4,920	3,681	36,153	3,287
Santa Clara	148	1,498	3,012	2,355	4,667	5,191	3,543	4,358	3,083	1,511	1,549	30,915	2,810
Stanislaus	3	521	738	569	1,578	3,886	1,827	2,215	1,548	3,512	1,036	17,431	1,585
San Joaquin	0	180	374	1,730	159	889	1,488	1,726	2,145	768	951	10,409	946
Los Angeles	948	1,440	1,157	184	137	44	1,023	144	9	40	25	5,150	468
Tulare	221	74	209	1,711	953	703		278				4,148	593
Merced				27	12	659				405	843	1,947	389
Santa Cruz	410	182	366	336	372	110	241	179	78	5	11	2,290	208
Shasta		420	626	407	585							2,037	509
Yolo	64	104	84	317	209	91	133	108	117	330	55	1,611	146
Siskiyou		330										330	330
Madera	223		3		1,013	392						1,630	408
Colusa	1,310	34		133							8	1,485	371
Kings				166						647	544	1,357	452
Modoc												0	0
Sacramento	24	390	24	60		25						523	105
Glenn			420									420	420
Sonoma	18		15	23	23	26	34	38	38		36	249	28
San Diego	23			21		9				38		91	23
Sutter											147	147	147
Contra Costa					0	35			16	15	23	89	18
San Mateo		35	12	16			11	11	6	5		95	14
Orange		3	1	0	12		1	2	1			20	3
Solano	18											18	18
Butte					18							18	18
Placer	0	1	2	2	2			1				8	1
Calaveras				6	1							7	3

Table 2. Total DCPA use (pounds) by crop from 2000 to 2010 (CDPR, 2017a).

Crop	DCPA Use (pounds)	Percentage Total Use (%)
BROCCOLI	967,953	46
ONION (DRY, SPANISH, WHITE, YELLOW, RED, ETC.)	469,723	22
CAULIFLOWER	152,078	7
CABBAGE	89,986	4
BROCCOLI RAAB (RAPA, ITALIAN TURNIP, RAPINI)	69,877	3
CHINESE CABBAGE (NAPPA, WON BOK, CELERY CABBAGE)	56,554	3
ONIONS (GREEN)	51,744	2
BOK CHOY (WONG BOK)	41,187	2
RADISH	38,166	2
N-OUTDR GRWN CUT FLWRS OR GREENS	32,235	2
ORNAMENTAL TURF (ALL OR UNSPEC)	32,197	2
PEPPERS (FRUITING VEGETABLE), (BELL,CHILI, ETC.)	22,273	1
GAI LON	18,465	1
KALE	13,999	1
TURNIP, GENERAL	8,177	0.4
MUSTARD, GENERAL	7,073	0.3
COLLARDS	5,693	0.3
CHINESE GREENS, CHINESE LEAFY VEGETABLES	5,461	0.3
GARLIC	5,264	0.2
LEEK	4,726	0.2
RAPE (ALL OR UNSPEC)	3,613	0.2
BRUSSELS SPROUTS	3,105	0.1
N-OUTDR CONTAINER/FLD GRWN PLANTS	3,087	0.1
KOHLRABI	2,553	0.1
LEAFY VEGETABLES (ALL OR UNSPEC)	1,811	0.1
PEPPERS (CHILI TYPE) (FLAVORING AND SPICE CROP)	1,551	0.1
TOMATOES, FOR PROCESSING/CANNING	1,307	0.1
N-OUTDR GRWN TRNSPLNT/PRPGTV MTRL	1,160	0.1
GAI CHOY (LOOSE LEAF)	1,004	< 0.1
WATERMELONS	998	< 0.1
CANTALOUPE	942	< 0.1
BEANS, SUCCULENT (OTHER THAN LIMA)	830	< 0.1
CHINESE RADISH/DAIKON (LOBOK, JAPANESE RADISH)	599	< 0.1
LETTUCE, HEAD (ALL OR UNSPEC)	498	< 0.1
STRAWBERRY (ALL OR UNSPEC)	496	< 0.1
RIGHTS OF WAY	492	< 0.1
UNCULTIVATED AGRICULTURAL AREAS (ALL OR UNSPEC)	483	< 0.1
EGGPLANT (ORIENTAL EGGPLANT)	432	< 0.1
SOIL APPLICATION, PREPLANT-OUTDOOR (SEEDBEDS,ETC.)	425	< 0.1
LANDSCAPE MAINTENANCE	416	< 0.1
MELONS	364	< 0.1
CUCUMBER (PICKLING, CHINESE, ETC.)	351	< 0.1
SQUASH (ALL OR UNSPEC)	326	< 0.1
SHALLOT, ONIONS (SHALLOT)	321	< 0.1
SQUASH (SUMMER)	300	< 0.1
CHERRY	300	< 0.1
LETTUCE, LEAF (ALL OR UNSPEC)	257	< 0.1
N-GRNHS GRWN PLANTS IN CONTAINERS	227	< 0.1
COTTON, GENERAL	166	< 0.1
OATS, GENERAL	158	< 0.1
RESEARCH COMMODITY	152	< 0.1
COLE CROPS (ALL OR UNSPEC)	138	< 0.1
GARBANZOS (INCLUDING CHICK PEAS)	102	< 0.1
TOMATO	91	< 0.1
N-GRNHS GRWN CUT FLWRS OR GREENS	84	< 0.1
PIMENTO (PIMIENTO TYPE PEPPER)	66	< 0.1
BEANS (ALL OR UNSPEC)	56	< 0.1
PEAS, GENERAL	48	< 0.1
UNCULTIVATED NON-AG AREAS (ALL OR UNSPEC)	44	< 0.1
VERTEBRATE PEST CONTROL	32	< 0.1
BEETS, GENERAL	32	< 0.1
YAMS, TRUE (LISBON & WHITE YAM)	30	< 0.1
GRAPES, WINE	30	< 0.1
CILANTRO (CHINESE PARSLEY, CORIANDER LEAVES)	21	< 0.1
STRUCTURAL PEST CONTROL	18	< 0.1
SPINACH	15	< 0.1
FLAVORING AND SPICE CROPS (ALL OR UNSPEC)	8	< 0.1
CHIVE (SIBERICUM)	8	< 0.1
DILL	5	< 0.1
MINT (ALL OR UNSPEC)	5	< 0.1
PECAN	4	< 0.1
CHICORY (ALL OR UNSPEC)	3	< 0.1
CORN, HUMAN CONSUMPTION	3	< 0.1
VEGETABLES (ALL OR UNSPEC)	1	< 0.1
N-GRNHS GRWN TRNSPLNT/PRPGTV MTRL	1	< 0.1
ENDIVE (ESCAROLE)	1	< 0.1

Table 3. Summary of sampling for DCPA, MTP, and TPA by CDPR (CDPR, 2015; 2018).

County	Sampling Date Range	Reporting Year	Unique Wells Sampled	Unique Wells with DCPA Detections	Unique Wells with MTP Detections	Concentration MTP (ppb)	Unique Wells with TPA Detections	Concentration TPA (ppb)
Los Angeles	5/9/1990-8/21/1990	1991	10	0	0	--	3	0.28-1.93
Santa Clara	5/9/1990-7/12/1990	1991	8	0	0	--	6	0.1-3.7
Monterey	8/6/1990-8/8/1990	1991	15	0	0	--	5	0.43-6.9
Fresno	8/13/1990-8/23/1990	1991	15	0	0	--	2	1.1-1.5
San Luis Obispo	8/14/1990	1991	3	0	0	--	1	1.5
Santa Barbara	8/14/1990-8/16/1990	1991	7	0	0	--	4	0.18-11
Kern	8/21/1990-8/22/1990	1991	10	0	0	--	5	0.8-15
Tulare	8/21/1990-8/22/1990	1991	6	0	0	--	0	--
Monterey	7/8/1991-7/11/1991	1992	2	0	0	--	0	--
San Luis Obispo	5/19/1992-5/20/1992	1993	6	0	0	--	1	1.28-4
Colusa	4/19/1994-4/28/1994	1994	8	0	0	--	0	--
Fresno	4/19/1994-6/9/1994	1995	147	0	0	--	2	0.11-6.88
Tulare	5/11/1994-6/8/1994	1995	31	0	0	--	0	--
Madera	7/16/1996-1/16/1997	1997	6	0	0	--	3	0.419-0.889
Monterey	1/9/17-6/15/17	2018	13	0	2	0.056-0.13	5	0.916-101
San Luis Obispo	10/11/17-11/29/17	2018	7	0	0	--	3	0.121-0.383
Santa Barbara	10/9/17-11/30/17	2018	16	0	3	0.063-0.101	10	0.435-159
		Total	310	0	5		50	

Table 4. Details of MTP and TPA detections from sampling by CDPR (CDPR, 2015; 2018).

County	Location (Meridian-Township/Range-Section)	First Year Sampled	Last Year Sampled	Number of Wells Sampled	Number of Wells MTP Detections	Highest MTP Concentration (ppb)	Number of Wells TPA Detections	Highest TPA Concentration (ppb)
Fresno	M-13S/22E-26	1994	--	1	0	--	1	6.88
Fresno	M-14S/19E-01	1990	--	1	0	--	1	1.1
Fresno	M-14S/19E-19	1990	--	1	0	--	1	0.11
Fresno	M-14S/20E-32	1990	--	2	0	--	1	1.5
Kern	M-26S/24E-32	1990	--	1	0	--	1	15
Kern	M-27S/23E-01	1990	--	1	0	--	1	5.05
Kern	M-27S/23E-04	1990	--	1	0	--	1	0.8
Kern	M-28S/25E-24	1990	--	1	0	--	1	1.5
Kern	M-31S/28E-13	1990	--	1	0	--	1	1.1
Los Angeles	S-01N/08W-33	1990	--	1	0	--	1	0.34
Los Angeles	S-01S/08W-03	1990	--	1	0	--	1	1.93
Los Angeles	S-01S/08W-04	1990	--	1	0	--	1	0.44
Madera	M-08S/20E-27	1996	--	1	0	--	1	0.76
Madera	M-08S/20E-34[a]	1996	1997	2	0	--	2	0.89
Monterey	M-14S/02E-34	1990	--	1	0	--	1	0.61
Monterey	M-15S/04E-17[b]	1990	2017	2	0	--	2	8.22
Monterey	M-15S/04E-29	1990	--	1	0	--	1	3
Monterey	M-16S/04E-15	1990	--	1	0	--	1	0.43
Monterey	M-18S/07E-28	1991	--	1	0	--	1	6.9
San Luis Obispo	S-11N/35W-25	1991	--	1	0	--	1	1.5
San Luis Obispo	M-32S/13E-33	1993	--	1	0	--	1	4
Santa Barbara	S-07N/35W-26	1991	--	1	0	--	1	0.18
Santa Barbara	S-10N/34W-07	1990	--	2	0	--	2	8
Santa Barbara	S-10N/34W-18	1990	--	1	0	--	1	11
Santa Clara	M-06S/01W-30	1990	--	2	0	--	2	1.51
Santa Clara	M-06S/02W-24	1990	--	1	0	--	1	0.16
Santa Clara	M-06S/02W-25	1990	--	3	0	--	2	3.7
Santa Clara	M-06S/02W-36	1990	--	1	0	--	1	0.66
Monterey	M-15S/04E-22	2017	--	1	0	--	1	0.916
Monterey	M-19S/07E-05[c]	2017	2017	1	1	0.13	1	22.7
Monterey	M-19S/06E-01[c]	2017	2017	1	1	0.073	1	101
Monterey	M-15S/03E-02	2017	--	1	0	--	1	10.9
San Luis Obispo	M-32S/13E-28	2017	--	1	0	--	1	0.383
San Luis Obispo	M-32S/13E-32	2017	--	1	0	--	1	0.121
San Luis Obispo	S-11N/35W-26	2017	--	1	0	--	1	0.147
Santa Barbara	S-10N/35W-08	2017	--	2	1	0.065	2	66.5
Santa Barbara	S-10N/34W-17	2017	--	2	0	--	2	15.3
Santa Barbara	S-10N/35W-09	2017	--	3	1	0.063	2	159
Santa Barbara	S-10N/35W-23	2017	--	1	0	--	1	13.1
Santa Barbara	S-07N/35W-25	2017	--	1	0	--	1	0.867
Santa Barbara	S-07N/35W-24	2017	--	1	0	--	1	0.435
Santa Barbara	S-10N/35W-10	2017	--	1	1	0.101	1	133

[a] Section 34 contained two different wells that were each sampled in 1996 and 1997 and both wells in both years had detections of TPA.

[b] Section 17 contained two different wells: one well sampled in 1990 with a concentration of 5.9 ppb and a second well sampled in 2017 with a concentration of 8.22 ppb.

[c] Well in the section was sampled during both the winter and spring of 2017.

Table 5. Physical and chemical properties of DCPA, MTP, and TPA, and Specific Numerical Values.

	Mobility Properties		Persistence Properties			
	Water Solubility (mg/L)	**Soil Adsorption Coefficient, Koc (cm^3/g)**	**Hydrolysis Half-life (days)**	**Aerobic Soil Metabolism Half-life (days)**	**Anaerobic Soil Metabolism Half-life (days)**	**Field Studies Half-life (days)**
Specific Numerical Values (SNVs)	**> 3**	**< 1,900**	**> 14**	**> 610**	**> 9**	**--**
DCPA	0.5[a]	2,963[b]	> 36[a]	17.7-38.8[a]	--	8-34.8[a]
MTP	3,000[b]	30[b]	--	2.8[c]	--	--
TPA	5,780[b]	0	--	> 300[c]	--	--

[a]Pesticide Chemistry Database, California Department of Pesticide Regulation (2017c)

[b]Pesticide Properties Database (PPDB), University of Hertfordshire (2018)

[c]Wettasinghe and Tinsley (1993)

Figures

Figure 1. Annual DCPA use in California Statewide from 1990 to 2016 (CDPR, 2017a).

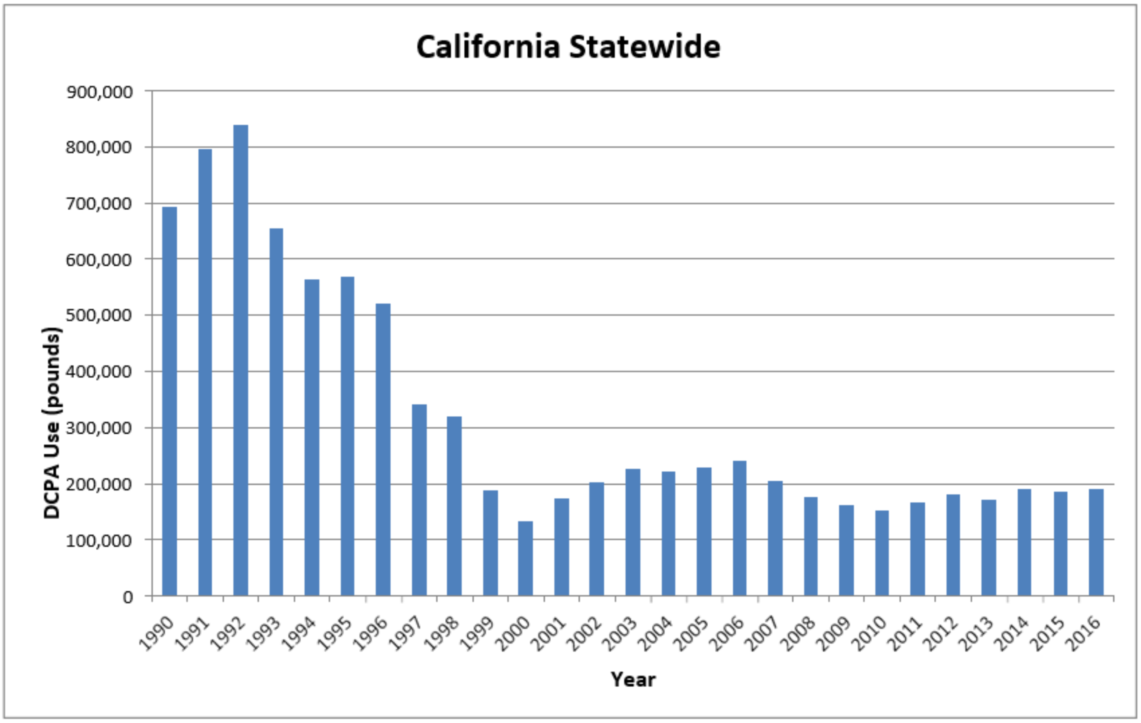

Figure 2. Annual DCPA use in Monterey County from 1990 to 2016 (CDPR, 2017a).

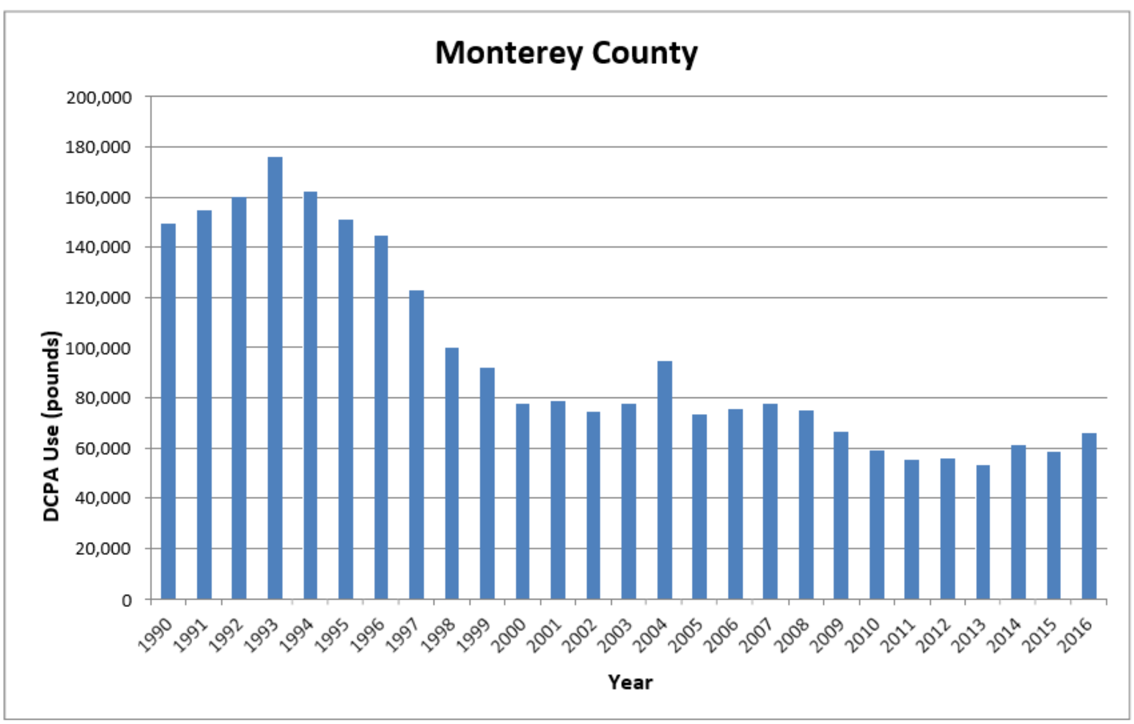

Figure 3. Annual DCPA use in San Luis Obispo County from 1990 to 2016 (CDPR, 2017a).

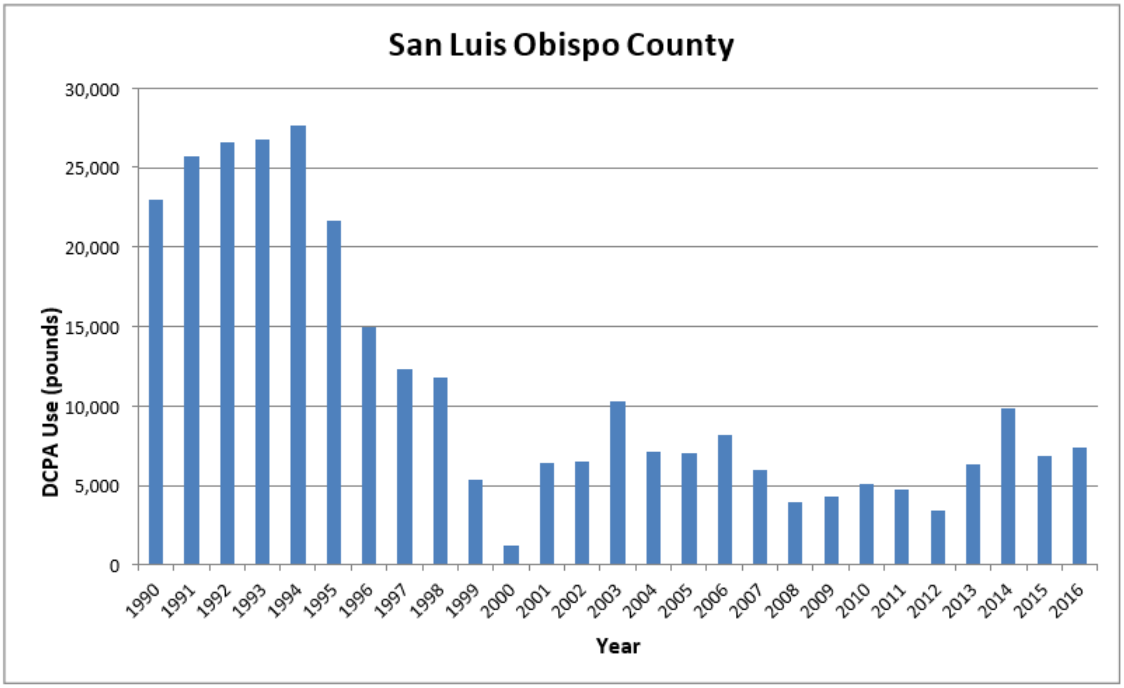

Figure 4. Annual DCPA use in Santa Barbara County from 1990 to 2016 (CDPR, 2017a).

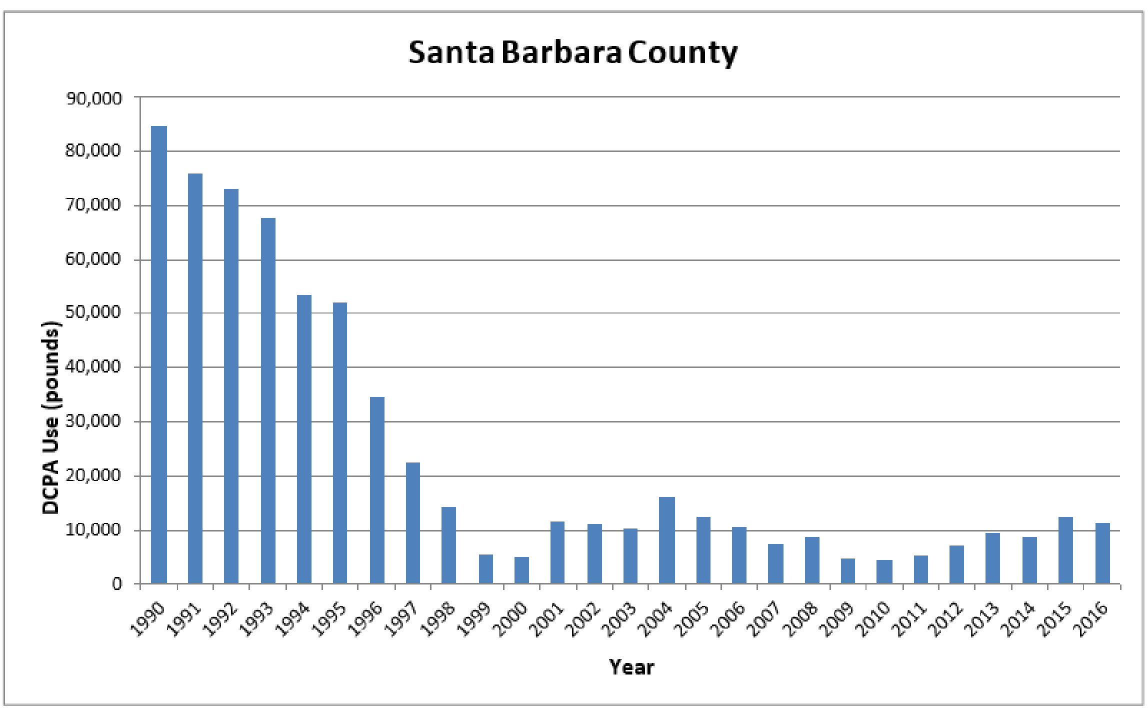

Figure 5. Total DCPA use (lbs per section) from 2000 to 2010 and locations of confirmed detections of TPA in the Salinas Valley area of Monterey County (CDPR, 2015; 2017a; 2018).

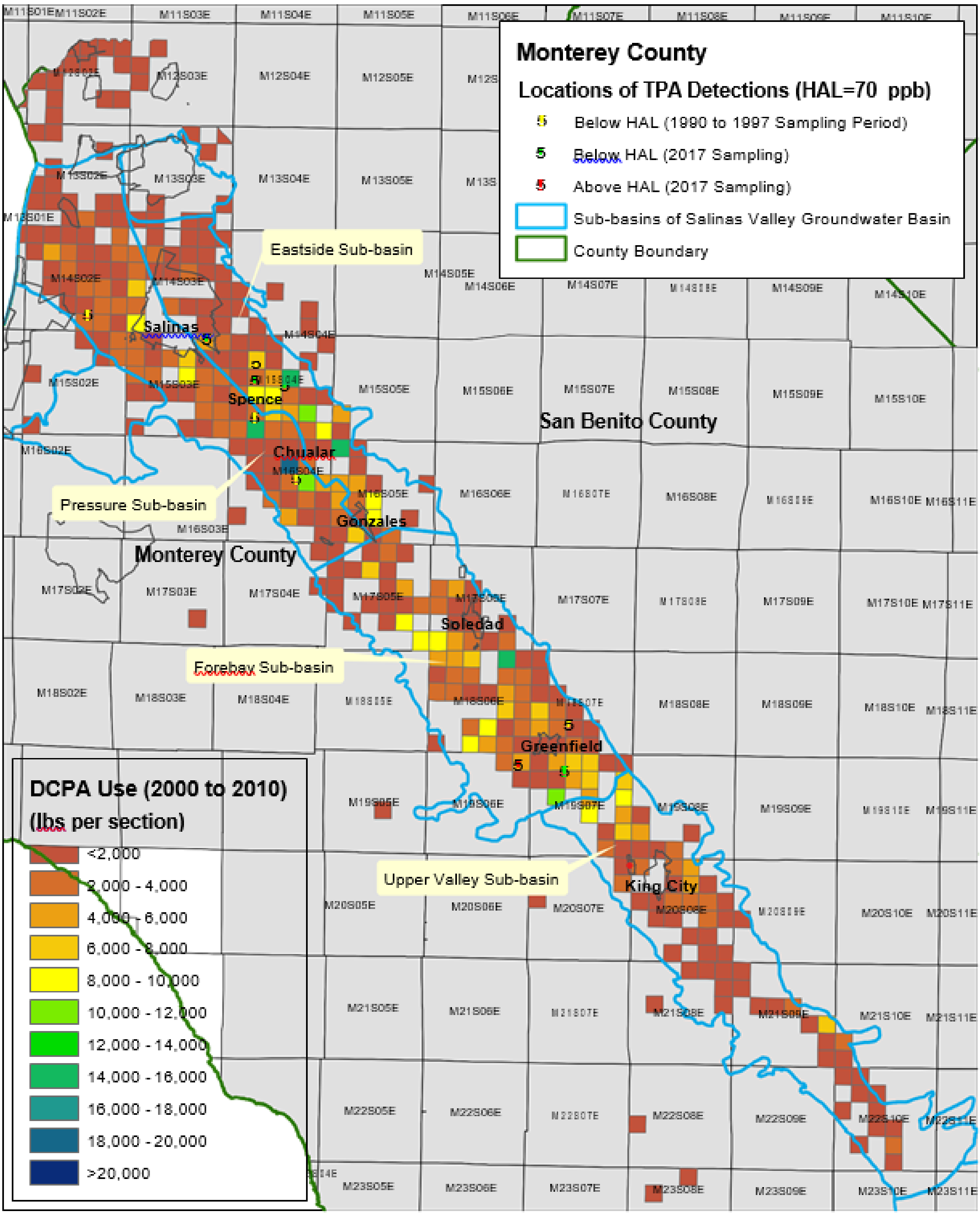

Figure 6. Total DCPA use (lbs per section) from 2000 to 2010 in Imperial County (CDPR, 2017a).

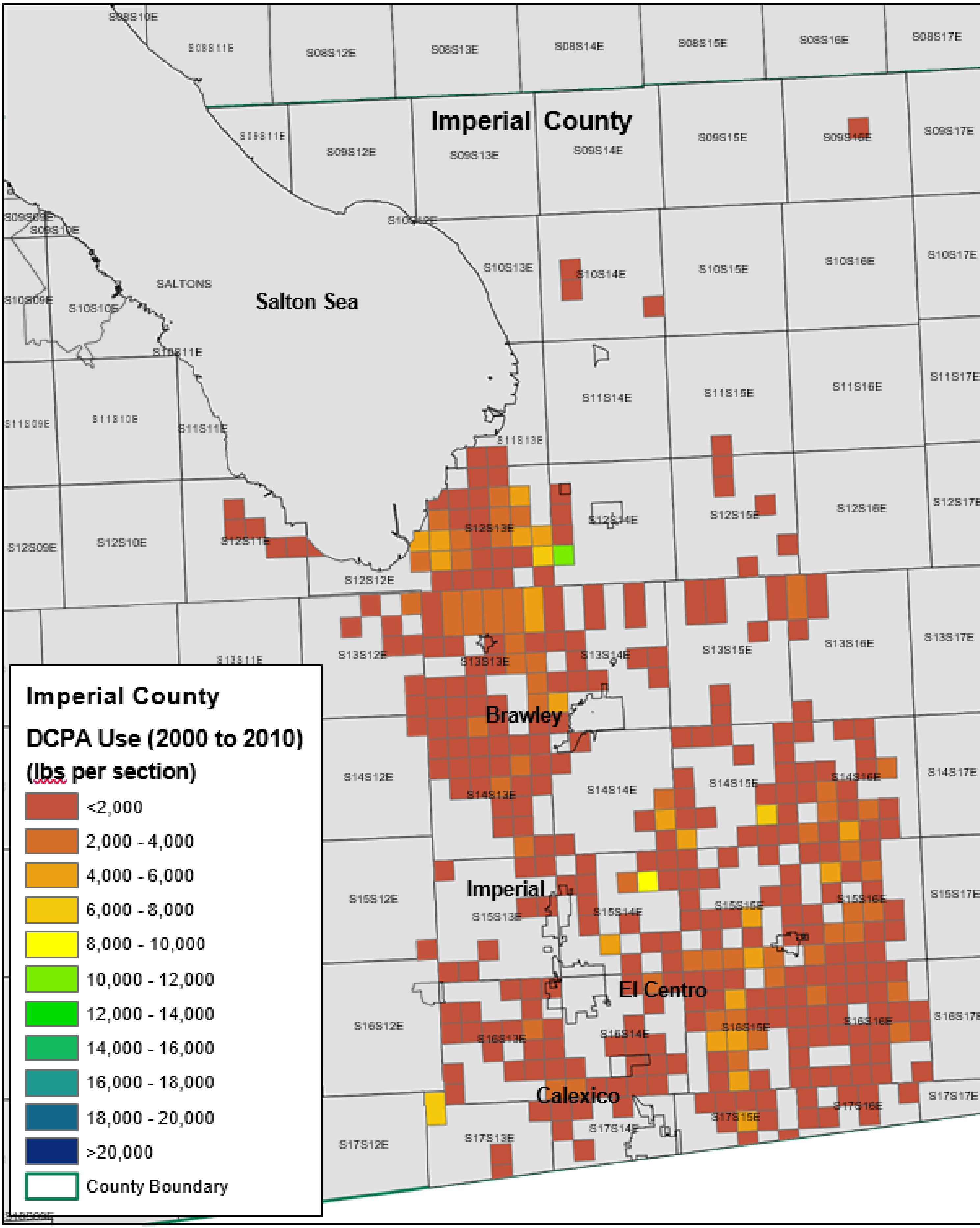

Figure 7. Total DCPA use (lbs per section) from 2000 to 2010 in Ventura County (CDPR, 2017a).

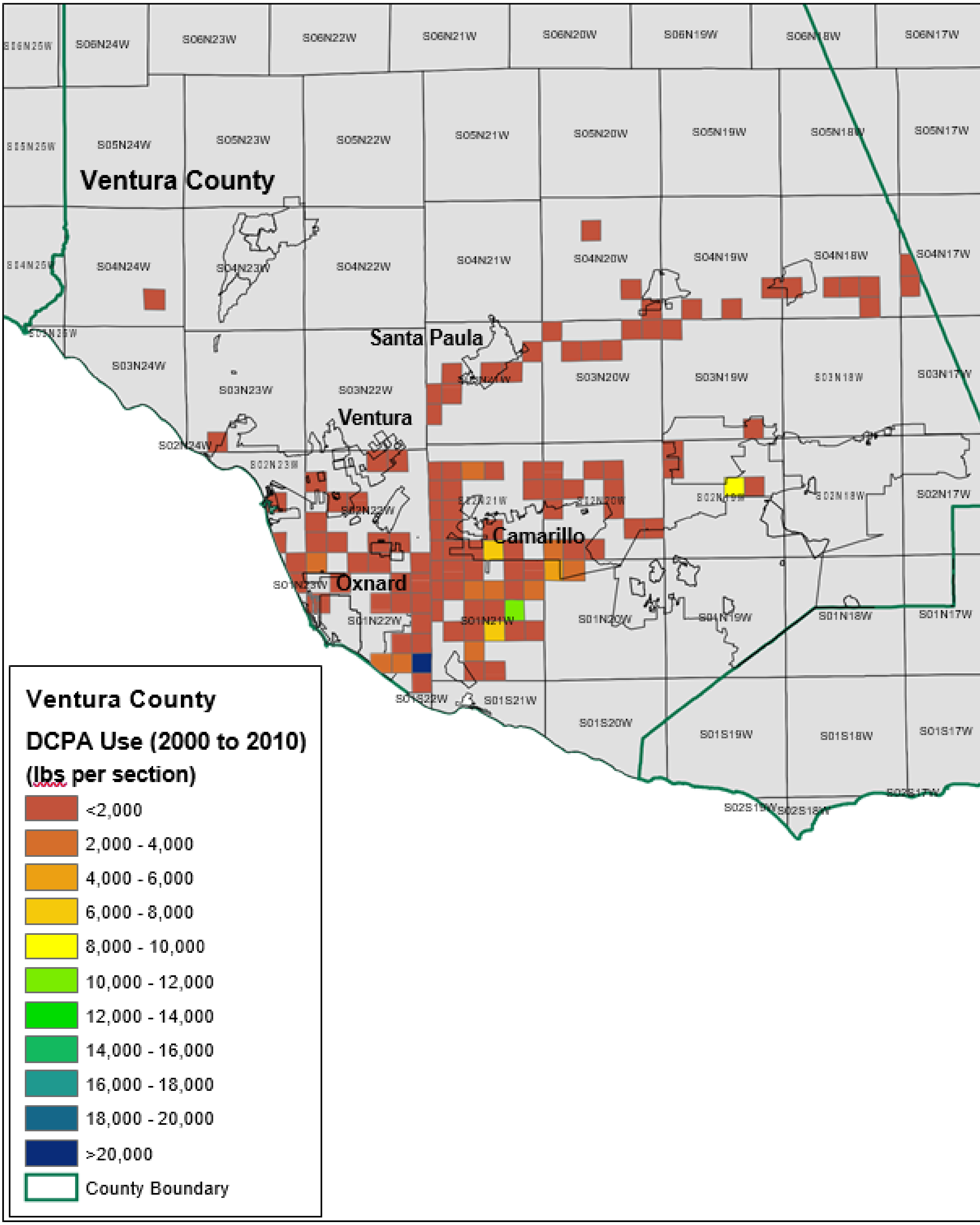

Figure 8. Total DCPA use (lbs per section) from 2000 to 2010 and locations of confirmed detections of TPA in Fresno County (CDPR, 2015; 2017a).

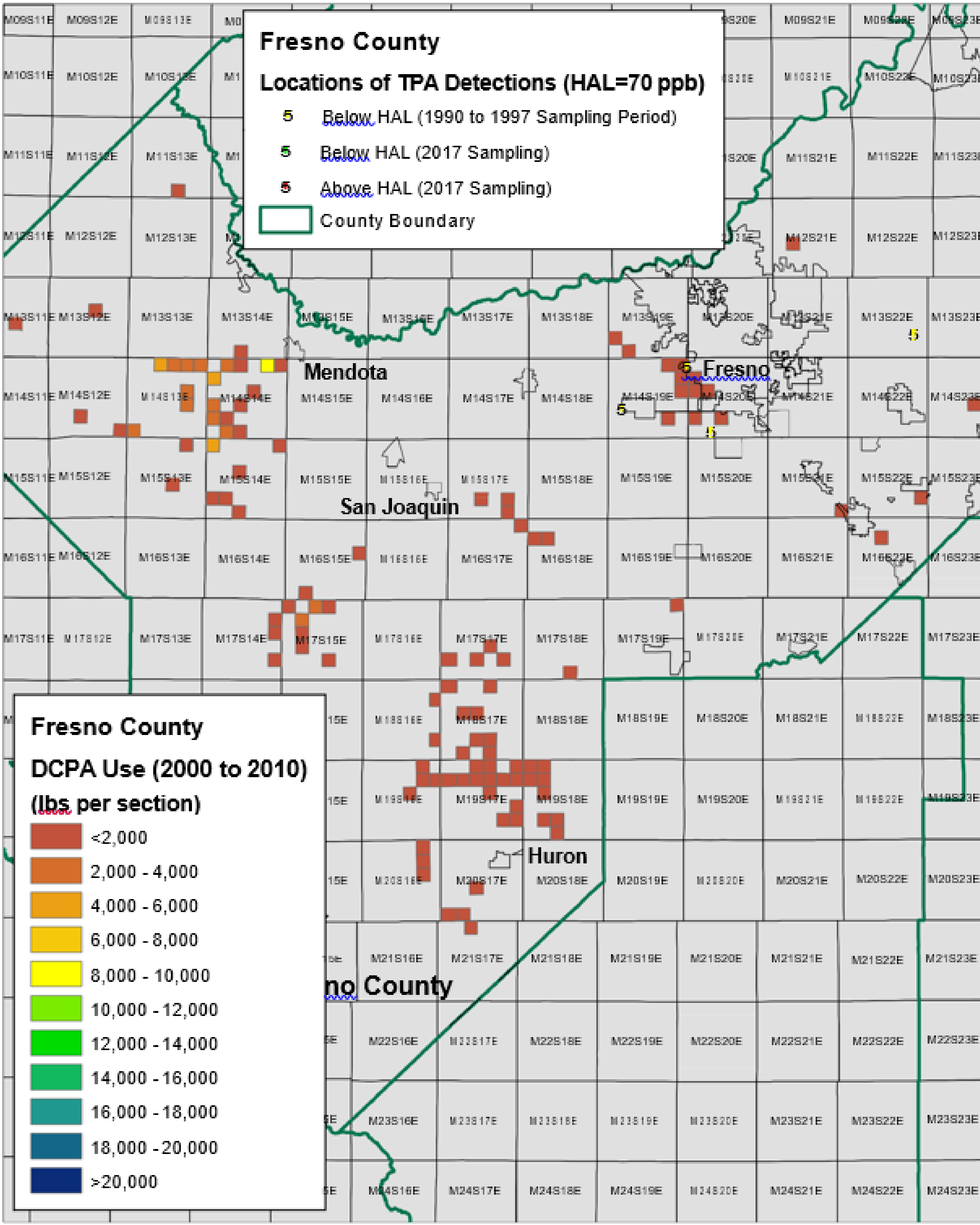

Figure 9. Total DCPA use (lbs per section) from 2000 to 2010 in Riverside County (CDPR, 2017a).

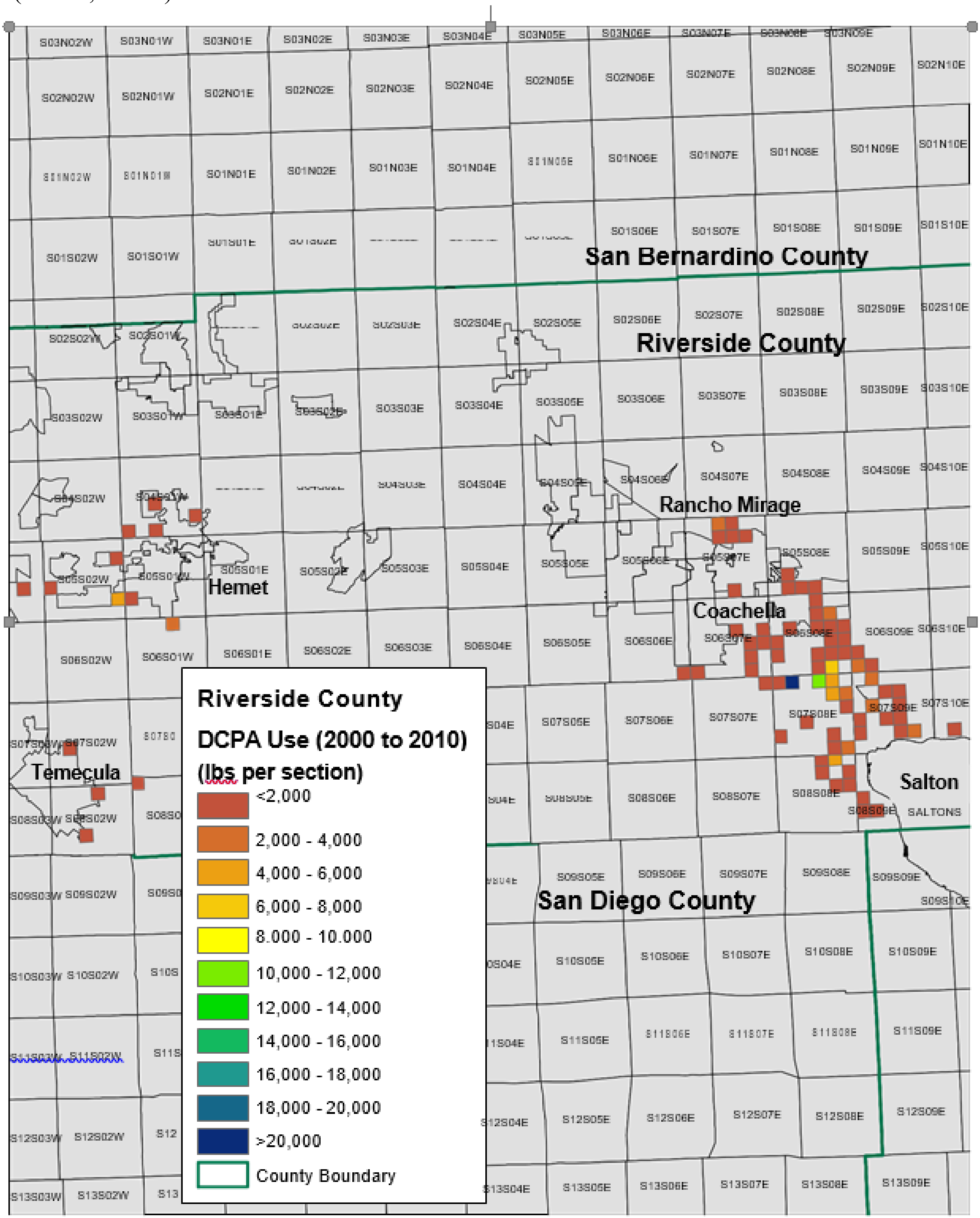

Figure 10. Total DCPA use (lbs per section) from 2000 to 2010 and locations of confirmed detections of TPA in San Luis Obispo and Santa Barbara counties (CDPR, 2015; 2017a; 2018).

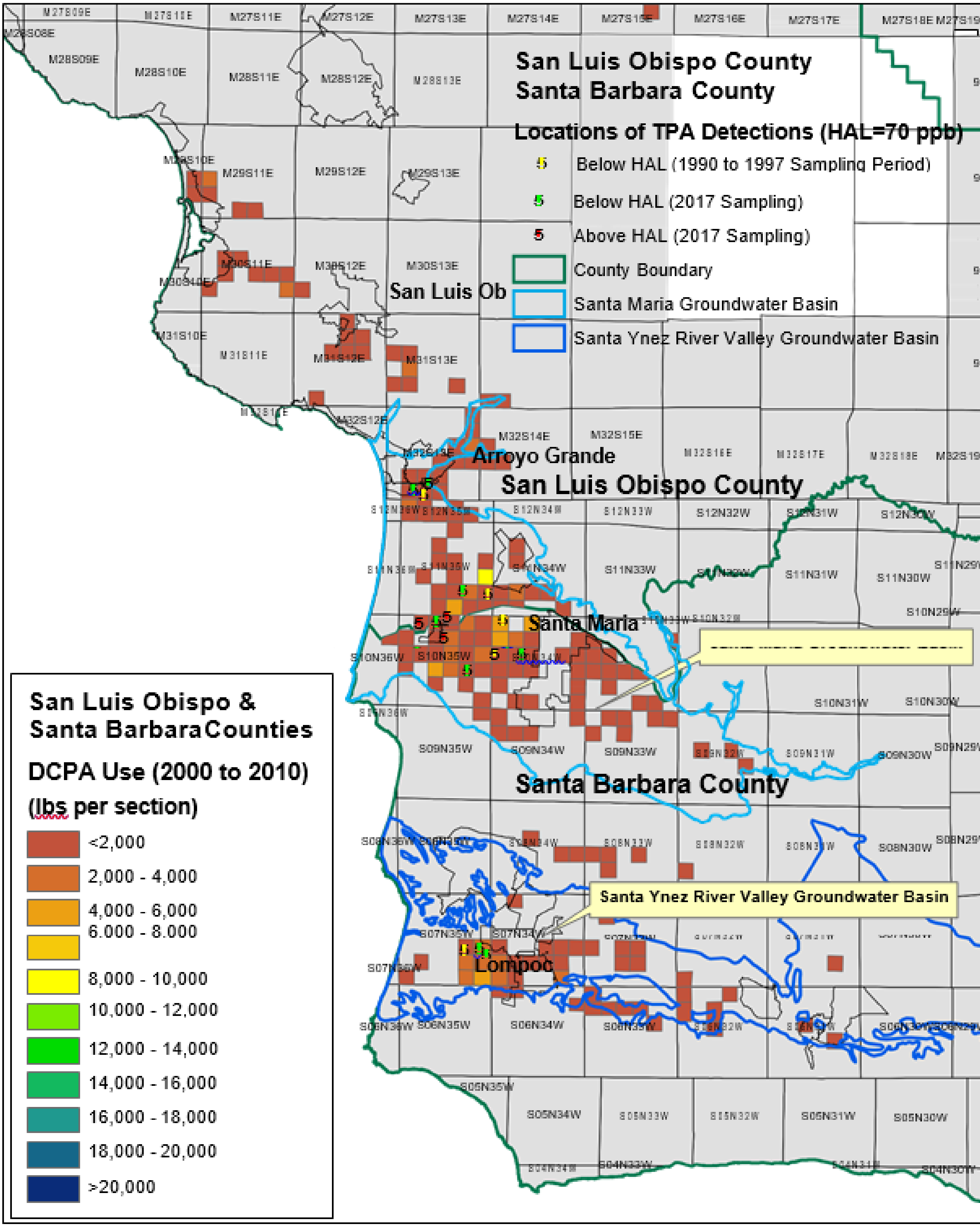

Figure 11. Locations of confirmed detections of TPA in the central region of California from sampling conducted between 1990 and 2017 (CDPR, 2015; 2018).

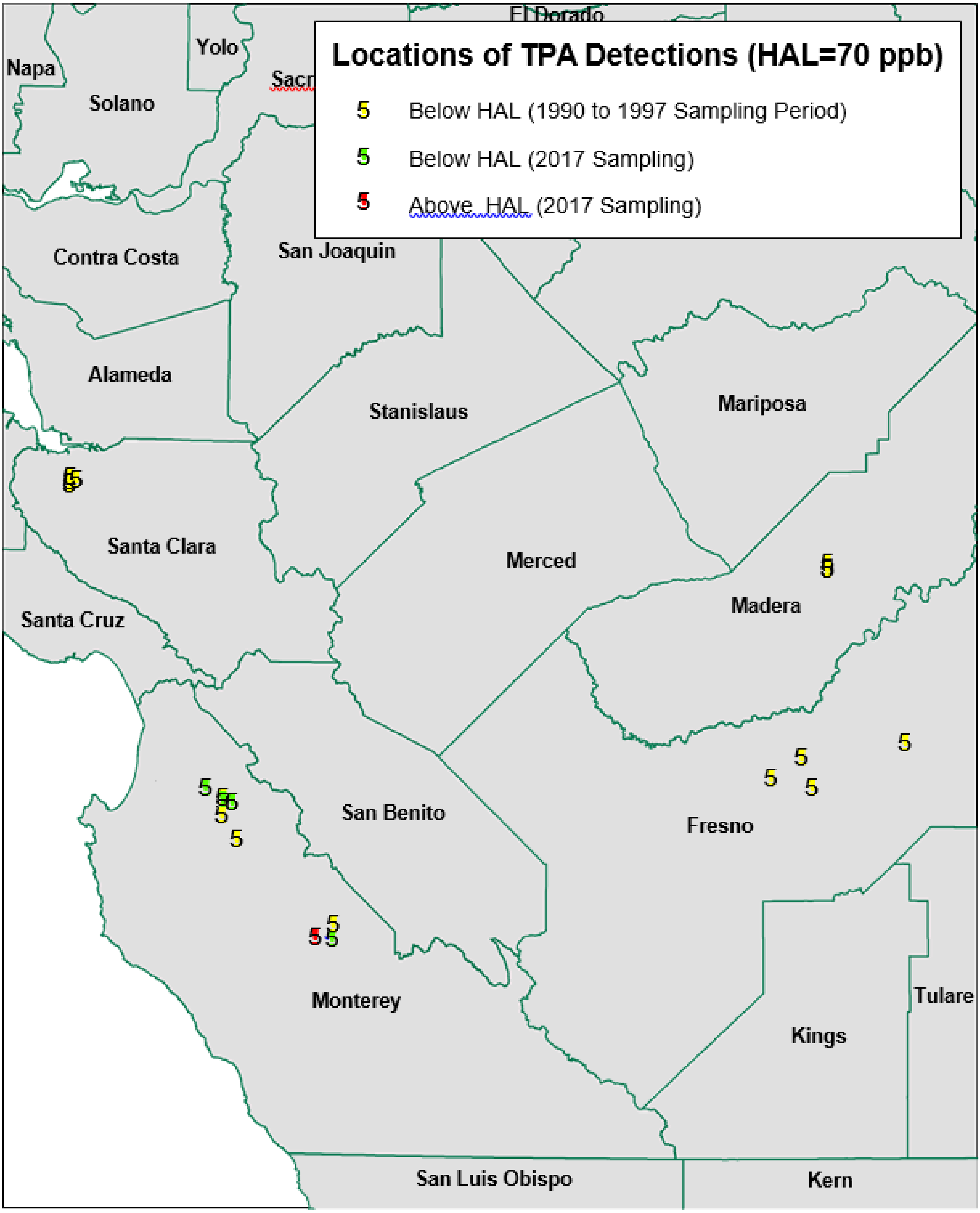

Figure 12. Locations of confirmed detections of TPA in the southern region of California from sampling conducted between 1990 and 2017 (CDPR, 2015; 2018).