

## **Community air monitoring for pesticides.**

### **Part 3: Using health-based screening levels to evaluate results collected for a year**

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## **ABSTRACT**

The CA Department of Pesticide Regulation (CDPR) and the CA Air Resources Board monitored 40 pesticides, including five degradation products, in Parlier, CA, to determine if its residents were exposed to any of these pesticides and, if so, in what amounts. They included 1,3-dichloropropene, acrolein, arsenic, azinphos-methyl, carbon disulfide, chlorpyrifos and its degradation product, chlorothalonil, copper, cypermethrin, diazinon and its degradation product, dichlorvos, dicofol, dimethoate and its degradation product, diuron, endosulfan and its degradation product, S-ethyl dipropylcarbamothioate (EPTC), formaldehyde, malathion and its degradation product, methyl isothiocyanate (MITC), methyl bromide, metolachlor, molinate, norflurazon, oryzalin, oxyfluorfen, permethrin, phosmet, propanil, propargite, simazine, SSS-tributylphosphorotrithioate, sulfur, thiobencarb, trifluralin, and xylene. Monitoring was conducted 3 days per week for a year. Twenty-three pesticides and degradation products were detected. Acrolein, arsenic, carbon disulfide, chlorpyrifos, copper, formaldehyde, methyl bromide, MITC, and sulfur were detected in more than half the samples. Since no regulatory ambient air standards exist for these pesticides, CDPR developed advisory, health-based non-cancer screening levels (SLs) to assess acute, subchronic and chronic exposures. For carcinogenic pesticides, CDPR assessed risk using cancer potency values. Amongst non-carcinogenic agricultural use pesticides, only diazinon exceeded its SL. For carcinogens, 1,3-dichloropropene concentrations exceeded its cancer potency value. Based on these findings, CDPR has undertaken a more comprehensive evaluation of 1,3-dichloropropene, diazinon, and the closely related chlorpyrifos that was frequently detected. Four chemicals—acrolein, arsenic, carbon disulfide, and formaldehyde—sometimes used as pesticides were detected, although no pesticidal use was reported in the area during this study. Their presence was most likely due to vehicular or industrial emissions.

**Keywords** Community air monitoring, pesticides, health-based screening levels, chlorpyrifos, diazinon, 1,3-dichloropropene

## 1. Introduction

In 2004, the CA Environmental Protection Agency (Cal/EPA) asked the CA Department of Pesticide Regulation (CDPR) to conduct air monitoring for 1 year in a farming community in the Central Valley (Segawa et al. 2013). Most of the state's agriculture and agricultural pesticide use occur in this region (CDPR 2007; Umbach 2002). Statutory law requiring Cal/EPA to incorporate environmental justice (EJ) principles into its policies and programs provided the impetus for the request (Cal/EPA 2004). This study was an opportunity for CDPR to conduct air monitoring for a much longer period than had been done in its previous monitoring studies. In 2006, CDPR in collaboration with the California Air Resources Board (CARB) initiated this community ambient air monitoring study in Parlier. It was designed to provide systematic air monitoring for up to 35 pesticides and five degradation products, with the resulting data serving as a more robust foundation for assessing exposure and risk. Hengel and Lee (2013) describe the analytical methods in detail and Segawa et al. (2013) provide information about how the pesticides and community were selected.

The study sought to answer three main questions:

- Are residents of the community exposed to pesticides in the air?
- Which pesticides are people exposed to and in what amounts?
- Do measured pesticide air levels exceed levels of concern to human health?

Federal law requires ambient air quality human health standards for six air pollutants: ozone, particulate matter, carbon monoxide, nitrogen oxides, sulfur dioxide, and lead (United States Environmental Protection Agency [US EPA] 2012). State law requires ambient air quality standards for those six and four more: hydrogen sulfide, sulfates, vinyl chloride, and visibility reducing particles (CARB 2009). With the exception of sulfur dioxide none of these chemicals have pesticidal uses. Although regulatory standards have not been set, federal and state laws also require the control of toxic chemicals in air, including pesticides. Since no state or federal ambient air standards exist for most of the pesticides analyzed by CDPR, CDPR developed an approach to evaluate its air monitoring results using non-cancer screening levels (SLs). To address carcinogenic potential of the pesticides monitored, CDPR reviewed the literature to develop cancer potency factors.

This article summarizes the public participation process; reports the monitoring results; describes the methods used to develop acute, subchronic, and chronic SLs, and cancer potency values; and evaluates the health risks due to the 35 pesticides and five degradation products monitored.

## 2. Methods

This section describes how CDPR incorporated public participation into this study, as well as the materials and methods used for (1) selecting the community, pesticides monitored, and monitoring sites; (2) sampling and chemical analyses; (3) quality control; (4) collecting weather and reported pesticide use data; and (5) developing non-cancer SLs, cancer potency values, and assessing risk.

### 2.1 Public participation

Public participation is a key component of EJ policy (Cal/EPA 2004). The CDPR formed two advisory groups to provide public input: a technical advisory group (TAG) and a local advisory group (LAG).

The TAG consisted of technical experts from governmental and nongovernmental organizations. It provided informal peer review on technical and scientific elements of the study (CDPR 2012b; Segawa et al. 2013). The TAG evaluated the study protocol to ensure that appropriate pesticides were included; the monitoring sites represented locations of relatively high potential exposure in Parlier; the number of samples and frequency of sampling were enough to determine exposures; and helped develop the SLs. The TAG held seven meetings between June 2005 and May 2007.

The LAG, composed of Parlier-area stakeholders, met nine times from June 2005 to November 2007. It assisted CDPR in finalizing the selection of pesticides and choosing sampling sites (CDPR 2012a, b; Segawa et al. 2013). The LAG also facilitated action on practical issues. For example, the LAG approved delaying the start of monitoring until January 2006, enabling CDPR to spread the study costs over two fiscal years, which, in turn, allowed more frequent monitoring at more sites. The LAG also added several objectives to the study, and CDPR addressed them as summarized below.

- *Inform the community of the study.* The CDPR did this in several ways. It sponsored a community forum in Parlier in January 2006 to tell residents about the air monitoring study; met with the LAG multiple times; translated LAG agendas, minutes, and other information into Spanish; and also made a public presentation to discuss the study at one of the three schools where monitoring was conducted.
- *Reduce pesticide risk.* As part of its work in Parlier, CDPR conducted a pest management assessment to develop, evaluate, and promote lower-risk alternatives to manage pests for Parlier's major crops: grapes, stone fruit and citrus (Matteson et al. 2007). Based on this

assessment, CDPR funded the use of innovative application equipment in the area to reduce pesticide use and funded research on alternatives to using highly toxic pesticides.

## 2.2 Study area and monitoring sites

Using a scoring system, based on (1) social demographics and human health data, (2) availability of data for cumulative impacts evaluation, and (3) pesticide use categories, CDPR evaluated the communities in the San Joaquin Valley (SJV), an area of high pesticide use in California (Segawa et al. 2013). The three categories were further divided into subcategories. First, CDPR ranked the communities in the SJV by reported pesticide use from highest to lowest. Then CDPR eliminated communities in the foothills that had little to no agriculture or pesticide use, or that were not feasibly close to sample; this produced a list of 83 communities. Next CDPR ranked the communities by the data available for each subcategory. For each subcategory, communities were divided into quartiles and each quartile was assigned one to four points. Four points represented the highest priority for monitoring. Subcategory points were summed and averaged to give an average score for each category. Category scores were summed for a final total score. Communities were then ranked from highest to lowest final total score. Such a process was designed to select a community that had a large number of children because this subgroup can be more sensitive to pesticides, a majority of its population non-white, a low median family income, and a high number of non-occupational illnesses caused by exposure to pesticides in air. These last two criteria were suggested by public comments. Segawa et al. (2013) fully describes this selection process.

Based on this selection method, CDPR chose Parlier. Of the 11,088 people living in Parlier in 2000, 38% were <18 years of age and 97% were Hispanic (US Census Bureau 2000) and its median income was \$24,275. The study area encompassed the City of Parlier (36.612N and -119.527E) and pesticide applications made within 8 km of the city boundary. About 78,000 kg of pesticides were applied within the study area in 2006, representing 200 chemicals used for agricultural production. Insecticides and fungicides are the most heavily used pesticides in the area (CDPR 2007). Parlier, 3.6 km<sup>2</sup>, is about 32 km southeast of Fresno. It has an elevation of about 104 m and receives 33 cm of average annual precipitation. Summer temperatures typically range from 10 to 36°C.

In consultation with its advisory groups, CDPR chose three Parlier elementary schools as sampling locations (Fig. 1). The CARB located its meteorological station and monitoring trailer at the Benavidez Elementary School in central Parlier. The San Joaquin Valley Air Pollution Control District station, located southeast of Parlier, measured wind speed and direction, air temperature, barometric pressure, relative humidity, and solar radiation.

## 2.3 Pesticides monitored

The CDPR selected 35 pesticides and 5 pesticide degradation products for monitoring based on: (1) statewide reported use, (2) volatility, (3) toxicity, (4) availability of an analytical method, (5) and input from the TAG and LAG (Table 1; Segawa et al. 2013).

## 2.4 Sampling

The design for sample collection is a product of the objectives of the study, the input of the community, and input from the TAG and LAG. Table 2 is divided into two sections, one for CDPR sampling parameters and one for CARB's.

### 2.4.1 CDPR sampling

The CDPR collected a total of 468 24-h samples 3 days a week on 156 days from January through December 2006. Each sample was analyzed for 25 pesticides and five breakdown products. The CDPR collected another 468 24-h samples on the same days at the same sites and analyzed them for methyl isothiocyanate (MITC), since it could not be analyzed by the multi-pesticide analytical method.

The most widely used procedure for atmospheric measurement of pesticides is to pass 2 to 100 L/min of air through a solid sorbent material onto which the pesticides are adsorbed (Keith 1996). Sorbent media typically used to trap pesticides include XAD resins and carbon sorbents such as charcoal (Baker et al. 1996; Majewski & Capel 1995). For this study, CDPR collected two types of samples according to the procedures described by Ganapathy (2003). The first type of sample, the multi-pesticide sample, was collected following CDPR's standard operating procedure (Wofford 2001). The multi-pesticide air monitoring was conducted with air sampling pumps (Andersen Series 110 Constant Flow Air Sampler Model 114) set at an airflow rate of 15 L/min equipped with a sample tube containing 30 mL of XAD-4 resin.

The second type of sample, the MITC sample, was collected using sample pumps (SKC Inc., #224-PCRX) equipped with coconut charcoal sorbent tubes (SKC Inc., #226-16-02) set at an airflow rate of 1.5 L/min (Table 2).

The use, operation, calibration and maintenance of air sampling pumps are described in CDPR's standard operating procedures (Wofford 2001, 2005). The CA Department of Food and Agriculture's (CDFA) Center for Analytical Chemistry washed, rinsed and packed XAD-4 resin into the sample containers. Sampling equipment was located in plastic storage boxes, modified to protect the

equipment and electrical supply from weather and to allow proper siting of the sampling tubes (CARB 2008a). The boxes were set on the roofs of the elementary schools. Sampling tubes were set at a height of 1 m above the equipment box and protected from sunlight and rain with PVC covers. Samples were collected and immediately placed on dry ice. They were kept on dry ice until they were delivered to the CDFA's Center for Analytical Chemistry in Sacramento, CA, at the end of the week. A temperature data-logger was placed in the dry ice container from sample collection to sample delivery. Staff followed CDPR's sample receipt login and verification procedures (Ganapathy 2005; Jones 1999).

#### 2.4.2 CARB sampling

The CARB collected up to 71 samples for five volatile organic compounds (VOCs, which include fumigants [1, 3-dichloropropene and methyl bromide], carbon disulfide, acrolein, and xylene); 64 samples for three metals (arsenic, copper and sulfur); and 65 samples for the carbonyl, formaldehyde (Table 2). The sampling frequency was once every sixth day, but increased to once every third day during those periods of highest expected pesticide use based on information CDPR provided<sup>1</sup>.

The CARB placed samplers and monitoring probes in accordance with the neighborhood spatial siting criteria (CARB 2008b). Twenty-four-hour integrated samples of VOCs, metals, and the carbonyl compound were collected every sixth day, except as specified above. Samples for VOCs were collected in 6-L Summa canisters; for metals on 37-mm Teflon filters; and for the carbonyl compound on Sep-Pak silica cartridges (Table 2). The CARB's Northern Laboratory Branch prepared all sample media following standard procedures detailed in laboratory standard operating procedures. The CARB (2008b; 2011) presents a complete description of field sampling procedures, including procedures for instrument set-up, calibration, and operation.

#### 2.5 Chemical analyses

The CDFA's Center for Analytical Chemistry analyzed the samples CDPR collected; CARB's Monitoring and Laboratory Division analyzed its samples. Table 2 describes analytical parameters and is divided into two sections, one for CDPR's samples and one for CARB's samples. Each laboratory determined the method detection limit (MDL) for each analyte by analyzing a standard at a concentration with a signal/noise ratio of 2.5:5. This standard was analyzed at least

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<sup>1</sup> The sampling frequency for pollutants monitored by CARB and collected on filters, cartridges, or in canisters was once every six days except for those periods (17 April to 11 May and 26 October to 22 November 2006) of expected highest use of 1,3 dichloropropene, methyl bromide, and sulfur in the immediate area of Parlier.

seven times, and the MDL was determined by calculating the 99% confidence interval of the mean. Similar to the MDL, the limit of quantitation (LOQ) is the smallest amount of the chemical that may be reliably measured. Samples with concentrations above the MDL but below the LOQ were identified as containing a *trace* amount, but the concentration couldn't be measured reliably. When calculating average concentrations and other statistics, CDPR assumed that samples with a trace concentration had a concentration at the midpoint between the MDL and the LOQ.

The University of CA Davis Trace Analytical Laboratory developed an analytical method to determine multiple chemicals from a single sample, which CDPR (2003) had used previously. The previous method analyzed each sample for 22 pesticides and five degradation products. The CDFA's Center for Analytical Chemistry modified the method to analyze for 30 of the pesticides and degradation products selected as chemicals of concern in Parlier (Hengel & Lee 2013). Lee (2004) describes extraction of MITC from sorbent tubes and its analysis. Storage stability studies also were performed by storing spiked sampling media in a freezer for the expected length of time between field sampling and laboratory analysis to determine the rate of sample degradation (Hengel & Lee 2013).

The CARB (2001, 2002, 2006) describes the methods used to analyze for VOCs, metals, and formaldehyde (the only carbonyl).

## 2.6 Quality control

During monitoring, CDPR collected trip blank samples, fortified field spikes, and co-located duplicate samples, as well as field samples. All trip blanks were nondetects; fortified field spikes ranged from 65.2 to 112.5% and duplicates had a maximum relative difference of 21%, all within acceptable range. The CARB (2008b) report describes its quality control procedures.

## 2.7 Weather and reported pesticide use data

The CDPR used weather and reported pesticide use data to help evaluate the air monitoring data. All agricultural pesticide applications must be reported to the state; CDPR (2007) maintains a database of these applications, including pesticide applied, date and amount applied, and application location. Meteorological data were collected and wind speed and direction, air temperature, barometric pressure, relative humidity, and solar radiation were measured.



## 2.8 Deriving non-cancer SLs for acute, subchronic, and chronic exposures

The CDPR evaluated the air monitoring data on a continuing basis throughout the study in order to promptly identify any detected concentrations that might pose a non-cancer health risk. To do this, CDPR used SLs it developed through extensive collaboration and consensus with the TAG, including technical experts from other agencies. The draft SLs and steps to develop them were also available for public comment before CDPR finalized them.

Screening levels were set for each pesticide and for various lengths of exposure—acute, subchronic or chronic. In this context, SLs are air concentrations at or below which adverse non-cancer health effects are not likely to occur in the general human population, including sensitive subpopulations such as children, for specified exposure durations. A central assumption is that a population threshold exists below which adverse effects will not occur in a population; however, such a threshold is not observable and can only be estimated. Areas of uncertainty in estimating effects among a diverse human population are addressed using extrapolations and uncertainty factors (UFs) (CA Office of Environmental Health Hazard Assessment 2001; CDPR 2011).

Since UFs are incorporated into SLs to address data gaps and other uncertainties, SLs may be 100 to 100,000 times lower than the levels of exposure observed to have no adverse effects in animal studies. So an exposure (i.e., measured air concentration) below the SL for a given pesticide is not considered hazardous and generally does not undergo further evaluation. A measured concentration above the SL does not necessarily indicate a significant health concern (because of health-protective assumptions used to derive the SL), but does indicate the need for further evaluation.

To the extent possible, SLs were developed using identified critical toxicology values or exposure levels taken from existing peer-reviewed documents. To identify the level at which an adverse human health effect is not expected to occur, CDPR used the following three primary sources of toxicology data listed in order of preference:

- (1) Human health risk assessments in the form of risk characterization documents completed by CDPR (2011);
- (2) Re-registration eligibility documents (REDs) completed by US EPA; and
- (3) Reference exposure levels established by CA's Office of Environmental Health Hazards Assessment and peer-reviewed by CA's Toxic Air Contaminant Scientific Review Panel.

The SLs were derived from the selected sources, listed above, and the corresponding No Observed Adverse Effect Level (NOAEL) to choose the most appropriate toxicology values. If a NOAEL was unavailable, then a Lowest Observed Adverse Effect level (LOAEL) was used. Applying an UF to the LOAEL generated an estimated NOAEL. Inhalation NOAELs generally are derived using laboratory animal studies. Children have the highest inhalation rate relative to body weight. The SLs are based on a child <1 year of age using a default inhalation rate of 4.5 m<sup>3</sup>/day and a default body weight of 7.6 kg. The resulting respiratory rate is (4.5 m<sup>3</sup>/day)/ (7.6 kg) = 0.59 m<sup>3</sup>/kg/day.

To make temporal adjustments CDPR used the following process. If the period of exposure in the animal study was less than a full 24 h, the NOAEL was normalized to a 24-h period. In general, rat inhalation NOAELs are derived from studies of either 4 or 6 h out of 24 h. No Observed Adverse Effects Levels based on studies less than 24 h duration were normalized to 24 h (Wofford et al. 2003). Similarly, subchronic SLs based on studies less than 7 days were normalized to represent 7 days (Wofford et al. 2003).

Dosimetric adjustments were made when only an oral reference dose was available by assuming inhalation and oral absorption rates are equal:

$$\text{RfC}^2 \text{ (or SL)} = \text{RfD} \times \text{body weight of subject} / \text{inhalation rate}$$

So, using the child breathing rate, the RfC is calculated as:

$$\text{RfC or SL (mg/m}^3\text{)} = \text{RfD (mg/kg/day)} \times (7.6\text{kg}) / (4.5 \text{ m}^3\text{/day)} = (1.7) \times \text{RfD}$$

Areas of uncertainty in data are accounted for by applying UFs. The methodology consists of identifying a point of departure, such as the highest exposure level in an animal experiment at which a NOAEL is observed. Extrapolation from this point of departure to a health protective level for the target human populations is by means of UFs. Extrapolations may include: a LOAEL to a NOAEL, between species, within a species, and a subchronic to a chronic value.

## 2.9 Developing cancer potency values to evaluate carcinogenic effects

Cancer risk was evaluated separately from non-carcinogenic risks because there is no assumed threshold mechanism of action. The CDPR determined carcinogens based on the US EPA Integrated

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<sup>2</sup> RfC = reference concentration, an estimate of the daily air concentration of a chemical likely to be without adverse effects to the exposed human population. RfD = reference dose, an estimate of the daily exposure of the human population to a chemical, usually by the oral route, that is likely to be without adverse effects.

Risk Information System (US EPA 2001). The carcinogenic risk was determined from the cancer potency of the chemical and the human exposure to the chemical.

$$\text{Risk} = (\text{cancer potency}) \times (\text{exposure})$$

$$\text{Exposure} = (\text{air concentration}) \times (\text{respiratory rate})$$

$$\text{Risk} = (\text{cancer potency}) \times (\text{air concentration}) \times (\text{respiratory rate})$$

Since exposure to a carcinogen takes place over a lifetime, adult respiratory rates were used (0.28 m<sup>3</sup>/kg/day). The CDPR's policy is to consider risk in the range of 10<sup>-5</sup> to 10<sup>-6</sup> or less to be negligible (CA Office of Environmental Health Hazard Assessment 2001).

### 3. Results and discussion

#### 3.1 Monitoring data

The study sought to answer three main questions, the first two of which are:

- Are residents of the community exposed to pesticides in the air?
- Which pesticides are people exposed to and in what amounts?

This section addresses these two questions.

The pesticides monitored accounted for 80% of the total kilograms of pesticides applied in Parlier and the surrounding 8-km agricultural study area in 2006 (CDPR 2007). Seventeen of the 40 pesticides and pesticide degradation products monitored were not detected at concentrations above the detection limit. Of the 17 pesticides monitored but not detected, 13 had reported use <454 kg and the remaining four had reported use ranging from 1,048 to 5,883 kg within the study area.

Twenty-three pesticides and degradation products were detected (Table 3) in the study area at or above trace levels. Four chemicals—acrolein, arsenic, carbon disulfide, and formaldehyde—sometimes used as pesticides were detected; however, no use of these compounds as pesticides was reported in the study area (CDPR 2007). Levels detected were comparable to those found statewide (CARB 2008a; Peck & Hornbuckle 2005; Royce et al. 1993) and their presence in the study area – like elsewhere in the state – is most likely the result of vehicular or industrial emissions. Since these compounds were not detected due to their use as pesticides, they are outside CDPR's regulatory authority and beyond the scope of this article.

Of the 19 detected compounds at or above trace concentrations that were used strictly as pesticides, copper and sulfur were found in 100% of the samples (Table 3). MITC (84%) was the next most frequently detected chemical. Methyl bromide (66%) and chlorpyrifos (64%) were the third and fourth most frequently detected. The remaining 14 pesticides were detected at or above trace concentrations in less than 50% of the samples. Xylene was detected, although no agricultural use was reported. Xylene is sometimes used in pesticide formulations as an inert ingredient. Dichlorvos was detected in 1% of the samples; however, no agricultural pesticide use was reported. Dichlorvos is used in some home products, which may have contributed to its detection.

Figures 2, 3, 4, 5 and 6 present the average of the concentrations detected at the three monitoring sites/week for malathion, MITC, chlorpyrifos, diazinon, and phosmet (the only pesticides detected at quantifiable amounts), overlaid with the total reported use/week of the pesticide in the 8-km study area. All of the pesticide detections corresponded with times of reported use except for those of MITC. Several detections of MITC (Fig. 3) did not correspond with reported use of field applications of any MITC-producing pesticides, which could indicate that applications made outside the 8-km boundary of Parlier may have influenced the concentrations of MITC detected.

### 3.2 Acute exposure SLs

The study sought to answer three main questions, the third of which is: Do measured pesticide air levels exceed levels of concern to human health? The “Acute”, “Subchronic”, and “Chronic exposure SL” sections and the “Carcinogenicity” section address this question.

To evaluate the potential health risk of exposure to the individual monitored pesticide, the highest 24-h concentration at any site was used (Table 3). Only diazinon exceeded its acute SL: One sample (out of 468) had a concentration above the acute SL. Based on this result, CDPR moved diazinon to the top of its high priority list for risk assessment and initiated a comprehensive risk assessment in 2008 for all exposure routes, including inhalation.

### 3.3 Subchronic exposure SLs

To calculate the subchronic exposure SLs for individual pesticides, a rolling average concentration for every 2-week period was calculated for all of the sampling sites and days. As a result, only pesticides monitored by CDPR (three times per week at three sites) are included in these

calculations. Table 3 lists the highest 14-day average concentrations. No 14-day average concentrations were above the subchronic SLs.

### 3.4 Chronic exposure SLs

The 1-year average of all the sampling sites and days was used to calculate the chronic air concentrations for individual pesticides. They are included in this evaluation of chronic exposure. The CARB sample 1-year average concentrations were calculated as a total average of all of the monthly averages. None of the 1-year average concentrations exceeded chronic SLs (Table 3).

### 3.5 Carcinogenicity

Only one of the carcinogenic pesticides posed a risk: 1, 3-dichloropropene. Its potency is 0.055 mg/kg/day, its air concentration was 0.001970 mg/m<sup>3</sup>; therefore, its risk is  $3 \times 10^{-5}$ .

This risk level is greater than the range of what CDPR would normally consider negligible (i.e.,  $1 \times 10^{-5}$ ). The CDPR has reopened its risk assessment of 1, 3-dichloropropene and is evaluating management plans, permitted uses, and application restrictions in light of these and other monitoring and modeling (Johnson 2009) results.

### 3.6 Reported pesticide use data

Table 3 summarizes reported pesticide use within 8 km of Parlier's boundary in 2006 for the pesticides detected. Pesticide detections generally corresponded to reported use during the study. MITC was frequently detected when use of its parent compounds [metam sodium (Vapam), potassium N-methyldithio-carbamate (K-Pam), or dazomet (Basamid)] were not reported during the times when it was detected (Fig. 3). Perhaps applications made outside the 8-km boundary of the study area influenced the concentrations of MITC detected. Figure 7 shows the monthly reported use of pesticides in Parlier that were monitored as well as those that were not monitored.

### 3.7 Summary

This study provided the following answers to the questions it addressed:

- (1) *Are residents of the community exposed to pesticides in the air?* Yes.
- (2) *Which pesticides are people exposed to and in what amounts?* Parlier residents were exposed to 19 compounds used as pesticides in amounts that ranged from highest 1-day concentrations of 16 to 23,601 ng/m<sup>3</sup>.

(3) *Do measured pesticide air levels exceed levels of concern to human health?* Of those detected compounds used strictly as pesticides, only diazinon exceeded a SL. However, chlorpyrifos, a closely related compound, approached its acute and subchronic SLs. Use of diazinon and other organophosphate pesticides has steadily decreased over the past decade as newer, more targeted compounds have been developed. Also, US EPA's RED for diazinon places additional restrictions on the agricultural uses of the pesticide (US EPA 2006). While CDPR had already initiated a risk assessment on chlorpyrifos, it increased its priority based on these findings and will continue working with US EPA. The air concentrations measured in Parlier are an integral part of the assessment. 1,3-dichloropene exceeded its cancer potency value. To address this health impact, CDPR has undertaken a more comprehensive evaluation of 1,3-dichloropropene.

The CDPR developed data collection and analytical methods for selecting communities for monitoring based on risk assessment priorities and related criteria, and detecting multiple pesticides in a single sample (Hengel & Lee 2013; Segawa et al 2013). The study was the first time CDPR or any other government agency in the US conducted pesticide air monitoring for 12 months in a single community, and it was the first study in the state to simultaneously monitor 30 pesticides. Particulate matter (PM) has been well studied in the SJV (Herner et al. 2005; Ying & Kleeman 2009; Zhao et al. 2010). Less is known about pesticides in air. This study provides some of the most comprehensive pesticide air monitoring data for this region.

The CDPR also developed SLs for pesticides for which no ambient air quality standards exist using a consensus approach that involved other agencies as well as other stakeholders. The SLs provide a transparent and systematic method to evaluate health risks. They also require much less time to develop than risk assessments, which can take several years to complete. Since SLs are calculated using clearly defined methods and identified data, they can be revised as updated toxicity information becomes available.

The analysis of hundreds of monitoring samples taken over a full year added substantially to CDPR's knowledge of pesticides in air, and not just in Parlier. Parlier is similar to many Central Valley towns, surrounded by agriculture and the associated use of pesticides, with its large number of children and large non-white population with a low median family income. Data from this study may represent pesticide air concentrations in other communities that share similar pesticide use, cropping, and weather patterns, as well as topography. These data and the SL approach can provide

valuable information to state agencies, the US EPA, and others interested in air quality and pesticides.

This study tested sampling protocols, expanded laboratory analytical methodology, fine-tuned approaches to data analysis, and developed effective ways to gain community input and assistance. It provided a foundation for CDPR to establish the first ongoing, statewide pesticide air monitoring network in the US (Vidrio et al. 2013). In 2011, CDPR began this monitoring network to sample ambient air for multiple pesticides in three communities on a regular schedule for several years. The CDPR plans to use the data gathered to evaluate and improve protective measures against pesticide exposure.

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**Table 1** The active ingredient, common trade name, use (action), and chemical class for each pesticide monitored. Pesticide degradation products are shown in italics.

	<b>Pesticide active ingredient</b>	<b>Common trade names</b>	<b>Use</b>	<b>Chemical class</b>
1	1,3-Dichloropropene	Telone, Inline	Fumigant	Halogenated organic
2	Acrolein	Magnacide	Algacide	Aldehyde
3	Arsenic			Elemental metal
4	Azinphos-methyl	Guthion	Insecticide	Organophosphate
5	Carbon disulfide	Enzone	Fumigant	
6	Chlorothalonil	Bravo, Daconil	Fungicide	Chloronitrile
7	Chlorpyrifos	Dursban, Lorsban	Insecticide	Organophosphate
8	<i>Chlorpyrifos oxygen analog</i>			
9	Copper		Fungicide	Elemental metal
10	Cypermethrin	Demon	Insecticide	Pyrethroid
11	Diazinon	Diazinon-various brands	Insecticide	Organophosphate
12	<i>Diazinon oxygen analog</i>			
13	Dichlorvos <sup>a</sup>	Vapona, DDVP, Dibrom	Insecticide	Organophosphate
14	Dicofol	Kelthane	Insecticide	Organochlorine
15	Dimethoate	Cygon	Insecticide	Organophosphate
16	<i>Dimethoate oxygen analog</i>			
17	Diuron	Karmex	Herbicide	Urea
18	Endosulfan	Thiodan	Insecticide	Organochlorine
19	<i>Endosulfan sulfate</i>			
20	EPTC	Eptam	Herbicide	Carbamate
21	Formaldehyde		Microbiocide	Aldehyde
22	Malathion	Malathion-various brands	Insecticide	Organophosphate
23	<i>Malathion oxygen analog</i>			
24	MITC <sup>b</sup>	Vapam, K-pam, Basamid	Fumigant	Dithiocarbamate
25	Methyl bromide	Brom-O-Gas, Pic-Brom	Fumigant	Halogenated organic
26	Metolachlor	Dual	Herbicide	Chloracetanilide
27	Molinate	Ordram	Herbicide	Thiocarbamate
28	Norflurazon	Solicam	Herbicide	Pyridazinone
29	Oryzalin	Surflan	Herbicide	Dinitroaniline
30	Oxyfluorfen	Goal	Herbicide	Diphenyl ether
31	Permethrin	Ambush, Pounce	Insecticide	Pyrethroid
32	Phosmet	Imidan	Insecticide	Organophosphate
33	Propanil	Duet, Wham	Herbicide	Anilide
34	Propargite	Omite, Comite	Insecticide	Organosulfite
35	Simazine	Princep	Herbicide	Triazine
36	SSS-	DEF, Folex, Tribufos	Defoliant	Organophosphate
37	Sulfur		Fungicide	Elemental mineral
38	Thiobencarb	Bolero, Abolish	Herbicide	Thiocarbamate
39	Trifluralin	Treflan	Herbicide	Dinitroaniline
40	Xylene		Solvent	Petroleum derivative

<sup>a</sup>Dichlorvos also may be present as a degradation product of the insecticide Naled (common trade name Dibrom).

<sup>b</sup>MITC, a degradation product, is the pesticidal active ingredient generated by the following compounds: metam sodium (Vapam), potassium N-methyldithio-carbamate (K-Pam) and dazomet (Basamid).

**Table 2** Sampling and analytical parameters for pesticides monitored by CDPR and CARB in Parlier, CA, 2006. MITC required different sampling and analysis methodology from the other VOCs.

	DPR samples		ARB samples		
Sampling & analytical parameters	Multi-pesticides <sup>a</sup>	MITC	VOCs <sup>c</sup>	Metals <sup>d</sup>	Carbonyls <sup>e</sup>
Sampler/media <sup>b</sup>	Anderson Series 110 Constant Flow air sampler model 114 pump /XAD-4 filter	SKC Inc. personal sample pump (SKC Inc., #224-PCRX)/coconut charcoal filter	XonTech 910A 6-L Summa canister	XonTech 924/ 37-mm Teflon filter	XonTech 924 Sep-Pak cartridge
Analytical method <sup>a</sup>	LC (19 analytes) and GC (11 analytes)	GC	GC/MS	X-ray fluorescent spectroscopy	HPLC
Extraction solvent	Ethyl acetate	0.1% CS <sub>2</sub> in ethyl acetate	NA	NA	Acetone-free acetonitrile
Detector	Tandem mass spectrometer (LC/MS/MS) Mass selective detector (GC + MSD)	GC + TSD	MSD	X-ray spectrometer	HPLC-UV
Flow rate or cartridge pressure	15 L/min	1.5 L/min	10.0 – 16.0 (PSIG)	9 – 14 (SLPM)	0.63 – 0.77 (SLPM)
Reference	Lee (2008)	Lee (2004)	CARB (2002)	CARB (2006)	CARB (2001)

<sup>a</sup> Multiple pesticides (30) = azinphos-methyl, chlorothalonil, chlorpyrifos, cypermethrin, diazinon, dichlorvos, dicofol, dimethoate, diuron, endosulfan, endosulfan sulfate, EPTC, malathion, metolachlor, molinate, norflurazon, oryzalin, oxyfluorfen, permethrin, phosmet, propanil, propargite, simazine, thiobencarb, trifluralin, chlorpyrifos oxygen analog, diazinon oxygen analog, dimethoate oxygen analog, malathion oxygen analog.

<sup>b</sup> Notes and abbreviations: XAD-4 is a resin; GC = gas chromatography; LC = liquid chromatography; HPLC = high-performance liquid chromatography; UV = ultraviolet detector; MS = mass spectrometry; NA = not applicable; TSD = thermospray detector; MSD = mass selective detector; L/min = liters per minute; PSIG = pounds per square inch; SLPM = standard L/min.

<sup>c</sup> VOCs (volatile organic compounds) (5) = acrolein, carbon disulfide, 1, 3-dichloropropene, methyl bromide, and xylene. Note: MITC, also a VOC, is not included in this group since it required different sampling and analytical methods.

<sup>d</sup>Metals (3) = arsenic, copper, and sulfur.

<sup>e</sup>Carbonyls (1) = formaldehyde.

**Table 3** The number of samples collected; percent of samples with detections; reported use in 2006; highest 1-day concentrations (conc), highest 14-day concs, and 1-year average concs; and acute, subchronic, and chronic screening levels for the 19 pesticides that were detected at or above trace levels in the air monitoring study in Parlier, CA, in 2006 due to pesticidal uses. The CDPR collected samples for all the pesticides, except for those shown in italics; CARB collected those. Chemicals whose concs  $\geq$  one or more SLs are shown in bold.

Pesticide or degradation product	Samples collected (no.)	Samples with detections (%) <sup>a</sup>	Reported use <sup>b</sup> (kg a.i.); Reported applications (no.)	Exposure					
				Acute		Subchronic		Chronic	
				Highest 1-day conc (ng/m <sup>3</sup> )	SL (ng/m <sup>3</sup> )	Highest 14-day conc (ng/m <sup>3</sup> )	SL (ng/m <sup>3</sup> )	1-year avg conc (ng/m <sup>3</sup> )	SL (ng/m <sup>3</sup> )
<i>1,3-Dichloropropene</i>	71	34	13,7019; 122	23,601	160,000	NSD	NSD	1,970	120,000
Chlorothalonil	468	17	2,372; 153	Trace (30-238)	34,000	30	24,000	11	34,000
Chlorpyrifos	468	64 <sup>c</sup>	14,252; 1,217	150	1,200	96	850	23	510
Chlorpyrifos OA	468	22 <sup>c</sup>	N/A; N/A	28	1,200	7	850	3	510
<i>Copper</i>	64	100	49,782; 2,159	550	100,000	NSD	NSD	44	10,000
<b>Diazinon</b>	468	32 <sup>c</sup>	1,565; 222	<b>172</b>	<b>130</b>	20	130	3	130
Diazinon OA	468	19 <sup>c</sup>	N/A; N/A	71	130	13	130	2	130
Dichlorvos	468	1	0; 0	Trace (25)	11,000	9	2,200	2	770
Malathion	468	1 <sup>c</sup>	302; 14	21	40,000	3	15,000	1	29,000
Malathion OA	468	5 <sup>c</sup>	N/A; N/A	16	40,000	3.60	15,000	1	29,000
<i>Methyl bromide</i>	71	66	5,661; 68	2,524	820,000	281	3,900	281	3,900
MITC	468	84 <sup>c</sup>	16,548; 16	5,010	66,000	377	3,000	38	300
Permethrin	468	1	101; 43	Trace (27)	168,000	7	90,000	4	90,000
Phosmet	468	19 <sup>c</sup>	14,452; 1,235	42	77,000	18	26,000	6	18,000
Propargite	468	15	3,211; 330	Trace (25)	14,000	25	14,000	5	14,000
Simazine	468	7	5,951; 1,063	Trace (3-6)	110,000	4	31,000	1	8,500
<i>Sulfur</i>	64	100	363,482; 6,197	1,800		NSD	N/A	692	N/A
Trifluralin	468	24	36; 16	Trace (23)	1,200,000	11.15	170,000	3.64	41,000
<i>Xylene</i>	71	49	0; 0	5,906	900,000	NSD	N/A	1,498	700,000

NSD = Not sufficient data. For most of the year, CARB took only 2 samples in any 14-day period, which were not sufficient to generate data for the subchronic analysis.

N/A = Not available.

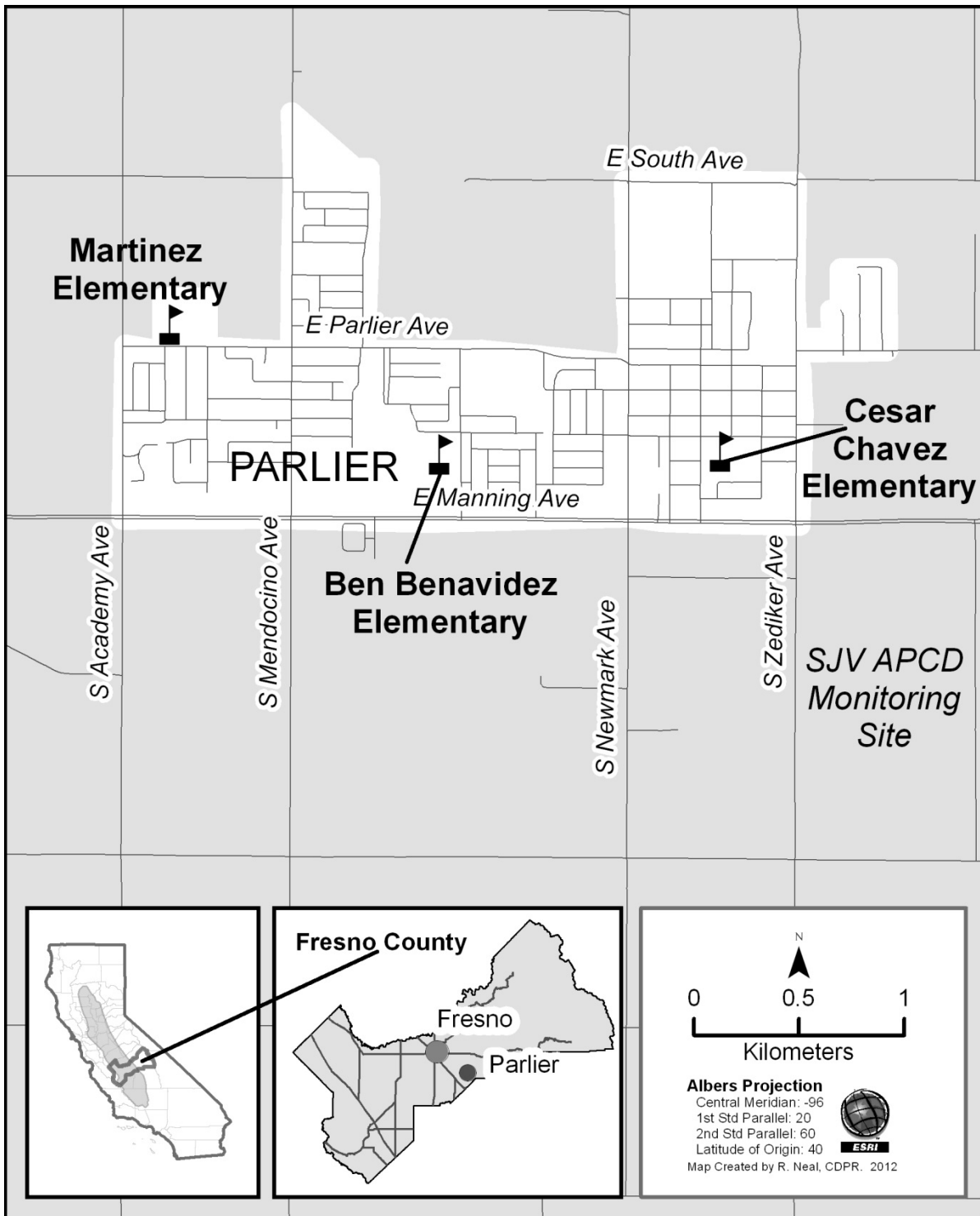
<sup>a</sup> Detections  $\geq$  trace concentration.

<sup>b</sup> Reported pesticide use from 2006 for applications made within 8 km of the city boundary.

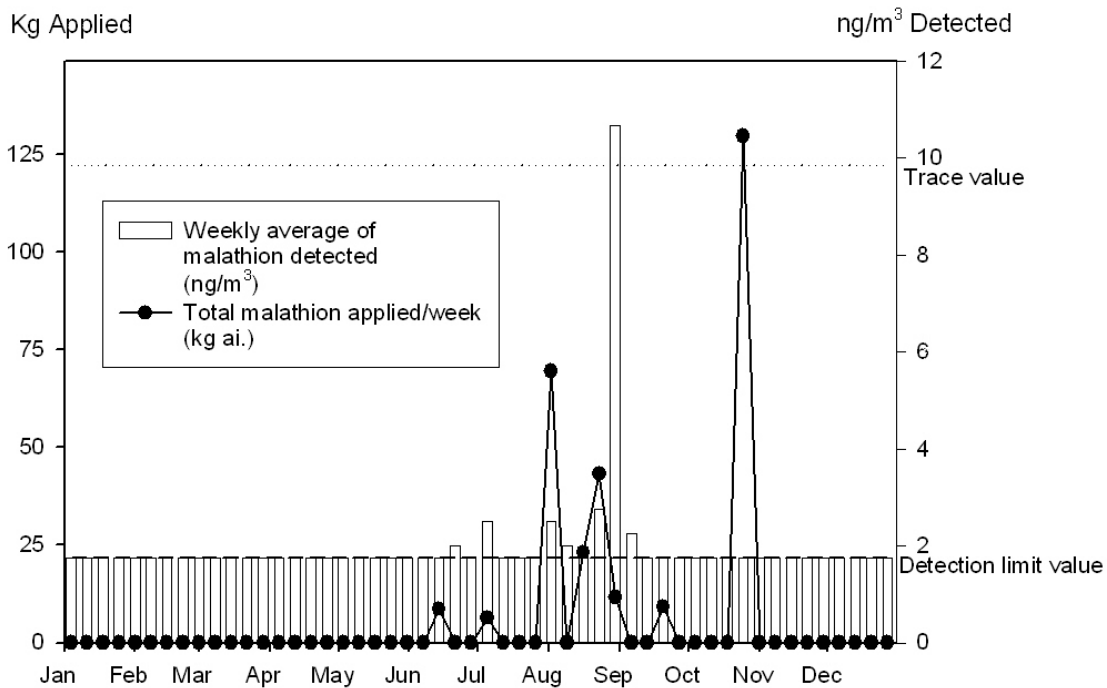
<sup>c</sup> Includes detections with quantifiable concentrations.

**Figure 1** Map of the City of Parlier showing locations of the monitoring sites.

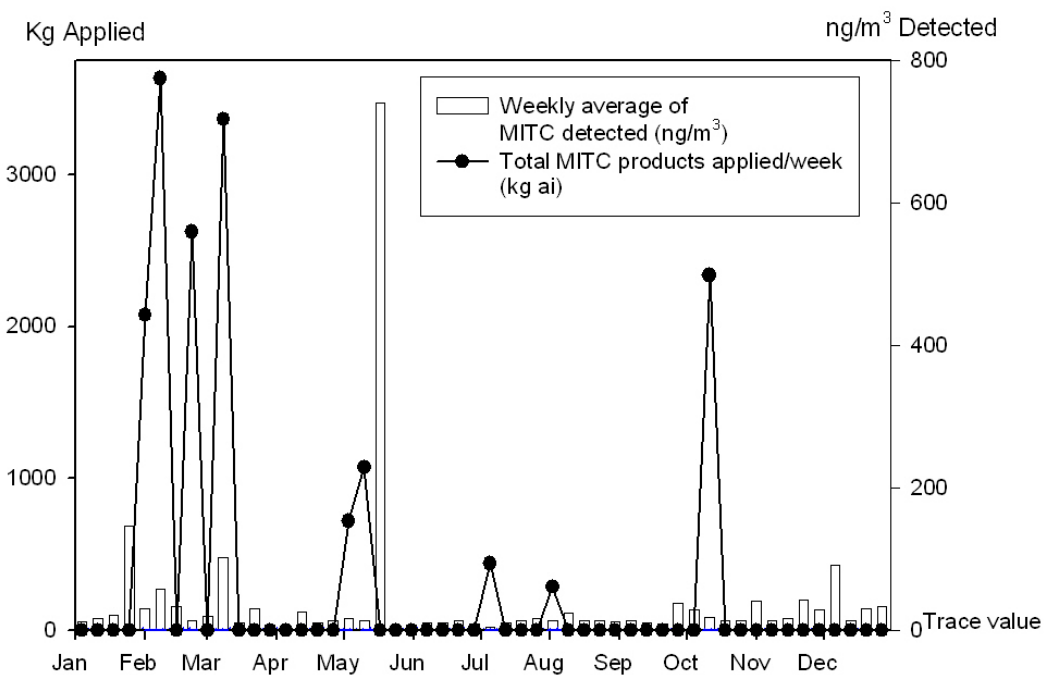
*Inserts:* map of CA with the Central Valley highlighted; map of Fresno County showing locations of Fresno and Parlier



**Figure 2** Malathion + oxygen analog: comparison of average concentrations detected at 3 monitoring sites/week and total reported use/week in the 8-km Parlier study area. Note: Malathion products are also registered for home use, which is not subject to use reporting requirements

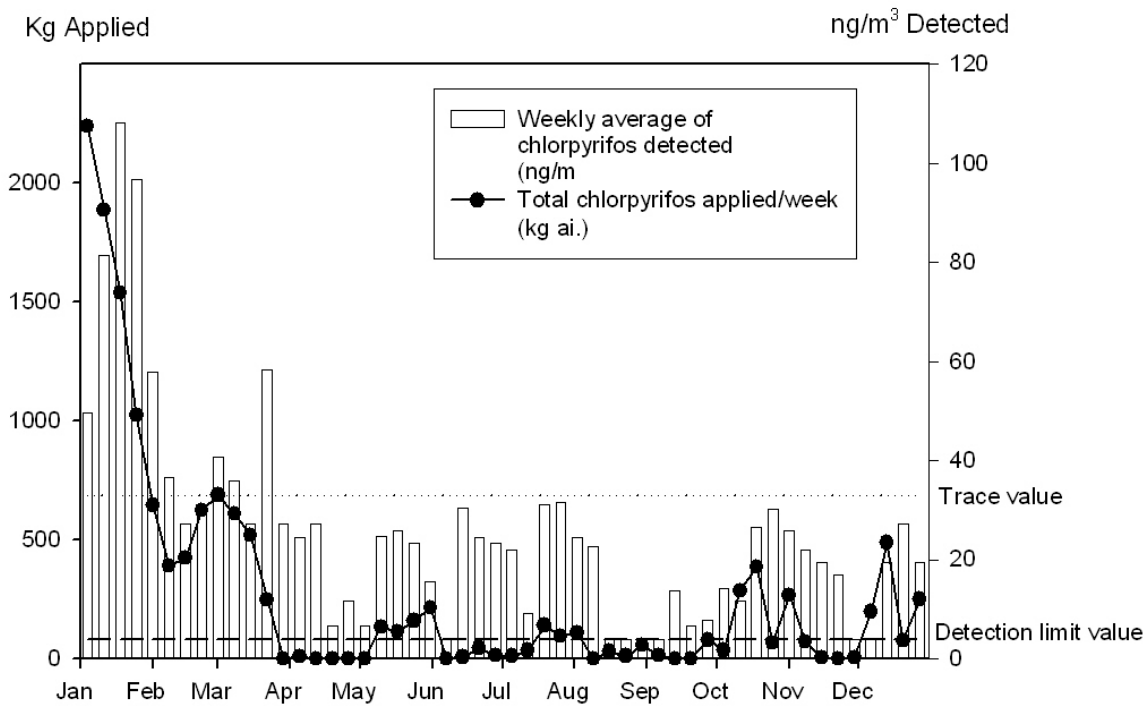


**Figure 3** MITC: comparison of average concentrations detected at 3 monitoring sites/week and total reported use/week in the 8-km Parlier study area. Note: This figure includes reported use of all MITC-generating products. The detection limit is too low to show at this scale.

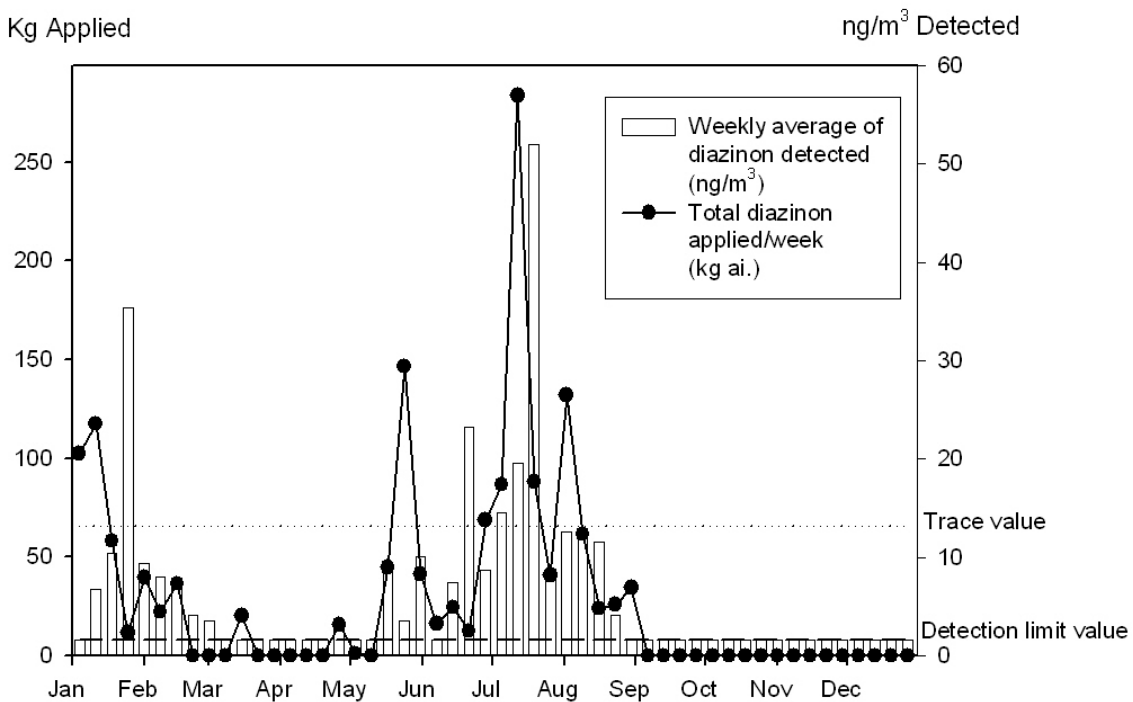




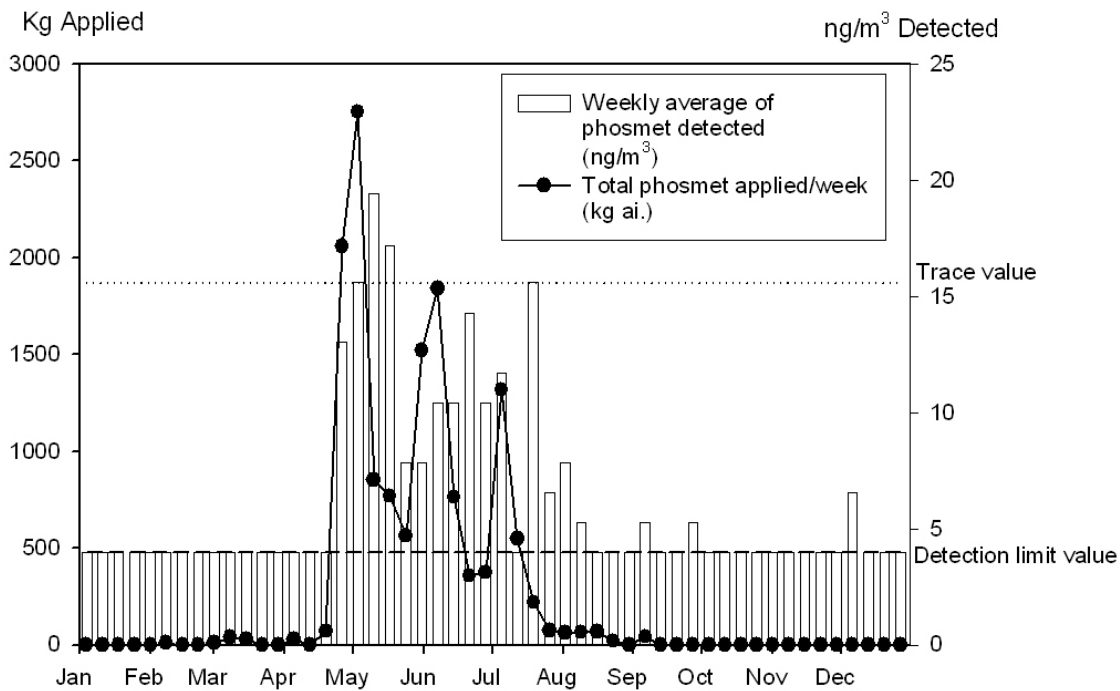
**Figure 4** Chlorpyrifos + oxygen analog: comparison of average concentrations detected at 3 monitoring sites/week and total reported use/week in the 8-km Parlier study area.



**Figure 5** Diazinon + oxygen analog: comparison of average concentrations detected at 3 monitoring sites/week and total reported use/week in the 8-km Parlier study area.



**Figure 6** Phosmet: comparison of average concentrations detected at 3 monitoring sites/week and total reported use/week in the 8-km Parlier study area.



**Figure 7** Monthly reported use of all--monitored and unmonitored--pesticides within 8 km of Parlier city boundary in 2006.

