

**ENVIRONMENTAL JUSTICE PILOT PROJECT  
PROTOCOL FOR PESTICIDE AIR MONITORING IN PARLIER**

**DECEMBER 30, 2005  
REVISED  
MARCH 1, 2006**

**PREPARED BY  
CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY  
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## **1. INTRODUCTION**

### **1.1 Background**

As part of the California Environmental Protection Agency's (Cal/EPA's) Environmental Justice Action Plan, the Department of Pesticide Regulation (DPR) will lead a pilot project in the Central Valley focusing on pesticides in a rural, farming community. This protocol describes the monitoring to be conducted for ambient air concentrations of pesticides in the Fresno County community of Parlier.

California rural communities may have higher concentrations of pesticides in ambient air compared to urban communities, due to their proximity to agricultural fields. DPR evaluated 83 communities in Fresno, Kern, Kings, Madera, Merced, Stanislaus, and Tulare counties as candidates for this project. The communities were prioritized based on population data, availability of cumulative impact data, and pesticide use – both local and regional use. DPR also considered other factors, including air sampling feasibility, weather patterns, and the potential for collaboration with other projects focused on environmental health. Based on an analysis of all these factors, DPR selected Parlier in Fresno County (DPR, 2005).

This project will focus on monitoring ambient air concentrations of as many as 40 pesticides and pesticide breakdown products. The data gathered will help DPR evaluate ambient air exposure to pesticides in order to better understand and identify opportunities to reduce environmental health risk, particularly to children. This project will include additional elements to address definitions of and guidance for cumulative impacts, precautionary approaches, and public participation.

### **1.2 Site Description**

Parlier is a small city (approximately 1.6 square miles in area) located in the San Joaquin Valley, approximately 20 miles southeast of Fresno (Figure 1). Parlier has an elevation of approximately 340 feet, with approximately 13 inches of precipitation annually. Temperatures during the summer typically range from 60 – 96 °F, and 35 – 50 °F during the winter. Winds are most frequently from the northwest at 5 – 8 miles per hour (Figure 2).

According to the 2000 U.S. Census the total population for Parlier is 11,088. Approximately 38 percent of the population is less than 18 years old, 97 percent are Hispanic, and the median family income is \$24,275 per year.

Parlier is a rural community surrounded by agriculture. The major crops grown in the area are grapes and tree fruit. In 2003, approximately 249 chemicals were used for agricultural production within 5 miles of the Parlier region, with approximately 2,388,000 pounds used per year. Table 8 lists the pesticides that will be monitored in this study, which account for approximately 1.3 million pounds of that total use in the area. Insecticides and fungicides are the most heavily used pesticides in the Parlier area. See Section 3.1 for a detailed description of pesticide use in the Parlier area.

## 1.3 Project Goals and Objectives

### 1.3.1 Overall Goals

The overall goal for this pilot project is to evaluate ambient air exposure to pesticides to better understand and identify opportunities to reduce environmental health risk, particularly to children. The Parlier project is one of six environmental justice pilot projects being done by boards and departments that are part of the California Environmental Protection Agency (Cal/EPA). All include some common elements: assessment of cumulative impacts, application of precautionary approaches, and public participation.

For the purposes of this and the other pilot projects, the Interagency Work Group on Environmental Justice (which includes the Cal/EPA secretary and heads of its boards, departments, and offices) adopted the following working definitions:

“Cumulative impacts means exposures, public health or environmental effects from the combined emissions and discharges, in a geographic area, including environmental pollution from all sources, whether single or multi-media, routinely, accidentally, or otherwise released. Impacts will take into account sensitive populations and socio-economic factors, where applicable and to the extent data are available.”

“Precautionary approach means taking anticipatory action to protect public health or the environment if a reasonable threat of serious harm exists based upon the best available science or other relevant information, even if absolute and undisputed scientific evidence is not available to assess the exact nature and extent of risk.”

A local advisory group (LAG) is key to ensuring meaningful public participation in this environmental justice project. The Parlier LAG includes representatives of the California Rural Legal Assistance Foundation; Californians for Pesticide Reform; Fresno County Agricultural Commissioner’s office; Fresno Metro Ministry; Latino Issues Forum; LUPE (La Unión del Pueblo Entero); Parlier City government; Parlier HEAL Asthma Project; and the Parlier Unified School District. The LAG also includes a local Realtor; a Parlier businessman; local health care provider; a Parlier vintner; and three farmers, including an organic farmer. In addition, a Technical Advisory Group (TAG) was formed to provide guidance on the scientific elements of the pilot project. The TAG is composed of staff from federal, state, and county agencies, as well as technical specialists from the local communities.

### 1.3.2 Specific Project Objectives

DPR based the selection of the pesticides and community on the following objectives:

- 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, particularly children?

After discussion with the LAG, DPR added the following additional objectives:

- Inform the community of project, including public forums
- Reduce pesticide risk
- Conduct follow-up actions, such as education and/or regulatory actions
- Evaluate the pesticide risk relative to other pollutants monitored

#### 1.3.4 Other Monitoring

The City of Parlier relies on ground water for its drinking water supply. The City of Parlier conducts routine monitoring of city municipal wells for pesticides and other potential water contaminants. In addition, during the study DPR will collect ground water samples from city wells and analyze them for pesticides not monitored by the City of Parlier and that may be groundwater contaminants.

DPR will check with other regulatory agencies to determine if Parlier has any unusual sources of pesticides or other environmental contaminants.

### **1.4. Previous Investigations**

This pilot project will provide more systematic air monitoring for a community in the Central Valley and therefore will serve as a more robust foundation for exposure assessment. DPR conducted a similar project in Lompoc (Santa Barbara County) and the U.S. Environmental Protection Agency is completing one in McFarland (Kern County). DPR will use similar methods for this study.

#### 1.4.1 Lompoc Air Monitoring

In 2000, DPR monitored ambient air concentrations of 22 pesticides and five breakdown products simultaneously during the peak use period for most of the pesticides in Lompoc (DPR, 2003). In addition, air concentrations of three fumigants were monitored following specific applications close to the city of Lompoc (DPR, 2003). Of the 31 pesticides or breakdown products monitored in the two-part study, DPR detected 27 of them in one or more of the 451 samples collected and analyzed. Four of the 31 chemicals were below any detectable concentrations, 11 detected at quantifiable concentrations (the smallest amount that can be measured), 16 were detected at trace amounts (detectable but not measurable). While many pesticides were detected, and some quite frequently, air concentrations were low compared to health screening levels.

#### 1.4.2 McFarland

The U.S.EPA monitored ambient air concentrations at two schools in McFarland from July 2001 to May 2002 during different agricultural seasons. The extensive study monitored 145

chemicals and took more than 900 samples (U.S.EPA, 2004). The chemicals monitored included; pesticides used in the McFarland area, volatile organic compound (VOCs), dioxins, polynuclear aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pesticide breakdown products, and dust. Of the 145 chemicals monitored, 79 were detected of which 11 were detected above a screening level, but within EPA's protective health range. The chemicals detected above their screening levels were four metals; cadmium, chromium, manganese, and arsenic, and six VOCs; carbon tetrachloride, formaldehyde, methylene chloride, benzene, para-dichlorobenzene, and methyl chloride. Methyl bromide was the only pesticide found above its screening level. Although, the levels were within EPA's protective health range, the data was not sufficient to fully evaluate community exposure to methyl bromide applications.

### 1.4.3 Pesticide Toxic Air Contaminant Monitoring

The Air Resources Board, in consultation with DPR, conducts ambient monitoring for a variety of pesticides in accordance with the Toxics Air Contaminant (TAC) monitoring program. Monitoring for pesticides is conducted in counties with the highest use for a particular pesticide to be monitored and during the season of highest use. ARB's ambient air monitoring of pesticides is conducted near agricultural areas where use of the pesticides being monitored is expected. Public buildings such as schools are used as monitoring sites if such locations represent potential public exposure to the target pesticides. Information is available from ambient air sampling conducted under the TAC program for 13 of the pesticides included in the monitoring study in Parlier: 1,3-dichloropropene, chlorpyrifos, diazinon, endosulfan, EPTC, malathion, MITC, methyl bromide, molinate, permethrin, propargite, simazine, and S,S-tributyl phosphorotrithioate. Summaries of the TAC monitoring are given in Attachment I.

## 2. PROJECT PERSONNEL

DPR's standard project organization and responsibilities are described in SOP ADMN002.00 (Attachment II). This project is under the overall management of John Sanders, Branch Chief, DPR-Environmental Monitoring Branch. Other key personnel assigned to this project include:

Project Leader:	Randy Segawa Senior Environmental Research Scientist, DPR (916) 324-4137 rsegawa@cdpr.ca.gov
Field Sampling Coordinators:	Clarice Ando and Pam Wofford Associate Environmental Research Scientists, DPR
Senior Scientist:	Bruce Johnson Senior Environmental Research Scientist, DPR
Laboratory Liaison and Quality Assurance:	Carissa Ganapathy Associate Environmental Research Scientist, DPR

Pesticide Risk Evaluation:	Jay Schreider Primary State Toxicologist, DPR
Pest Management Analysis:	Pat Matteson Associate Environmental Research Scientist, DPR
Environmental Justice Coordinator:	Veda Federighi External Affairs Director, DPR
Chemical Analysis:	Department of Food and Agriculture, Center for Analytical Chemistry Air Resources Board, Monitoring and Laboratory Division

Air Resources Board personnel will conduct the monitoring for air toxics chemicals which includes volatile organic compounds and metals/elements. Personnel from the San Joaquin Valley Air Pollution Control District will conduct the monitoring of several criteria air pollutants and hydrocarbons as part of their Photochemical Assessment Monitoring Stations program.

In addition, to the personnel described above, other people have key roles for this specific project. DPR formed the LAG to assist with the project. The LAG advises DPR on overall project goals and priorities. The TAG will assist DPR in the planning of pesticide air monitoring and evaluation of results. DPR will also establish a multi-agency quality assurance team to perform audits of the monitoring.

### **3. SAMPLE COLLECTION DESIGN AND METHODS**

The design for sample collection is a product of community and technical input from the TAG and LAG. This section describes the pesticides and other chemicals that will be monitored, types of samples to be collected, sample measurement details, monitoring locations and frequency, and other information pertinent to field collection and shipment of samples.

#### **3.1 Pesticides and Other Chemicals Included in the Project**

During the study, monitoring will be conducted for 20 pesticides and five pesticide breakdown products that were among the top 100 used within five miles of Parlier during 2003. Table 1 lists these pesticides and breakdown products and gives some key chemical and physical characteristics. The monitoring will include an additional 13 pesticides not among the top 100 used within five miles of Parlier because they are easily included at no extra cost with the methods and many have high use in other areas. DPR selected the pesticides for monitoring based on: (1) toxicity, (2) vapor pressure (volatility), (3) use, (4) availability of sampling and laboratory methods, and (5) ability to include a pesticide in a multi-residue method. DPR selected the pesticides for monitoring in two phases. Pesticides selected in the first phase were used as part of the criteria for selecting a community for monitoring. The pesticides selected in the first phase were based in part on statewide use. Once DPR selected Parlier for monitoring,



the second phase refined the pesticides selected for monitoring based on pesticide use in the Parlier area.

Following discussions with the LAG and TAG, DPR selected 24 pesticides and six pesticide breakdown products (Table 2) for monitoring in a single multi-residue method. DPR also selected metam-sodium for monitoring as a single chemical. Metam-sodium rapidly breaks down to methyl isothiocyanate (MITC), the primary pesticidal agent. DPR will monitor for MITC rather than metam-sodium. In addition, the Air Resources Board (ARB) will assist DPR by monitoring for toxic air pollutants, that includes 33 volatile organic compounds (VOCs) and 33 metals/elements (Table 3). As indicated in Table 3, ARB's VOC and metals/elements methods include several pesticides. The ARB and San Joaquin Valley Air Pollution Control District (SJVAPCD) also conduct monitoring near Parlier for 57 hydrocarbons and 12 aldehydes (Table 4) as part of the Photochemical Assessment Monitoring Stations program. A number of the VOCs and hydrocarbons included in the monitoring are likely inert ingredients in some of the pesticide products used in the Parlier area. ARB and SJVAPCD will also monitor for several criteria air pollutants in or near Parlier, including ozone and particulate matter (Table 5).

A number of important pesticides are not included in the monitoring due to resource limitations. DPR evaluated the top 100 pesticides used statewide as candidates for monitoring by rating these pesticides on toxicity, volatility and statewide use. Those pesticides with higher toxicity, higher volatility, and higher use were rated higher for monitoring. Table 6 shows the highly rated pesticides and which ones are included in the monitoring. While most of the pesticides with high use statewide also have high use in the Parlier area, a few pesticides have high use in Parlier, but not statewide. Table 7 shows the high-use pesticides in the Parlier area and which ones are included in the monitoring. Most of the high-use pesticides in the Parlier area not included in the monitoring are not highly rated for monitoring due to low toxicity and low volatility, with captan, chloropicrin, paraquat, and ziram being the exceptions.

Tables 8 and 9 show the amounts of pesticides reported and crops treated for the monitored pesticides. Figures 3 – 6 show the locations of high pesticide use in the Parlier area. Similar to other areas in the state, copper, sulfur, and the fumigants are the highest use pesticides, by far. In the Parlier area, grapes and fruit trees are the predominant crops treated with pesticides. Attachment III summarizes the products, crops, and target pests for the monitored pesticides.

### **3.2 Sampling Locations and Frequency**

DPR considered several monitoring locations in Parlier, assessing each site based on the following criteria:

- Close proximity to high use areas for multiple pesticides monitored
- Close proximity to populated areas
- Sampling point meets all U.S. EPA ambient air siting criteria
  - 2 – 15 meters above ground
  - At least 1 meter horizontal and vertical distance from supporting structure
  - Should be at least 20 meters from trees
  - Distance from obstacles should be at least twice the obstacle height
  - Unobstructed air flow for 270°

- Accessible to sampling personnel during time of sampling
- Accessible to electrical outlets
- Secure from equipment loss or tampering
- Permission of property owner

Air monitoring will occur at four locations in or near Parlier: Martinez Elementary School, Chavez Elementary School, Benavidez Elementary School, and Kearney Agricultural Center (Figure 7). DPR will conduct pesticide monitoring at Martinez School, Chavez School, and Benavidez School. ARB will conduct VOC, metal/element, and criteria air pollutant monitoring at Benavidez School. SJVAPCD will conduct hydrocarbon, aldehyde, and criteria air pollutant monitoring at the Kearney Agricultural Center.

DPR selected Martinez, Chavez, and Benavidez schools because they are in the northwest corner, southeast corner, and center of Parlier, respectively. DPR gave priority to placing monitoring locations at the edge of town and near agricultural areas, where the highest pesticide air concentrations are expected. While pesticides are applied in all areas surrounding Parlier, greater amounts of certain pesticides are applied west of Parlier, and other pesticides are applied in greater amounts east of Parlier (Figures 3 – 6). In addition, the predominant wind direction is from the northwest, so that Martinez Elementary School may have higher concentrations compared to the rest of Parlier, all other factors being equal. Benavidez Elementary School was selected because it is located near the center of Parlier and is likely the most representative single location in Parlier. VOCs, metals/elements, and particulate matter can only be monitored at a single location. Benavidez School will provide comprehensive data for both pesticides and other air pollutants at a single location. Kearney Agricultural Center was selected because SJVAPCD currently conducts its monitoring there on a routine basis.

DPR will collect 24-hour samples three consecutive days a week at each of the three schools for 52 weeks. The weekly starting day will vary through the week, but one of the DPR sample days each week will correspond with ARB's scheduled 24-hour air toxics samples. One of DPR's sampling days will also correspond with every other SJVAPCD sampling day.

As described in ARB (2005), ARB will operate an air monitoring station in Parlier for the one-year duration of DPR's pilot project and will collect samples typical of other monitoring sites for air toxics. Monitoring will be conducted at the Benavidez School as a site representative of general community exposure in central Parlier. ARB's standard toxics monitoring method for gaseous pollutants includes about 30 volatile organic compounds and includes two pesticides - methyl bromide and 1,3-dichloropropene (Telone). Air sampling filters are also routinely analyzed by ARB at air toxics monitoring sites for metals, some of which will give DPR information on metal-based pesticides such as sulfur and copper, used near Parlier. At ARB's air toxics monitoring sites throughout California, 24-hour samples are collected every 12 days. Data are used to establish annual average concentrations, which can be evaluated for trends from year to year. In some special projects, samples are collected every 6 days. In Parlier, ARB will collect 24-hour samples every 6 days, which will provide DPR with more data than would be typical of ARB's routine air toxics monitoring sites. Also, during the expected peak month of use of 1,3-dichloropropene and sulfur, ARB will collect 24-hour samples every 3 days. Figures 8-10 present historical daily application data for methyl bromide, 1,3-dichloropropene and sulfur, respectively. ARB will ship samples to ARB's lab in Sacramento,

analyze the samples, and include results of the monitoring on ARB's web site, making the results available to DPR and the public.

SJVAPCD routinely conducts monitoring for hydrocarbons and aldehydes at the Kearney Agricultural Center as part of the Photochemical Assessment Monitoring System (PAMS). SJVAPCD collects four sequential 3-hour samples (12 consecutive hours during the day) every three days between July and September. ARB's sampling days will correspond with SJVAPCD's sampling days.

Table 10 shows the frequency of all of the monitoring.

### **3.3 Sample Type**

The most widely used procedure for atmospheric measurement of pesticides is to pass 2 to 100 liters of air per minute through a solid sorbent material onto which the pesticide is adsorbed (Keith, 1988). Sorbent media typically used to trap pesticides include XAD resins and carbon sorbents such as charcoal (Majewski and Capel, 1995; Keith, 1988; Baker *et al.*, 1996). Sorbent tube samples will be collected according to procedures listed in DPR's SOP EQAI001.00 (Attachment II). The multi-residue air monitoring will be conducted using Andersen air sampling pumps equipped with a sampling tube containing 30 mL of XAD-4 set at a flow rate of 15 L/min. MITC samples will be collected with SKC Inc. personal sample pumps equipped with 200/1800 mg coconut charcoal tubes (SKC Inc., #226-16-02) set at an air flow rate of 1.5 liters per minute (L/min). The use, operation, calibration and maintenance of SKC air sampling pumps are described in DPR's SOP EQAI001.00 (Attachment II).

Prior to monitoring, sample labels with the study number and sample identification numbers will be attached to the tubes. Preparation of sorbent tubes for use with air sampling pumps is described in DPR's SOP FSAI001.01 (Attachment II). Chain of custody forms, and sample analysis request forms will be supplied to field sampling personnel. Field personnel will collect field notes on sampler location and weather observations during the monitoring study.

Once samples are collected, each tube opening will be tightly capped and samples will be placed on dry ice and remain frozen until analysis. Sample handling and shipping will follow procedures defined in DPR's SOP QAQC004.01 (Attachment II). Samples will follow the tracking procedures outlined in DPR's SOP QAQC003.02 (Attachment II). Samples will be transported to the analytical laboratory once a week.

With ARB's assistance, DPR will obtain data for VOCs, including the fumigants 1,3-dichloropropene and methyl bromide. These samples will be 24 hours in duration and most VOCs will be collected in stainless steel Summa canisters. Carbonyl compounds will be collected on Sep-Pak silica cartridges (ARB 2005).

With ARB's assistance, DPR will obtain data for metals/elements, including the copper and sulfur-based pesticides. These samples will be 24 hours in duration and collected on Teflon® filters. Samples for chromium VI will be collected on cellulose fiber filters (ARB 2005).

### **3.4 Additional Sampling**

In addition to the collection of air samples, DPR will collect ground water samples from the five municipal wells that supply drinking water for the city of Parlier. The samples will be collected once or twice during the 52-week monitoring study. The chemicals to be analyzed for are: atrazine, bromacil, diuron, hexazinone, metribuzin, norflurazon, prometon, simazine, and breakdown products desmethyl norflurazon, deethyl atrazine (DEA), deisopropyl atrazine (ACET), and diamino chlorotriazine (DACT). The samples will be analyzed by Department of Food and Agriculture, Center for Analytical Chemistry.

### **3.5 Field Tests**

The flow rate for each sampler will be measured before and after each sampling period and recorded on the chain of custody. Flows will be measured with a DryCal® primary flowmeter. All equipment will be checked and initially calibrated in the laboratory. Samples will be considered valid if the ending flow rate is within 20 percent of the starting flow rate.

### **3.6 Quality Control for Field Sampling**

In addition to field samples collected during monitoring, trip blank samples, fortified field spikes and (co-located) duplicate samples will be collected.

A trip blank sample is used to provide information on contamination of samples. For the charcoal sample tubes, the ends will be broken open, capped and placed on dry ice with the field samples. The multi-residue XAD tubes will be left capped and also placed on dry ice to be stored and shipped with the field samples. A trip blank will be collected for each sample type during one of every three weeks of sampling. Blank samples containing detectable amounts of any of the pesticides will trigger a reassessment of the field and laboratory procedures.

A fortified field spike is a laboratory spike, which is sent to the field and placed on an air sampler with air flowing through the sorbent tube. Shipped on dry ice to the field, it is treated just like a field sample, including storage and shipping conditions. The fortified spike, in comparison with the respective field sample, gives us some information about any change in the ability to recover the analyte during air sampling. DPR will collect one fortified field spike for each sample type during one of every three weeks of sampling. Spike samples outside the control limits established from the validation data for each pesticide will trigger a reassessment of the field and laboratory procedures.

A duplicate sample is a sample that is co-located with a field sample. These samples serve to evaluate overall precision in sample measurement and analysis. DPR will collect one duplicate sample for each sample type during one of every three weeks of sampling. Duplicate samples that are greater than 50 percent different will trigger a reassessment of the field and laboratory procedures.

The quality assurance team will conduct a field audit of the sampler air flow rates.

### **3.7 Meteorological Monitoring**

Meteorological stations will be located at SJVAPCD's monitoring station at the Kearney Agricultural Center and ARB's monitoring station at Benavidez School, as shown in Figure 7. The SJVAPCD station collects hourly data on wind speed, wind direction, air temperature, and relative humidity at a height of 10 meters. In addition, a sampling trailer supplied by ARB to collect air samples for analysis by the ARB laboratory will also be equipped with meteorological equipment to measure wind speed and direction, and temperature at a height of approximately 7 meters.

In addition, a California Irrigation Management Information Systems (CIMIS) station is located at the Kearney Agricultural Center. The CIMIS station provides hourly data for precipitation, solar radiation, vapor pressure, air temperature, relative humidity, dew point, wind speed, wind direction, and soil temperature.

### **3.8 Pesticide Use Data**

Universal use reporting, required by the state of California, directs all growers to submit details of pesticide usage to the County Agricultural Commissioner. All pesticide use data will be collected for the agricultural area within five miles from Parlier. The township, range and sections that will be used to define the agricultural boundary of the study area are listed in Table 11 and mapped in Figure 11. Pesticide use reports contain the following information:

- Operator identification
- Date of application
- County of application
- Pesticide product applied
- Amount of pesticide product applied
- Area/amount treated
- Site/commodity treated
- Field identification
- Location – meridian/township/range/section

## **4. SAMPLE ANALYSIS DESIGN**

### **4.1 Laboratory Analysis Methods**

Chemical analysis will be performed by the California Department of Food and Agriculture Center for Analytical Chemistry (CDFA). For the XAD cartridges, the laboratory will follow method SOP EMON-SM-05-002 (Attachment II). Pesticides will be extracted from the sorbent using ethyl acetate and analyzed with a liquid chromatograph – mass spectrometer and gas chromatograph – mass selective detector. The method will likely be revised after analysis of initial field samples

CDFA will analyze MITC samples following SOP EM 41.9 (Attachment II). In this method, the MITC is extracted from the charcoal tubes using one percent carbon disulfide in ethyl

acetate and analyzed using a gas chromatograph with a nitrogen/phosphorous detector. The method will likely be revised after analysis of initial field samples

Well water samples will be analyzed by CDFA following SOP EM 62.9 (Attachment II). The method uses two conditioned waters cartridges to retain the analytes from the water sample. The chemicals are eluted with 5% ammonium hydroxide in methanol and analyzed using liquid chromatography – Atmospheric Pressure Chemical Ionization Mass spectrometry.

ARB will analyze the VOC and metal/element samples as described in ARB (2005).

#### **4.2 Criteria Air Pollutant Monitoring**

The ARB and SJVAPCD will monitor for the criteria air pollutants ozone, nitrogen dioxide, and particulate matter-2.5 microns. Ozone will be monitored continuously and recorded as hourly averages using ultraviolet photometry. Nitrogen dioxide will be monitored continuously and recorded as hourly averages using gas phase chemiluminescence. Particulate matter, less than 2.5 microns in diameter will be monitored continuously and recorded as hourly averages using a beta attenuation monitor.

#### **4.3 Quality Assurance**

The CDFA laboratory will follow DPR's standard laboratory quality control procedures, described in SOP QAQC 001.00 (Attachment II). Prior to the analysis of field samples, the laboratory will validate the method by analyzing a series of spikes (samples containing known amounts of pesticides) to document the precision and accuracy of the methods. Trapping efficiency tests will be performed to ensure breakthrough (pesticides not adsorbed to the sorbent tube) does not occur and to check for chemical transformation of the adsorbed pesticides. Storage stability tests will be performed to document the degradation of samples between the time of sample collection and the time of sample analysis. The laboratory will include quality control samples with each batch of field samples analyzed, including blank samples (samples containing no pesticides) to check for contamination, and spikes to check the precision and accuracy.

The other laboratories will follow standard, validated methods for analysis. All laboratories will include their standard quality assurance oversight.

Additionally, DPR will establish a quality assurance team to perform audits of the project procedures. ARB will lead the quality assurance team and it will submit a questionnaire to the laboratories participating in this study. Subsequent to mailing this questionnaire, the quality assurance team will visit the laboratories before or near the beginning of the study. The audit will result in a list of items that will assist the laboratories in their efforts to produce quality data. The quality assurance team will schedule another audit during sample analysis for each laboratory. A review of raw data and laboratory tracking procedures will be conducted on a minimum of five percent of all samples collected.

#### **4.4 Method Detection Limit and Limit of Quantitation**

The laboratory determined the method detection limit for each analyte by analyzing a standard at a concentration with a signal to noise ratio of 2.5 to 5. The spiked matrix is analyzed at least seven times, and the method detection limit is determined by calculating the 99% confidence interval of the mean. This procedure is described in detail in U.S. EPA (1990). The limit of quantitation is set a certain factor above the method detection limit. The level of interference found in the samples determines this factor: the more interference, the higher the factor. The method detection limits and limits of quantitation for each pesticide are given in Table 12.

## **5. DATA ANALYSIS**

### **5.1 Calculation of Air Concentrations**

Twenty-four-hour air concentrations will be calculated from the weight of analyte per sample (determined in the chemical analysis) divided by the volume of air drawn through an air sampler during the corresponding sampling period. Concentrations will be reported in nanograms per cubic meter ( $\text{ng}/\text{m}^3$ ). Gaseous compounds will also be converted to parts per billion, volume per volume. Samples below the limit of detection will normally be treated as having one-half the detection limit, except in cases where a specific pesticide is not detected and not applied in the Parlier area, in which case DPR will likely assume that the concentration is zero. Samples with concentrations less than the limit of quantitation (reporting limit), but greater than limit of detection will be reported as having a “trace” concentration. For calculation purposes, DPR will normally assume that trace samples contain a concentration that is the average of the quantitation limit and the detection limit. Except, DPR’s monitoring methods include some pesticides not used in the Parlier area, such as molinate that is only used on rice.

DPR will estimate the pesticide air exposure for acute, seasonal, and chronic scenarios. Acute exposure will be estimated for each monitoring location from the individual 24-hour samples by calculating the 95<sup>th</sup> percentile concentration for each pesticide. Seasonal exposure will be estimated for each monitoring location from the individual 24-hour samples by calculating the average concentration during the peak season of use for each pesticide. Chronic exposure will be estimated for each monitoring location from the individual 24-hour samples by calculating the average concentration of all samples (one year) for each pesticide. Figure 12 illustrates the relationship between the detection limit, quantitation limit, and screening levels, using chlorpyrifos as an example.

### **5.2 Health Evaluation Methods**

DPR will compare these measured ambient air concentrations to human health screening levels to determine what, if any, action to take (Table 13, Attachment IV). No state or federal agency has established regulatory health standards for pesticides in ambient air (some agencies have developed occupational standards, or site-specific standards). Therefore, DPR in consultation with the TAG, has developed health screening levels for monitored pesticides to place the results in a health-based context. Although not regulatory standards, these screening levels can be used in the process of evaluating the air monitoring results. A measured air level that is below the screening level for a given pesticide would generally not be considered to represent a

significant health concern and would not generally undergo further evaluation, but also should not automatically be considered “safe” and could undergo further evaluation. By the same token, a measured level that is above the screening level would not necessarily indicate a significant health concern, but would indicate the need for a further and more refined evaluation. Significant exceedances of the screening levels could be of health concern and would indicate the need to explore the imposition of mitigation measures.

To the extent possible, the screening levels are based on toxicology values taken from existing documents. The three primary sources are risk assessments, in the form of Risk Characterization Documents (RCDs) conducted by DPR, Reregistration Eligibility Documents (REDs) completed by USEPA, and Reference Exposure Levels (RELs) established by OEHHA and peer reviewed by the Toxic Air Contaminant (TAC) Scientific Review Panel. These documents specified the studies and toxicity values to be used for various exposure scenarios (e.g. acute inhalation, chronic exposure, etc.). When REDs or RCDs are not available or appropriate values are not available, the primary source was the DPR Toxicology Database. A description of how the screening levels were calculated and the data used to determine the levels for each monitored chemical are presented in Attachment IV.

The potential health risk of a chemical(s) in air is a function of both the inherent toxicity of the chemical(s) as well as the level of exposure to the chemical(s). The potential health risk to community residents from exposure to pesticides in the air can be evaluated by comparing the air concentration measured over a specified time (e.g. 24 hours, one month, one year) with the screening level derived for a similar time (acute, seasonal, chronic). The ratio of an exposure level for a chemical (measured air concentration of a pesticide) to a reference concentration or screening level for that pesticide is called the Hazard Quotient (HQ). In this case,

$$\frac{\text{Air concentration}}{\text{Screening level}} = \text{Hazard quotient}$$

A hazard quotient is the air concentration detected expressed as the percentage of the screening level. For example, if the air concentration were 25 percent of the screening level, then the hazard quotient would be 0.25. When the hazard quotient is greater than one, the air concentration would exceed the screening level and further analysis of the data would be required.

Overexposure to pesticides can cause a variety of adverse health effects. An overview of the potential health effects for pesticides included in the monitoring is given in Attachment IV. Pesticides may exhibit toxic effects independently, or they may interact in an additive, synergistic, or antagonistic manner. As a preliminary approach, DPR will estimate risk from multiple pesticides by adding all of the hazard quotients for the individual pesticides:

$$\text{Hazard Index} = \begin{array}{l} \text{Hazard Quotient of Pesticide 1} \\ + \text{Hazard Quotient of Pesticide 2} \\ + \text{Hazard Quotient of Pesticide 3} \dots \text{(and so forth)} \end{array}$$



This approach assumes that toxicity and risk of all monitored pesticides are additive, although only a subset of the monitored pesticides (including organophosphate insecticides and oxygen analog breakdown products toxic to the nervous system) are known to act in an additive manner. U.S. EPA has developed more refined methods for analyzing cumulative impacts of pesticides, and these, the hazard quotient approach, and other avenues will be explored.

Should levels of pesticides be found above screening levels, it can trigger additional data collection and evaluation, in Parlier and elsewhere. The data helps DPR to evaluate the geographic scope, timing and use factors that contributed to the air concentrations. These and other data can establish parameters of problematic residues. The data are necessary to develop effective measures to minimize or eliminate unacceptable air exposures, and are required by law to support regulatory action.

### **5.3 Methods for Estimating Air Concentrations for Locations, Time Periods, and Pesticides Not Monitored**

In some studies, computer modeling can be attempted to estimate ambient air concentrations from pesticide applications made during monitoring, provided meteorological measurements and application/sampling site information are available. Thus, modeling can be used to supplement measured air concentrations to determine potential concentrations at places and time periods other than the ones monitored, or in the event a large application, or one close to the city limits occurs. The strength of this approach is the flexibility afforded by modeling. It can provide air concentration estimates within city limits given application scenarios that occur outside of the monitoring period.

Using the data collected from the County Agricultural Commissioner's Office on pesticide use within the study area, an attempt will be made to use modeling to estimate air concentrations expected at locations other than sampling sites within the city area of Parlier. Modeling may be able to estimate concentration of the applied pesticides during times when samples were not collected. The U.S. EPA gaussian plume dispersion model, Industrial Source Complex Short Term model (U.S. EPA, 1995) may be used to estimate the modeled concentrations. As model inputs, DPR will use the following: 1) flux rates back-calculated from application site monitoring using the procedures described in Ross, et al. 1996, or measured flux rates from other studies; 2) weather data recorded during the monitoring period. Additional parameters and modifications to this proposed modeling scheme could be addressed in future TAG meetings.

### **5.4 Estimating Cumulative Impacts**

Under Cal/EPA's Environmental Justice Action Plan, the Office of Environmental Health Hazard Assessment (OEHHA) has been designated to develop approaches to the evaluation of cumulative impacts for the regional /pilot projects, including DPR's Parlier project. As part of this process, OEHHA is examining the feasibility of using existing statewide data sources to characterize the potential for cumulative impacts from pollutant hazards from multiple sources and routes of exposure across different geographic areas (e.g., contaminants in drinking water or nearby stationary sources of air pollution). The Parlier pilot project is also evaluating the potential for adverse health effects based upon the pesticide and air toxics data that will be

accumulated during the 2006 monitoring. These data will be evaluated using a traditional hazard assessment approach, as described in Section 5 (Data Analysis).

## **6. RELATED PROJECTS**

DPR hopes to coordinate with several others to provide additional information on potential health effects of pesticides and other pollutants in Parlier.

### **6.1 University of California, Davis (UCD)**

Kent Pinkerton of UCD's Center for Health and the Environment is interested in collaborating on this project to examine the potential health effects of exposure to ambient airborne particles to the respiratory system in the Parlier area. In collaboration with engineers at UCD and the University of Southern California, the Center for Health and the Environment has acquired a special mobile system that allows them to concentrate in real-time, airborne particles to levels 20 to 40-fold above ambient concentrations. The system is designed to uniformly capture and concentrate particles from ultrafine (20 nanometer) to coarse (10 micron) size. These particles are concentrated without ever letting the particles deposit on a surface. In this manner small laboratory animals can be exposed to these concentrated particles in real time while the particles are passing through this system. In essence, with this system animals can be exposed to real world particles under conditions that might mimic a bad air pollution day. DPR will work with UCD to find a suitable location for this system in or near Parlier.

### **6.2 University of California, San Francisco (UCSF)**

Tim Tyner of UCSF's Valley Air Pollution and Health Effects Research (VAPHER) Institute in Fresno proposes a study on the health impacts of cumulative pesticide exposures on children in Parlier. This case-crossover study will assess the acute effects of pesticide/pollutant exposures on the probability of a health event. VAPHER will collect children's health data in Parlier from the United Health Center clinic, four elementary schools, and asthma data from the Health Education and Access for Life program. VAPHER will attempt to evaluate the recorded health events with pesticide air concentrations to determine if there are any correlations.

## **7. RISK REDUCTION AND PRECAUTIONARY APPROACHES**

### **7.1 Pest Management Analysis**

DPR's Pest Management Analysis and Planning Program will conduct a study in the project area of cropping patterns, pest pressures, pest control practices, pesticide use, application methods, and alternative pest management techniques, with a focus on integrated pest management. DPR will coordinate its study with ongoing work already being done in the Parlier area: for example, the Almond Pest Management Alliance and Outreach Project; DPR's federally funded project to develop organophosphate alternatives for stone fruit; the Code of Sustainable Winegrowing Practices developed by the California Association of Winegrape Growers and the Wine Institute; and research and extension activities by the world-renowned

University of California Kearney Agricultural Center in Parlier, in particular those directed towards the development of ecologically-based pest management systems for insect pests in orchards and vineyards.

## **7.2 Evaluation of Results and Follow-up Actions**

The monitoring results will be evaluated to determine the exposure and risk from individual as well as multiple pesticides. The data will be compared to historical monitoring results from other areas. DPR will also evaluate the results and pesticide use patterns at the time of monitoring to determine possible mitigation measures, as well as other potential areas and time periods for future monitoring. DPR is developing sampling and laboratory methods that provide flexibility so that they can be used in other areas with minimal additional work.

With assistance from ARB, DPR will also compare air concentrations of criteria pollutants, volatile organic compounds, and metals in Parlier with other areas of the state and determine if Parlier has elevated levels of these pollutants.

In situations where ambient air levels of pesticides lead to exposures of regulatory concern, DPR determines options to reduce ambient air concentrations. The options range from regulatory restrictions on the use of certain pesticides to seeking grant monies to promote alternative pest management strategies. While the focus of these efforts may be derived from the results of air monitoring, if other datasets evaluated by DPR (for example, groundwater pesticides data) demonstrate the need for further action, DPR addresses these also.

This project presents a number of opportunities for exploring the precautionary approach and supporting growers in the process. The type of actions DPR may take to change pesticide use practices can include:

- Collaborative efforts can be pursued with UC Cooperative Extension and the United States Department of Agriculture Natural Resources Conservation Service on education and financial support for growers on pest management alternatives. Evaluating and promoting the use of alternatives is a key element of precaution.
- DPR may seek grant monies to support public/private partnerships to develop and promote pest management alternatives.
- DPR's study of pest management practices in the Parlier area is intended in part to identify lower-risk alternatives. Outreach efforts will be explored to ensure that farmers are aware of the availability of and familiar with the use of these alternatives.
- A risk reduction approach could be focused on local and state enforcement efforts on eliminating illegal pesticide application practices that result in problematic levels of pesticides in air.

- Training pesticide applicators on best management practices (BMPs) can also be expanded. (BMPs are management and cultural activities and practices, general good housekeeping practices, pollution prevention and educational practices, maintenance procedures, and other management practices or devices, or prohibitions of practices, to prevent or minimize harm to health and the environment. These practices are defined by research and field testing to be the most effective and practicable methods.)
- DPR can also work with the registrant and the U.S. Environmental Protection Agency to make improvements to the pesticide product label. Among other elements, the label includes instructions and restrictions on product use. (Under federal law, states are precluded from mandating changes in pesticide labels.)

These and other risk reduction measures can be used singly or in combination.

## 8. SCHEDULE

The following is the estimated schedule for completing this project. All dates are subject to change.

Activity	Start Date	End Date
Write protocol	August 1, 2005	December 16, 2005
Collect field samples	January 1, 2006	December 31, 2006
Conduct laboratory analysis	January 2006	February 2007
Conduct QA audits	January 2006	January 2006
Public Forum in Parlier	January 28, 2006	
Conduct data analysis	March 2006	August 2007
Issue first progress report	April 2006	
Conduct QA audits	April 2006	August 2006
Issue second progress report	October 2006	
Issue third progress report	April 2007	
Write final report	July 2007	October 2007
Conduct public forum	October 2007	

## REFERENCES

ARB. 2005. Parlier Community Air Monitoring Project, Air Monitoring Plan for S. Ben Benavidez Elementary School. Air Resources Board, Monitoring and Laboratory Division.

Baker, L.W., D.L. Fitzell, J.N. Seiber, T.R. Parker, T. Shibamoto, M.W. Poore, K.E. Longley, R.P. Tomlin, R. Propper, and D.W. Duncan. 1996. Ambient air concentrations of pesticides in California. *Environ. Sci. Technol.* 30:1365-1368.

DPR. 1995. Pesticide Use Reporting: An Overview of California's Unique Full Reporting System. State of California. Department of Pesticide Regulation

DPR. 2003. Ambient Air Monitoring for Pesticides in Lompoc, California. Volumes 1 - 4. State of California. Department of Pesticide Regulation. March 2003. EH03-02.

DPR. 2005. Environmental Justice Pilot Project – Project Objectives, Pesticides, and Community for Monitoring. State of California. Department of Pesticide Regulation. June 2005.

Keith, L.H. 1988. Principles of Environmental Sampling. American Chemical Society. 458 pp.

Kollman, W.S. 1995. Pesticide air monitoring results. Report EH 95-10. State of California. Department of Pesticide Regulation.

Majewski, M.S. and P.D. Capel. 1995. Pesticides in the Atmosphere. Distribution, Trends, and Governing Factors. Ann Arbor Press, Inc. Chelsea, MI. 214 pp.

Ross, L.J., B. Johnson, K.D. Kim and J. Hsu. 1996. Prediction of methyl bromide flux from area sources using the ISCST model. J. Environ. Qual. 25(4):885-891.

U.S. EPA. 1990. Definition and Procedure for the Determination of the Method Detection Limit, Revision 1.11. Code of Federal Regulations, Title 40, Part 136, Appendix B.

U.S. EPA. 1995. User's Guide for the Industrial Source complex (ISC3) Dispersion Models. Volume 1. User Instructions. USEPA Office of Air Quality Planning and Standards; Emissions, Monitoring and Analysis Division, Research Triangle Park, North Carolina.

U.S. EPA. 2004. Results of Air Sampling. MacFarland Outdoor Air Investigation (Fact sheet 2 of 2). Dated October 2004. U.S. EPA, Region IX. San Francisco, CA