Air Monitoring for Chlorpyrifos in the Yakima Valley, Washington, April 2006

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Executive Summary

This report presents the results of air monitoring in populated areas in the towns of Tieton and Cowiche in the Yakima Valley, Washington for chlorpyrifos and its oxon degradation product during April 2006. Monitoring was conducted to coincide with the spring use of chlorpyrifos as an insecticide pre-bloom for the control of coddling moth and leafroller pests.

Chlorpyrifos is an organophosphorus insecticide that is neurotoxic to both insects and mammals, inhibiting acetyl cholinesterase, an enzyme necessary for proper transmission of nerve impulses. High levels of exposure to these types of pesticides are among the leading causes of acute pesticide poisonings in the U.S. Low levels of exposure during fetal and infant development have been linked to developmental deficits of the nervous system.

The US Environmental Protection Agency (EPA) recently banned all residential uses of chlorpyrifos; however, agricultural use continues. Nationwide in 2001, US EPA estimated that 11-16 million pounds of chlorpyrifos were used, second only to malathion for US insecticide use.

Sample results from air monitoring in Tieton and Cowiche, WA are reported in Tables 5 and 6.

Of the 21 samples collected (spikes and blanks excluded) between April 3rd and April 23rd in Cowiche, all were found to be above the limit of quantitation (LOQ) of 20 nanograms (ng) of chlorpyrifos per sample (equivalent to an air concentration of 7 ng/m^3 for a 24-hour sample at a 2 L/min flow rate and using a 2.65 mL solvent extraction volume). Thirty three percent of the samples were above the 24-hour acute and sub-chronic child REL of 170 ng/m^3, calculated from the US Environmental Protection Agency's inhalation No Observed Adverse Effect Level (NOAEL), as shown in Appendix 2. The highest concentration observed for a 24-hour period was 572 ng/m^3 (3.4 times the 24-hour acute child REL) on April 12, 2006.

Of the 21 samples collected (spikes and blanks excluded) between April 1st and April 21st in Tieton, all were found to be above the limit of quantitation (LOQ) of 20 nanograms (ng) of chlorpyrifos per sample (equivalent to an air concentration of 7 ng/m^3 for a 24-hour sample at a 2 L/min flow rate and using a 2.65 mL solvent extraction volume). Thirty eight percent of the samples were above the 24-hour acute and sub-chronic child REL of 170 ng/m^3, calculated from the US Environmental Protection Agency's inhalation No Observed Adverse Effect Level (NOAEL), as shown in Appendix 2. The highest concentration observed for a 24-hour period was 475 ng/m^3 (2.8 times the 24-hour acute child REL) on April 13, 2006.

The chlorpyrifos oxon degradation product was not detected in any of the samples.

About Chlorpyrifos

Chlorpyrifos is an organophosphorus insecticide used in agriculture primarily on cotton, oranges, corn, and almonds, among many other crops. Also known as Dursban (residential products) or Lorsban (agricultural use products), among other trade names, and manufactured predominantly by Dow AgroSciences, chlorpyrifos is one of the most widely used insecticides in the U.S.[1] Nationwide in 2001 (prior to the cancellation of residential uses), US EPA estimated that 11–16 million pounds of the insecticide were used, second only to malathion for insecticide use.[2]

Chlorpyrifos was widely used in residential insecticide products until U.S. EPA reached an agreement with the registrants in 2000 to change residential uses, including a phase-out of use in and around homes by the end of 2005 due to high risks to children, and the cancellation of chlorpyrifos use in schools, parks and other places where children might be exposed. U.S. EPA estimates that these residential uses accounted for about 50% of the total nationwide in 2001.[3] Major agricultural uses altered by this phase-out agreement include elimination of use on tomatoes and changes in use patterns for apples and grapes to reduce residue levels in harvested produce.

Chlorpyrifos Use in Washington State

In 2003 (the most recent data available) 269,000 pounds of chlorpyrifos were applied to apples, cherries and pears in Washington State.[4] Sixty-three percent, 57 % and 42 % of the acres for each of those crops respectively were treated with chlorpyrifos (Table 1).

Table 1: Use of Chlorpyrifos in Washington State in 2003

Crop	% treated acres	Total active ingredient applied, 1000 lb/year
Apples	63	217
Cherries	57	31
Pears	42	21

Source: National Agricultural Statistics Service.

According to an EPA Fact Sheet published in 2002 to accompany the IRED for chlorpyrifos, approximately 10 million pounds of chlorpyrifos are applied annually in agricultural settings in the United States.[5] The data available on chlorpyrifos use on apples, cherries and pears nationally is shown in Table 2. For these crops, Washington state has the highest use of chlorpyrifos in the nation.

Table 3 shows changes in chlorpyrifos use between 1991 and 2005.[6] Use on apples has declined since 1997, although new restrictions on permitted uses of azinphos-methyl may lead to increased chlorpyrifos use in the future. There are no apparent trends in chlorpyrifos use on cherries and pears.

Table 2: Use of Chlorpyrifos on Apples, Cherries and Pears in the U.S.

State/Area (Crop)	% treated acres	Total active ingredient applied, 1000 lb/year
APPLES		
California	12	6.0
Michigan	57	27.0
New York	32	14.0
North Carolina	46	6.0
Oregon	73	9.0
Pennsylvania	27	5.0
Washington	63	217.0
Subtotal Apples		**284**
CHERRIES		
California	1	-
Michigan	3	-
Oregon	64	18.0
Washington	57	31.0
Subtotal Cherries		**49.0**
PEARS		
California	12	3.0
Oregon	12	4.0
Washington	42	21.0
Subtotal Pears		**28.0**
Total (Apples, Cherries, Pears)		**361.0**

Source: US Department of Agriculture.[7]

Table 3: Changes in Chlorpyrifos use in Washington State Over Time

	1991	1993	1995	1997	1999	2001	2003	2005
	Percentage of acres treated							
Apples	65	85	80	91	65	68	63	55
Cherries	15	74	49	59	59	48	57	44
Pears	12	28	37	57	59	33	42	22
	Total active ingredient applied, 1000 lbs/yr							
Apples	234.6	276.6	268.5	360.2	250.9	234	217	186.7
Cherries	4	19.1	14	17.2	20.6	21.6	31	26.5
Pears	5.2	16.6	16.6	28.7	28.3	17.1	21	13.2

Physical Properties

Technical chlorpyrifos [O,O-diethyl O-(3,5,6-trichloro-2-pyridinyl) phosphorothioate] is a crystalline solid, white to amber in color, with a mild mercaptan-like odor. Physical properties of chlorpyrifos are shown in Table 4.[8]

Table 4: Properties of Chlorpyrifos

Property	Value
Molecular Weight	350.59 g/mole
Water Solubility	1,390 μg/L
Specific Gravity	1.398 @ 43.5 °C
Henry's Constant	4.16×10^{-6} atm-mol/m^3 @ 25°C
Vapor Pressure	1.7×10^{-5} mm Hg @ 25°C
Avg. Hydrolysis Half Life	58 days
Avg. Aerobic Soil Half Life	113 days
Avg. Anaerobic Soil Half Life	136 days

Chlorpyrifos is a semi-volatile chemical that, under conditions of use in the Yakima Valley with upwards of 95°F temperatures common during summer months, readily volatilizes from leaf and soil surfaces to become airborne. It does not degrade quickly in the environment and is transported away from the application site by prevailing winds. Because of their volatility, chlorpyrifos products are substantial contributors to Volatile Organic Compounds (VOCs). VOCs are precursors to ground-level ozone, a major contributor to asthma.

Health Effects

Chlorpyrifos is an organphosphorus compound that inhibits acetyl cholinesterase, an enzyme necessary for proper transmission of nerve impulses in both insects and mammals.[9] Symptoms of low-dose exposure may include headaches, agitation, inability to concentrate, weakness, tiredness, nausea, diarrhea and blurred vision. At higher doses, abdominal cramps, vomiting, sweating, tearing, muscular tremors, pinpoint pupils, low blood pressure, slow heartbeat and breathing difficulty may be observed.[10]

The Association of Occupational and Environmental Clinics (AOEC) lists all organophosphorus compounds generally and chlorpyrifos specifically as capable of causing asthma in previously unaffected individuals.[11] Exposure can also exacerbate asthmatic symptoms in individuals who already have the disease.

In addition to acute symptoms from high exposures, many recent studies indicate that low-level exposure to chlorpyrifos interferes with the development of the nervous system in fetal and neonatal rats. Neural cell replication and differentiation are both affected, with a reduction in the number of neural connections observed in exposed rats. [12] Substantial progress is being made in understanding the mechanism of these effects.[13]

Human epidemiological studies on pregnant mothers exposed to chlorpyrifos through involuntary home pesticide use demonstrate a link between *in utero* exposure to chlorpyrifos and low birth weights and reduced head circumference of newborns in the study, most significantly for mothers whose genetic makeup is such that they produce low levels of PON1, the enzyme that is responsible for detoxifying chlorpyrifos and its oxon in the body.[14] Evaluation of this cohort of children at one, two and three years of age showed statistically significant cognitive and psychomotor delays in highly exposed children. These children were also significantly more likely to be diagnosed with attention deficit hyperactivity disorder and pervasive developmental disorders than the lower exposed group.[15]

Chlorpyrifos is also a suspected endocrine disrupting compound; moderate doses have been shown to alter hormone levels in animal studies.[16]

A study of children in Oregon and North Carolina found that children of farm workers "performed poorer on measures of response speed (Finger tapping) and latency (Match-to-Sample) compared to children not living near fields. These results demonstrate modest differences in farm worker children compared to control group that are consistent with functional effects seen in adults exposed to low concentrations of organophosphate pesticides."[17]

A study of adults in Oregon found that "the neurobehavioral performance of Hispanic immigrant farmworkers to be lower than that observed in a nonagricultural Hispanic immigrant population, and within the sample of agricultural workers there was a positive correlation between urinary organophosphate metabolite levels and poorer performance on some neurobehavioral tests."[18]

An analysis of data from over 18,000 applicators in the Agricultural Health Study found a higher incidence of neurologic symptoms associated with cumulative lifetime days of insecticide use.[19] Among classes of insecticides, associations were strongest for organophosphates. Associations with cumulative exposure persisted after excluding individuals who had a history of pesticide poisoning or had experienced an event involving high personal pesticide exposure. These results suggest that self-reported neurologic symptoms are associated with cumulative exposures to moderate levels of organophosphates, even in the absence of an acute poisoning episode.

Preliminary findings from a study in North Dakota indicate that children exposed to agricultural pesticides used near their homes have lower IQs compared to the children not experiencing those exposures. The pesticide-exposed children had lower full scale IQ in general, and also did more poorly than the less-exposed children in terms of scores on various neurobehavioral tests such as for verbal comprehension, perceptual reasoning, working memory and processing speed.[20]

In addition to heightened vulnerability to chlorpyrifos because of their developing nervous systems, children are likely to be exposed to higher levels of chlorpyrifos than adults for several reasons. Children eat, breathe, and drink more per pound of body weight than adults, so the effects of any chlorpyrifos-contaminated food, water or air is magnified relative to that experienced by adults. Children also play on the floor and in the grass where pesticide residues collect and exhibit hand-to-mouth behaviors that increase their potential for exposure.

In a risk assessment finalized in 2002,[21] U.S. EPA determined an "acceptable" dose of chlorpyrifos via inhalation to be 0.1 milligrams per kilogram of body weight per day (mg/kg-day), which translates into a Reference Exposure Level (REL) of 3,880 ng/m^3 for a 70 kg adult and 170 ng/m^3 for a one-year-old child (see Calculations section). Sub-chronic and acute RELs are identical for this pesticide. These values include an additional uncertainty factor of 10 to allow for the particular vulnerability of children to chlorpyrifos.[22] Recent research indicates that this factor of ten is insufficient to protect children. According to a University of California, Berkeley research team, newborns can be 65 to 164 times more vulnerable than adults to the common organophosphate pesticides chlorpyrifos and diazinon.[23]

Chlorpyrifos Airblast Applications Associated with Cholinesterase Depression in Workers

Washington State began medical monitoring for farm workers who regularly handle organophosphates and/or carbamates in 2004. The program tracks levels of cholinesterase through blood tests. In the first year of the program, 20% of workers tested showed depressions in cholinesterase after handling those pesticides that triggered action under the state program. In 2005, 10% of a larger pool of workers tested had cholinesterase depressions high enough to trigger state action.[24]

While in most cases affected workers had handled a number of different pesticides, chlorpyrifos was the pesticide most implicated in nervous system impacts in both years. In 2004, 62 of 65 workers (95.38%) had handled chlorpyrifos. In 2005, 44 of 55 workers (80%) for whom use data was available had handled chlorpyrifos. In a report to the state legislature in January of 2006, the state Department of Labor & Industries noted that “The majority of significant cholinesterase depressions occurred during the beginning of the tree fruit application season (dormant season spraying)….During dormant season spraying, the organophosphate Lorsban™ (chlorpyrifos) is used. The fact that the majority of significant cholinesterase depressions were due to depression of serum cholinesterase is consistent with the use of chlorpyrifos as it has an affinity to bind with serum cholinesterase.”[25]

The Washington State medical monitoring results raise concerns about airborne chlorpyrifos not only for pesticide handlers but also for others working or living near applications. Even with respirators and other protective gear, handlers experience significant nervous system impacts associated with airblast applications of chlorpyrifos. Individuals nearby who lack protective gear may face risks that are as high or even higher than those of the handlers.

Prior Chlorpyrifos Air Monitoring

As part of the implementation of the California Toxic Air Contaminant act, application site monitoring of a chlorpyrifos application to a Tulare County orange grove, as well as longer-term, seasonal monitoring in an area of high chloryprifos use was conducted by the California Air Resources Board (ARB) in the Lindsay area during June 1996. The results of this study indicated the potential for high exposures both immediately adjacent to application sites and even in areas of high use that were not directly adjacent to an application site.[26]

Application Site Monitoring by ARB

Figure 1 shows ARB monitoring results from a chlorpyrifos application to an orange grove in terms of measured air concentrations of chlorpyrifos over time for sampling sites approximately downwind of the grove (see Appendix 1 for the full data set and application parameters). Because of high winds, the application was stopped after approximately half the orchard was sprayed. The application was completed the next day, with lighter winds coming from a different direction. Air concentrations peaked at 30,950 ng/m^3 at the east downwind site 30 feet from the field boundary during the 2.5 hour sampling period after completion of the first application.[27] A slightly lower peak concentration of 27,700 ng/m^3 at 57 feet from the field boundary was observed during the second application on the north (downwind) side of the field. High winds quickly cleared much of the chlorpyrifos out of the air near the application site between the two applications, but concentrations following the second application remained high much longer due to lighter wind conditions.

Concentrations exceeded RELs in 95% of samples, with three-day, time-weighted averages ranging from 5,312 to 8,112 ng/m^3 (depending on the location of the monitoring station), 31 to 48 times the child REL and 1.4 to 2.1 times the 24-hour adult REL. Concentrations of chlorpyrifos were still above both the adult and child RELs at the downwind site at the end of the monitoring period, at 4,900 ng/m^3 (29 times the child REL and 1.3 times the adult REL). These data indicate that those who live, work, or go to school near application sites risk acute nervous system toxicity from airborne exposure to this pesticide. The developing fetus, infants and children are especially at risk because their nervous systems are still developing.

ARB only conducted a single application site monitoring study for chlorpyrifos; however, the fact that the application occurred in two distinct time periods provides essentially two applications in one study. The similar peak concentrations observed for the two applications under different wind conditions (30,950 ng/m^3 vs. 27,700 ng/m^3) suggest that peak air concentrations may be quite predictable. The breakdown product chlorpyrifos oxon was observed in 100% of the samples, but the toxicity of this substance was not taken into account in this analysis because no RELs are available for comparison. However, because the oxon is more acutely toxic than the parent compound, neurotoxic effects associated with breathing air contaminated with both chlorpyrifos and its oxon at the measured levels will be greater than chlorpyrifos concentrations alone would suggest.

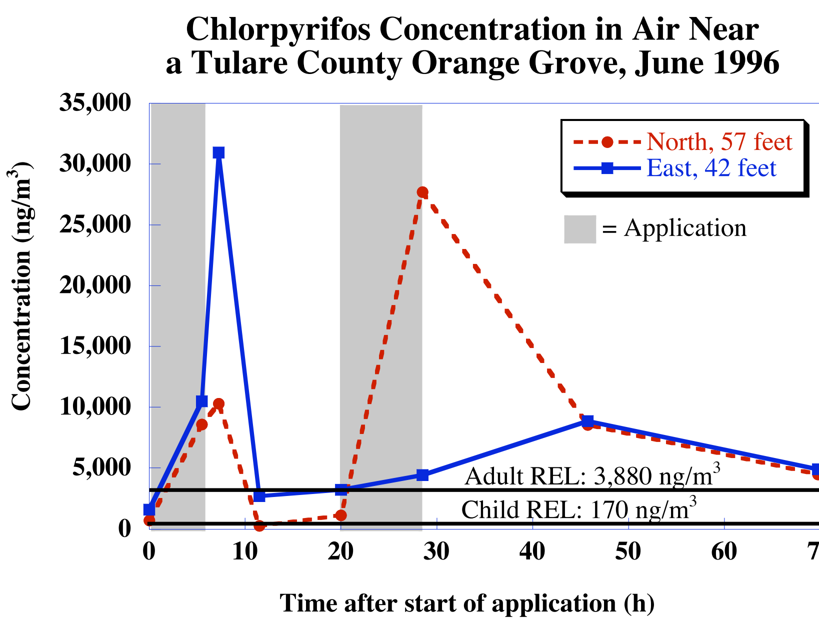


Figure 1: Chlorpyrifos air concentrations peaked approximately 2.5 hours after the end of the first application and again during the second application, with maximum concentrations on the downwind side of the orchard exceeding the adult acute REL by a factor of eight and the child acute REL by 184. Off-gassing continued for several days after application and exceeded RELs for both adults and children for much of the sampling period. (Data source: Reference 25.)

Seasonal Air Monitoring by ARB

ARB also sampled seasonal concentrations of chlorpyrifos in ambient air by placing monitoring stations on several schools somewhat distant from direct applications but in regions of high use. Monitoring occurred over the course of four and a half weeks, which serves as an estimate of sub-chronic exposure (Figure 2). For chlorpyrifos, acute and sub-chronic RELs are the same. Average concentrations were below both adult and child RELs over the time frame of the monitoring study, averaging 38% of the one-year-old child REL over all sites. The maximum measured 24-hour concentrations equaled or exceeded the child REL at four of the five monitoring sites and ranged from 0.23 to 4.8 times the child REL, exposures that may have acute neurotoxic effects in some children. Because chlorpyrifos is also present as residues on foods, and because other OP pesticides with a similar mechanism of action are also used on foods and are present in the air, aggregate exposures will be higher for some individuals.

Based on the ARB data, scientists at the California Department of Health Services concluded that short-term exposures to chlorpyrifos were above the REL for 50% of children in the areas near the monitoring stations, which were placed on fire stations and at schools in the town.[28] The scientists noted that combining the results of their analysis with census data suggest a potential for similar exposures and risks for hundreds of thousands of people in California. They pointed out that farm workers and their children may be at higher risk than the general population and urged Washington State to pay heed to their results given parallels in pesticides usage in Washington

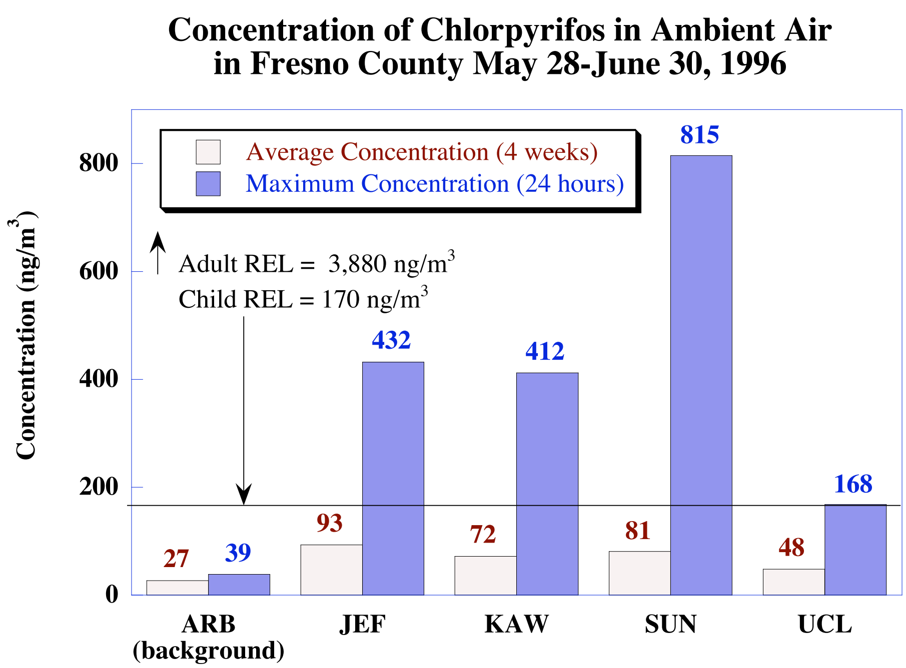


Figure 2: Four-and-a-half-week average chlorpyrifos concentrations in ambient air in Tulare County ranged from 16 to 55% of acute and sub-chronic RELs for a one-year-old child. Concentrations occasionally exceeded the child acute REL during a 24-hour monitoring period, with the maximum 24-hour concentration at each site ranging from 23 to 485% of the acute REL. Monitoring sites included ARB, the ARB office in downtown Visalia; JEF, Jefferson Elementary School in Lindsay; KAW, Kaweah School in Exeter; SUN, Sunnyside Union Elementary School in Strathmore; UCL, University of California, Lindcove Field Station. (Data source: Reference 25.)

Siting the Cowiche and Tieton Studies

The study locations were selected as the result of outreach in the Cowiche area outside of Yakima, Washington, a rural location with many different orchards. There is a high concentration of farm worker homes near the orchards.

The Cowiche Drift Catching project was carried out by a former farm worker in the backyard of the home he shares with his wife and three children (ages 3, 8 and 12). An apple orchard is located southwest of the family's home, approximately 19 feet from their yard, and 115 feet from their house. The Drift Catcher was set up next to the garage 57 feet southeast of the orchard. Prevailing winds shifted several times during the 3-week sampling period. The house was predominantly upwind of the orchard from April 3-10, downwind from April 11-16, and no predominant wind direction was noted from April 17-23. Peak concentrations correlated with winds blowing from the orchard.

The Tieton air monitoring was done at the home of two farm workers. At the time of the testing, the family had three children (ages 2, 5 and 8) and the mother was pregnant with a fourth child. The Tieton home is surrounded by orchards, with the nearest being less than 46 feet from the house. The Drift Catcher was set up immediately next to the house at a point that was 46 feet from the nearest orchard trees, and the sample tubes were changed daily for three weeks. Winds were light and variable during the sampling period.

Drift Catcher at Tieton house.

View of back of house in Tieton from orchard.

Orchard from back of Tieton house.

Drift Catcher next to garage behind house in Cowiche

View of garage, Drift Catcher and orchard in Cowiche..

Unknown pesticides being applied to the orchard after drift catching project had ended.

Results

Of the 21 samples collected (spikes and blanks excluded) between April 3rd and April 23rd in Cowiche, 81% were found to be above the limit of quantitation (LOQ) of 20 nanograms (ng) of chlorpyrifos per sample in the PANNA lab (equivalent to an air concentration of 7 ng/m^3 for a 24-hour sample at a 2 L/min flow rate and using a 2.65 mL solvent extraction volume). Thirty three percent of the samples were above the 24-hour acute and sub-chronic child REL of 170 ng/m^3, calculated from the US Environmental Protection Agency's inhalation No Observed Adverse Effect Level (NOAEL), as shown in Appendix 2. The highest concentration observed for a 24-hour period was 572 ng/m^3 (3.4 times the 24-hour acute child REL) on April 12, 2006. Duplicate Cowiche samples were analyzed by EMA Labs, Inc. Because PANNA's lab chlorpyrifos recoveries averaged 102% and EMA Labs' chlorpyrifos recoveries averaged 65% (probably because of the different solvents used in the two labs), the EMA labs results were corrected to 100% to account for low recoveries.

Of the 21 samples collected (spikes and blanks excluded) between April 1st and April 21st in Tieton, all were found to be above the LOQ of 20 ng/sample (equivalent to an air concentration of 7 ng/m^3 for a 24-hour sample at a 2 L/min flow rate and using a 2.65 mL solvent extraction volume). Thirty eight percent of the samples were above the 24-hour acute and sub-chronic child REL of 170 ng/m^3, calculated from the US Environmental Protection Agency's inhalation NOAEL, as shown in Appendix 2. The highest concentration observed for a 24-hour period was 475 ng/m^3 (2.8 times the 24-hour acute child REL) on April 13, 2006. Duplicates were run by the PANNA lab for most samples.

Complete results are provided in Tables 5 and 6, and plots of the daily chlorpyrifos concentration for each site are presented in Figures 3 and 4 for most days during the sampling periods. No chlorpyrifos oxon was detected in any of the samples. No chlorpyrifos was detected in any of the rear beds of the XAD-2 resin tubes, indicating that there was no breakthrough of chlorpyrifos from the front resin bed to the rear, i.e. no overloading of the sampling tubes. Samples with concentrations above the method detection limit (MDL) but below the Limit of Quantitation (LOQ) were estimated at half the LOQ, according to standard procedure.[29]

For the samples analyzed in the PANNA lab, the Method Detection Limit (MDL) was 1.4 ng/m^3. The Limit of Quantitation (LOQ) was estimated at five times the MDL or 7 ng/m^3. The MDL for EMA Labs was 1.7 ng/m^3, with an LOQ of 9 ng/m^3.

Table 5: Chlorpyrifos Air Concentrations in Cowiche, WA, April 3–April 23, 2006

Sample Name	Start Date	Start Time	Total Time (min)	Total Volume (m^3)	Conc. (ng/m^3) PANNA	Conc. (ng/m^3) EMA	Comment
Ama	4/3/06	5:04 PM	1630	3.42	19	9	
Tiempo	4/4/06	8:55 PM	1420	3.09	54	60	
Vaca	4/5/06	8:59 PM	1407	3.08	20	15	
Arroz	4/6/06	8:49 PM	1328	2.84	203	180	
Musica	4/7/06	7:20 PM	1473	3.24	168	157	
Azucar	4/8/06	8:12 PM	1235	2.72	86	68	
Pan	4/9/06	5:02 PM	1375	2.94	140	79	
Yunta	4/10/06	4:14 PM	1678	3.67	145	114	
Una	4/11/06	8:27 PM	1443	3.21	338	187	
Hueso	4/12/06	8:45 PM	1404	2.93	462	681	
Primo	4/13/06	8:24 PM	1397	3.00	---	261	"A" tube broke.
Papel	4/14/06	7:58 PM	1392	3.08	320	192	
Mango	4/15/06	7:23 PM	1379	3.02	216	169	
Coche	4/16/06	6:39 PM	1456	3.19	228	187	
Futbol	4/17/06	7:15 PM	1488	3.20	140	117	
Lengua	4/18/06	8:23 PM	1128	2.48	133	93	
Bola	4/19/06	3:24 PM	1716	3.67	178	128	
Copa	4/20/06	8:13 PM	1207	2.66	179	122	
Rapido	4/21/06	4:33 PM	1359	2.92	32	33	
Santo	4/22/06	3:25 PM	1690	3.59	19	26	
Mejor	4/23/06	7:49 PM	1270	2.76	16	20	

Table 6: Chlorpyrifos Air Concentrations in Tieton, WA, April 1-April 21, 2005

Sample Name	Start Date	Start Time	Total Time (min)	Total Volume (m^3)	Conc. (ng/m^3)	Comment
Hombre	4/1/06	2:40 PM	1423	3.06	194	Duplicate. Average of 194 and 194 ng/m^3.
Zona	4/2/06	2:44 PM	1515	3.26	46	Duplicate. Average of 50 and 41 ng/m^3.
Puro	4/3/06	4:20 PM	1489	3.28	156	Duplicate. Average of 161 and 151 ng/m^3.
Pico	4/4/06	5:25 PM	1331	3.29	220	Duplicate. Average of 228 and 211 ng/m^3.
Oido	4/5/06	3:53 PM	1436	3.09	149	Duplicate. Average of 146 and 151 ng/m^3.
Ejido	4/6/06	4:09 PM	1526	3.24	55	Duplicate. Average of 51 and 59 ng/m^3.
Fuego	4/7/06	5:51 PM	1231	2.65	182	
Caldo	4/8/06	2:37 PM	1584	3.48	120	
Fin	4/9/06	5:15 PM	1336	2.87	100	
Rosa	4/10/06	3:41 PM	1426	3.14	403	
Linea	4/11/06	3:42 PM	1453	3.20	366	
Bolsa	4/12/06	4:08 PM	1434	3.08	156	Duplicate. Average of 307 and 4 (<LOQ value) ng/m^3.
Mujer	4/13/06	4:16 PM	1387	2.98	475	Duplicate. Average of 501 and 448 ng/m^3.
Codo	4/14/06	3:37 PM	1311	2.82	168	Duplicate. Average of 152 and 183 ng/m^3.
Lunes	4/15/06	1:39 PM	1329	2.92	184	Duplicate. Average of 185 and 182 ng/m^3.
Jugo	4/16/06	12:00 PM	1762	3.88	151	Duplicate. Average of 160 and 141 ng/m^3.
Tapa	4/17/06	5:35 PM	1501	3.23	129	Duplicate. Average of 116 and 142 ng/m^3.
Furia	4/18/06	6:45 PM	1268	2.76	164	Duplicate. Average of 174 and 154 ng/m^3.
Frase	4/19/06	4:08 PM	1467	3.15	143	Duplicate. Average of 126 and 160 ng/m^3.
Manga	4/20/06	4:47 PM	1162	2.53	195	Duplicate. Average of 195 and 194 ng/m^3.
Manta	4/21/06	12:21 PM	1685	3.71	55	Duplicate. Average of 52 and 58 ng/m^3.

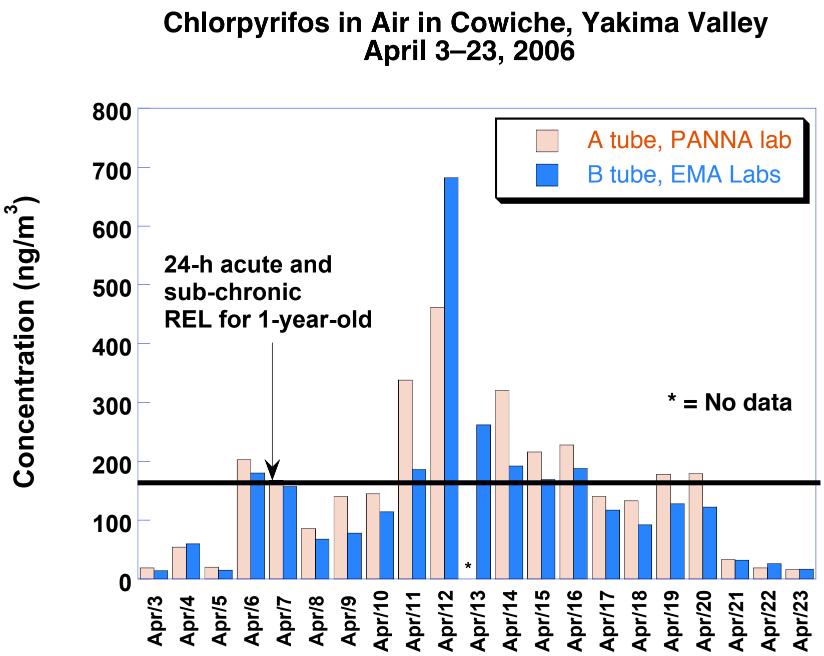


Figure 3: Chlorpyrifos concentrations in Cowiche, April 3-23, 2006. REL = Reference Exposure Level calculated from US EPA's "acceptable" daily dose for acute and sub-chronic exposures. EMA Labs results corrected to account for average recoveries of 65%.

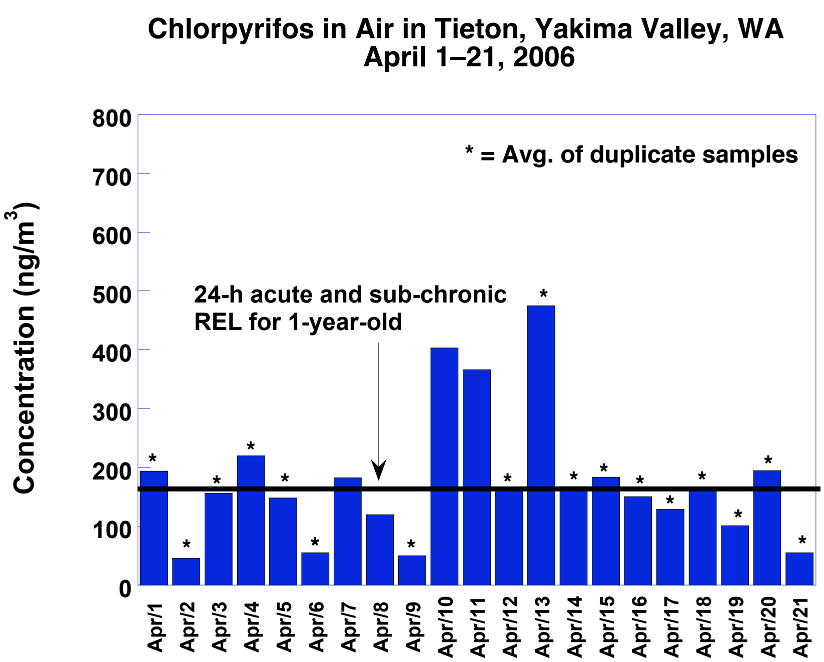


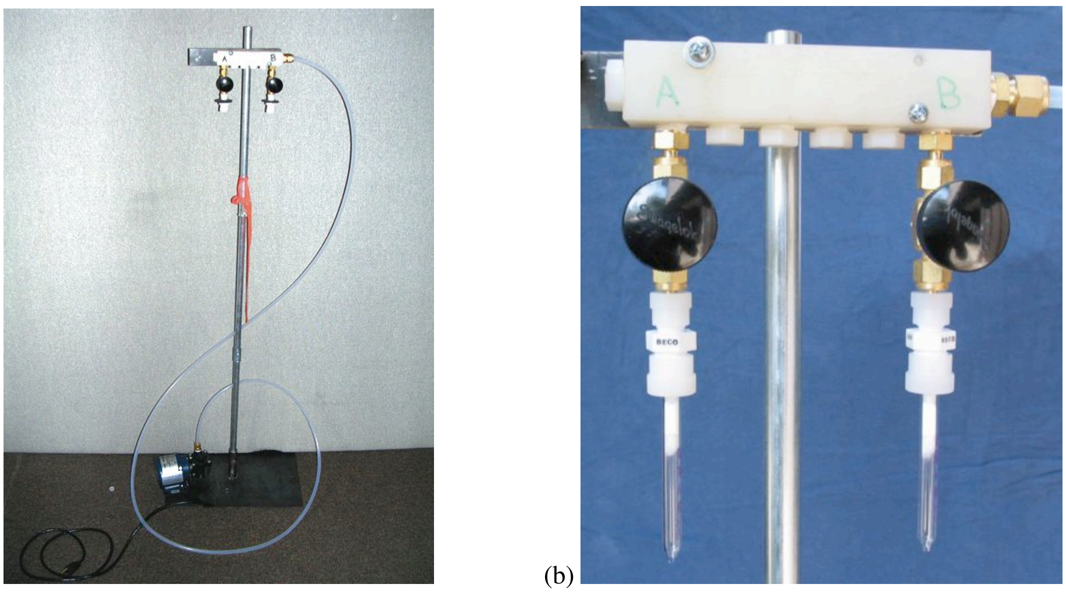
Figure 4: Chlorpyrifos concentrations in Tieton, April 1-21, 2006. REL = Reference Exposure Level calculated from US EPA's "acceptable" daily dose for acute and sub-chronic exposures.

Methods

Sample Collection

Samples were collected by passing a measured volume of air through XAD-2 resin tubes obtained from SKC Inc. (75/150 mg, Cat. #226-30-05). Sample tubes were changed once a day during the sampling period in approximately twenty-four hour intervals. This sampling method was based on NIOSH method 5600 for organophosphorus insecticides.[30]

The air sampling device consists of a vacuum pump (Barnant, Cat. #400-1901) connected with 3/8" Teflon tubing and compression fittings to a manifold equipped with two Cajon-type, vacuum-tight Teflon fittings (Beco Mfg.) as tube holders. Flow controller valves for each sample allowed for adjustment of air flow to each tube independently (Figure 15).



(a) (b)

Figure 15: (a) The air monitoring device used in this experiment, the Drift Catcher™, was designed based on sampling equipment used by the California Air Resources Board. This design has been evaluated by a Scientific Advisory Committee comprised of scientists from the California Department of Pesticide Regulation, the California Air Resources Board, US EPA Region 9, the US Geological Survey, and the California Department of Health Services. (b) Drift Catcher manifold with flow regulation control valves.

Pre-labeled sample tubes were attached to the manifold, which stood approximately 1.5 meters off the ground. Flow rates were measured with a 0–5 L capacity rotameter (SKC Inc., Cat. #320-4A5) pre-calibrated with a mass flow meter (Aalborg, cat. #GFM17A-VADL2-A0A). The initial flow rate through each of the tubes was set to 2.20 liters per minute. The flow rate was set at the beginning of the sampling run and then measured at the end to check for any changes. If the difference between the start and stop flow rates was less than 10%, these two values were averaged together to calculate an average flow rate. If the ending flow rate differed by >10% from the starting flow rate, the sample was discarded.

Sample tubes were covered with mylar light shields during the sampling period to prevent any photolytically catalyzed degradation of the sample. Sample identification, start and stop times, and flow rates were recorded on the Sample Log Sheet (SLS, Appendix 2). In addition, wind speed and direction, as well as temperature, weather conditions and any additional observations were noted at the beginning and end of each sampling period. At the end of each sampling period, labeled tubes were capped and placed in a zip-lock plastic bag with the completed SLS.

Within 10 minutes of removal from the sampling manifold, samples were placed into either a –10°C freezer or into a cooler at 0°C for transport to freezer storage. After storage for no more than two weeks, samples were shipped to the laboratory at –10 to 0°C by overnight express mail for analysis. A chain of custody form (Appendix 3) accompanied each batch of samples during handling and transport. In the laboratory, samples were stored in a –20°C freezer prior to processing and analysis. Prior sample storage stability assessments conducted by the California Air Resources Board indicate that no degradation of chlorpyrifos on XAD-2 resin occurred during storage at –20°C for up to 37 days.[31]

Sample Analysis

Detailed Standard Operating Procedures (SOPs) for processing of sorbent tubes containing organophosphorus pesticides such as chlorpyrifos were developed from NIOSH method 5600[32] and the methods used by CA ARB[33] and are attached as Appendix 4. Briefly, the front and rear XAD-2 resin beds were each extracted with either 2.65 mL of pesticide-grade ethyl acetate (PANNA lab) or 3.00 mL of 10% acetone in toluene (EMA Labs) using sonication, and the extracts were analyzed using a Varian 3800 gas chromatograph equipped with an 8400 autosampler using splitless injection (PANNA lab) or a gas chromatograph equipped with a nitrogen-phosphorus detector (EMA Labs). Samples were quantified using either an electron capture detector (ECD) (PANNA lab) or a nitrogen-phosphorus detector (NPD). Confirmation of peak identity was made by mass spectrometry. The details of instrumental conditions can be found in Appendix 6.

Concentrated stock standards of chlorpyrifos and chlorpyifos oxon for use in analysis were obtained directly from Accustandard (Catalog numbers P-094S and P-700S respectively), at a concentration of 100 μg/mL in MeOH. Dilute analytical standards at concentrations of 0.05, 0.1, 0.2, 0.5, and 0.7 ng/μL were prepared from the stock solution using pesticide-grade ethyl acetate as diluent. One chlorpyrifos oxon standard was prepared at 0.1 ng/μL and was analyzed with all sample sets to identify its presence or absence in the samples. None of the oxon was detected in any of the samples, so quantitation was unnecessary.

Calculations

Air Concentrations

Chlorpyrifos concentrations in air were calculated from the GC results as shown below:

$$\text{Air concentration, ng/m}^3 = \frac{\text{Extract concentration, ng/}\mu\text{L} \times \text{Solvent volume, } \mu\text{L}}{\text{volume of air sampled, m}^3}$$

Reference Exposure Levels (RELs)

In order to compare observed concentrations of chlorpyrifos in air with concentrations likely to be associated with adverse effects, the US EPA inhalation NOAELs for acute and sub-chronic exposures to chlorpyrifos of 0.1 mg/kg-day (based on plasma and red blood cell cholinesterase inhibition)[34] were used to calculate Reference Exposure Levels (RELs) for a sensitive receptor, a one-year-old infant weighing 7.6 kg, breathing on average 4.5 m^3 of air per day.[35] This calculation takes into account the 10-fold intraspecies, 10-fold interspecies and 10-fold FQPA uncertainty factors used by US EPA for chlorpyrifos.

$$\text{REL (1-year-old)} = \frac{0.1 \ mg/kg \bullet day}{10_{\text{intra-UF}} \times 10_{\text{inter-UF}} \times 10_{\text{FQPA}}} \times \frac{10^6 \ ng/mg \times 7.6 \ kg}{4.5 \ m^3/day} = 170 \ ng/m^3$$

The calculated concentration is the equivalent of a concentration in air below which no adverse effects on cholinesterase inhibition are anticipated by US EPA. Note, however, that the developmental neurotoxicity observed for chlorpyrifos[36] is not mediated by cholinesterase inhibition and may occur at lower doses.

Method Detection Limit (MDL)

The method detection limit (MDL) is the "minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from replicate analyses of a sample in a given matrix containing the analyte."[37] For air samples, the MDL takes into account the total amount of sampling time, the air flow rate through the sorbent tube, the volume of extraction solvent used to desorb the analyte, and the sensitivity of the instrument used to quantify the amount of analyte in a sample. For this experiment, the MDL was determined for a 24-hour sample taken with a flow rate of 2.00 L/min, and extracted with 3.00 mL of solvent. The sensitivity of the gas chromatograph equipped with an electron capture detector, the Instrument Detection Limit (IDL), was calculated by determining the standard deviation (σ) of the results of seven sequential injections of the extract from a low-level matrix spike and multiplying this value times 3.14, the student T value at the 99% confidence interval for seven replicates:

$$\text{IDL (ng/}\mu\text{L)} = 3.14 * \sigma$$

These parameters were then used to calculate the MDL for the entire method in units of concentration of pesticide in air, e.g. ng/m^3. The calculation is shown below for a low concentration matrix spike with a calculated IDL of 0.006 ng/μL:

$$\text{MDL (ng/m}^3\text{)} = \frac{(0.006 \ \text{ng}/\mu\text{L}) \times (3{,}000 \ \mu\text{L})}{(2.0 \ \text{L/min}) \times (60 \ \text{min/h}) \times (24 \ \text{h}) \times (1 \ \text{m}^3/1000 \ \text{L})} = 6 \ \text{ng/m}^3$$

The Limit of Quantitation (LOQ) was estimated at five times the MDL or 30 ng/m^3.

Quality Assurance–Quality Control

Operator Training

All Drift Catcher Operators participated in a hands-on training workshop on the operation of the Drift Catcher at which they were provided with a Drift Catcher Users' Manual. They were then tested on their knowledge of the procedures and practices by a PANNA scientist. Partipicants were certified if they could successfully demonstrate:

(1) Mastery of the technical set-up and operation of the Drift Catcher

(2) Correct use of Sample Log Sheets and Chain of Custody Forms

(3) Ability to troubleshoot and solve common operational problems

(4) Knowledge of the scientific method

Sample Labels

Sample labels were affixed directly to the sorbent tubes and to the corresponding sample log sheets prior to the start of sampling. The following information was contained on the labels: Sample ID, project name, and project date.

Sample Check-In

On arrival in the laboratory, samples were checked into a Sample Log Database organized by project and sampling dates. Sampling dates and times, extraction dates, analysis dates, analytical methods and sample results were all logged in the database. Appendix 5 shows a screen shot of the main data page.

Leak Check

All monitoring equipment was fully leak-checked prior to use by attaching the tubing-manifold combination to a pump generating a positive airflow and testing for leaks at each connection point with a soap solution.

Flow Calibration

Rotameters used in the field to determine flow rates were calibrated using an Aalborg mass flow meter, Model No. GFM17A-VADL2-A0A with totalizer attachment TOT-10-0C. All rotameters used in this experiment deviated less than 5% (the rated accuracy for these rotameters) from the mass flow meter readings.

Field Spikes

Field spike data from prior California Air Resources Board chlorpyrifos sampling indicated that there was no significant loss of sample under similar field sampling conditions.[38]

Lab Spikes

Ten lab spikes were prepared at 300 ng of chlorpyrifos, spiked onto the front resin bed. These samples were extracted and analyzed according to the same procedures used for samples. Lab spike recoveries are shown in Table 7. The average recovery was 106% and ranged from 82% to 117%.

Table 7: Chlorpyrifos Lab Spike Recoveries

Sample ID	Fortification (ng)	Recovery (ng)	Recovery (%)
l-spike-1	300	340	112
l-spike-2	300	330	110
l-spike-3	300	290	95
l-spike-4	300	320	107
l-spike-5	300	350	116
l-spike-6	300	300	100
l-spike-7	300	350	116
cp-spike-8	300	250	82
cp-spike-9	300	310	104
cp-spike-10	300	350	117
		Average	**106**
		Standard deviation	**11**

Trip Blanks

Two trip blank tubes per sampling week were prepared at each location at the end of the first 24-hour sampling period. These tubes were stored and transported with the batch of samples from that location, then processed and analyzed as part of the batch on arrival in the lab. No pesticide residues were detected in any of the trip blanks.

Lab Blanks

For each batch of samples processed, two blank tubes of the same lot number as that of the tubes used in the experiment were processed and analyzed according to the same procedures used for the samples. No pesticide residues were detected in any of the lab blanks.

Solvent Blanks

A sample of the solvent used for extraction was analyzed with each batch of samples to check for possible impurities in the solvent. No pesticide residues were detected in any of the solvent blanks.

Replicate Samples

Duplicate samples were taken for all sampling periods, and selected duplicates were extracted and analyzed to check agreement between samples. The results of duplicate sampling are provided in Tables 4 and 5.

Instrumental QA/QC

Quantification of chlorpyrifos was conducted either using an electron capture detector (ECD) or a nitrogen-phosphorus detector (NPD) (EMA Labs), calibrated with a set of five standards.

Positive identification of chlorpyrifos was established by mass spectrometry, as well as by comparison of retention times between two different columns. Reproducibility was determined by comparison of five replicate injections of two standards. Linearity of the standard curve was confirmed by inspection and evaluation of the regression coefficient, which was required to be at least 0.99. A new set of standards was analyzed for each 30–40 samples, with a mid-level calibration verification standard analyzed every 10th sample. See Appendix 6 for detailed instrument parameters.

Appendices

Appendix 1: Application Conditions and Monitoring Data for Chlorpyrifos Application Conducted by the California Air Resources Board, June 1996

Table A-1: Application Site Monitoring Conditions for Chlorpyrifos*

Location of application	Tulare County
Date of application	June 4 and 5, 1996
Time of application	06:30–10:30 (June 4) and 04:30–10:30 (June 5)
Type of application	Ground-rig blower
Distance of monitoring stations from field boundaries	North, 57 feet; East, 42 feet (two co-located samplers); and South, 30 feet. West sampler was stolen and not replaced during the study
Size of treated area	60 acres, orange grove
Product applied	Lorsban 4E
Product application rate	1.5 gallons per acre in 750 gal of water
Active ingredient (AI)	Chlorpyrifos, 50%
Vapor pressure of AI	1.7 x 10^{-5} mm Hg at 25°C
AI application rate	6 lbs. chlorpyrifos per acre (3–4.5 lbs/acre is typical for oranges)
Total amount of AI applied	360 lbs
Temperature range during first 24 hours	Not reported in summary data, but 60–105°F is common at this time of year in Tulare County
Winds	Light from the southeast at application start, shifting to high winds from the south and west 4–5 hours after start of first application. Winds light and from the east-southeast during second application.

**Source:* Reference 25.

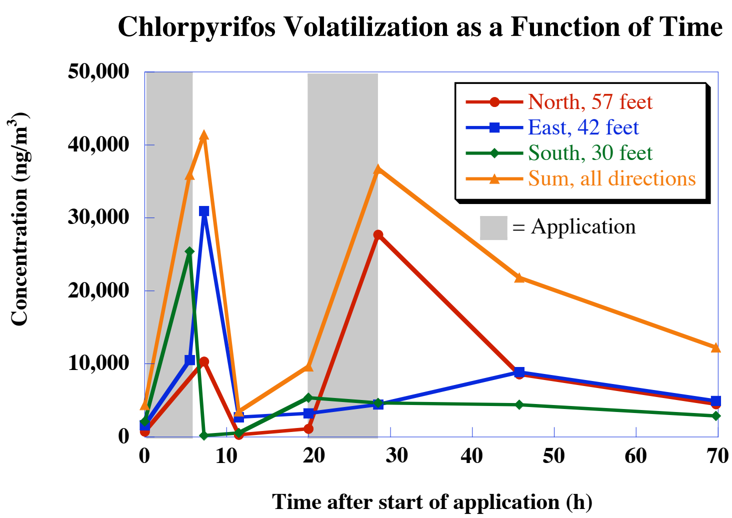


Table A-2: Application Site Monitoring Data for Chlorpyrifos*

Sampling Period	Direction Wind Coming From[a]	Time after Start of Application (h)	Concentration (ng/m³) North, 57 feet	East, 42 feet[b]	South, 30 feet	Sum, all directions	% Drift per Period (by mass)
Background	SE	NA	690	1,570	2,070	4,330	---
1	SE	5.5	8,580	10,500	25,400	44,480	17.85
2	S	7.25	10,300	30,950	160	41,410	4.98
3	W/NW	11.5	250	2,680	510	3,440	1.04
4	SE/NW	20	1,100	3,200	5,320	9,620	7.06
5	SE	28.5	27,700	4,410	4,620	36,730	22.02
6	W/E/SE	45.75	8,550	8,850	4,390	21,790	26.58
7	W/E/SE	69.75	4,470	4,905	2,840	12,215	20.48
		Time-weighted average	8,112	6,572	5,312	19,996	100.00

**Source:* Reference 25.

a. Underlined wind direction is the predominant one, if any.
b. Average of two co-located samples.

Appendix 2: Sample Log Sheet

Drift Catcher Sample Log Sheet

STARTING THE SAMPLE

Project: ______________________________ Location: ______________________________

YOU NEED: A Drift Catcher, a sample bag with pre-labeled tubes, caps, and labels, a tube cracker, a rotameter, two light shields, orange flag material, a compass, and a wind meter.

❒ **1. LABELS:** Make sure the labels included in the sample bag MATCH the labels on the pre-labeled tubes. If they match, affix the labels to this log sheet under Steps 4 & 11.

❒ **2. TUBES:** Break the tips of the glass sample tubes and insert them into the manifold.

❒ **3. PUMP:** Plug in the pump and note the EXACT TIME using the clock on the compass.

Today's Date		Exact Pump START Time	**AM or PM?**

❒ **4. ROTAMETER:** Use the rotameter to measure the flow rate for each tube.

	Tube Name	Starting Flow Rate	
Tube A	[stick label here]	**L/min**	**NOTE: Adjust the flow rates so that they are equal to each other!**
Tube B	[stick label here]	**L/min**	

❒ **5. LIGHT SHIELDS:** Attach both light shields.

❒ **6. COMPASS & ORANGE FLAG:** Use these to find the direction of the wind.

Which direction is the wind blowing FROM?	N NE E SE S SW W NW calm

❒ **7. WIND METER:** Face the wind meter into the wind for 2 minutes.

What is the wind speed?	maximum: mph	average: mph
What is the temperature? **(Remember to wave wind meter back and forth!)**		°F

❒ **8. YOUR SENSES:** Use your own senses to answer the following questions.

What is the weather like?	foggy sunny mix of sun and clouds cloudy rainy humid other:
Do you smell anything?	sweet rotten eggs perfume skunk none other:

There is space for other observations and notes at the bottom of the other side of this page.

Name: ______________________________ Initials: ______________

STOPPING THE SAMPLE (cont'd from other side)

❒ **9. PUMP:** Is the pump running? ❒ Yes ❒ No (If not, skip to Step #13)

❒ **10. LIGHT SHIELDS:** Remove both light shields.

❒ **11. ROTAMETER:** Use the rotameter to measure the flow rate for each tube.

	Tube Name	Ending Flow Rate	
Tube A	[stick label here]	L/min	**DO NOT adjust the flow rates. Just measure them.**
Tube B	[stick label here]	L/min	

❒ **12. PUMP:** Unplug the pump and note the EXACT TIME, using the clock on the compass.

Today's Date		Exact Pump STOP Time	**AM or PM?**

❒ **13. TUBES:** Remove the sample tubes, cap them, place them in the sample bag.

❒ **14. COMPASS & ORANGE FLAG:** Use these to find the direction of the wind.

Which direction is the wind blowing FROM?	N NE E SE S SW W NW calm

❒ **15. WIND METER:** Face the wind meter into the wind for 2 minutes.

What is the wind speed?	maximum: mph	average: mph
What is the temperature? **(Remember to wave wind meter back and forth!)**		° F

❒ **16. YOUR SENSES:** Use your own senses to answer the following questions.

What is the weather like?	sunny mix of sun and clouds cloudy rainy humid other:
Do you smell anything?	sweet rotten eggs perfume skunk none other:

❒ **17. TRIP BLANK:** If this is the first sample of your sample run in this location, prepare a Trip Blank sample (follow instructions on Trip Blank form).

Name: ____ Initials: ______________

- -

OBSERVATIONS AND NOTES

Please record observations or notes below (known pesticide applications nearby, equipment failure, nearby activities that could interfere with the sample, etc.)

Date	Time	Observation/Note

Appendix 3: Freezer Log and Chain of Custody Form

Chain of Custody Form and Freezer Log

This form is used to keep track of where all your samples are and who has been responsible for them at all times.

Name: ______________________________ Phone Number: ____________________

Project Name: ____

Sample Site (Include full address): ______________________________________

____

Date Sampling Started: _______________ Date Sampling Finished: _______________

Freezer Log

Sample Name	Sample Placed in Freezer on Date	Time (am/pm)	Notes or Comments	Initials
Ejemplo – A	6/8/05	8:18 pm	This is an example entry.	JD

Pesticide Action Network, 49 Powell Street, Suite 500, San Francisco, CA 94102, (415) 981-1771

Chain of Custody Form

This section tracks who has control of the batch of samples as they are being transported and how they are handled.

When you receive the samples,
- Make sure all samples are accounted for.
- Record the time and date and put your initials in the **Received by** column.
- If you are unpacking samples from a shipping box, note the temperature of the ice packs.

When samples are passed from one person to another, you should record the method of storage (freezer, cooler, dry ice, etc). If you change the method of storage (i.e. from a freezer to a cooler) please also record this along with the date and time of change, even though the samples are still in your custody.

Date Sent	Time Sent	Sent by (Initials)	Storage Before Transfer	Storage During Transfer	Storage After Transfer	Date Received	Time Received	Received by (Initials)	Temperature upon arrival (Circle one)*
6/9/05	2:43 pm	JD	Freezer	Cooler	Freezer	6/10/05	9:08 am	SK	(1) - 2 - 3 - 4
									1 - 2 - 3 - 4
									1 - 2 - 3 - 4
									1 - 2 - 3 - 4
									1 - 2 - 3 - 4

*note the shipping container temperature by choosing the ice pack description that best describes the condition of the ice packs.
1: Fully frozen; 2: Partially frozen; 3: Not frozen but still cold; 4: Room Temperature

Names and signatures of sample handlers:

Each person who handles the samples will need to sign off on this form. Your signature and initials are your verification that the samples were handled as indicated on the form.

	Name (Please print)	Phone Number	Signature	Initials
Example	Juan Diego	(234) 567-8901	Juan Diego	JD
1				
2				
3				
4				

Appendix 4: Standard Operating Procedures for Organophosphate Pesticides (NIOSH Method 5600)

QuickView

- ❑ Label extraction vials
- ❑ Enter extraction date, solvent and volume into DCD database
- ❑ Print sample processing form and put in project notebook
- ❑ Record extraction in lab notebook
- ❑ Prepare lab blanks & lab spikes
- ❑ Crack tubes into vials, add solvent, allow to sit
- ❑ Optional: Sonicate, make sure labels won't fall off
- ❑ Label GC vials, 2 for each resin bed (front/back)
- ❑ Transfer samples to GC vials. Check caps for tightness (dent in cap).

1. Label a set of 6 mL vials (Teflon-lined caps)—two for each sample tube, one for the front resin bed and one for the back resin bed. The labeling convention is as follows: the sample name, tube letter (A or B), and the front or back bed specification. For example, if the tube has a label that says TREE-A, the name on the first sample vial containing the front bed would be labeled TREE-A-F and the back bed vial would be labeled TREE-A-R.
2. Enter the extraction date, solvent and solvent volume into the Drift Catcher Data (DCD) database. Also, record the extraction in the lab notebook.
3. Prepare two lab blanks using sorbent tubes (or filters) with the same lot number(s) as your samples, labeling them with the lot number in the name, e.g. Blank3658-1, Blank3658-2, for two blanks of lot number 3658. Crack the tube open by using a glass file to score the tube near the front glass wool plug, then snapping the tube in two. Using a dental pick, remove the glass wool plug and then pour the front resin bed (the glass wool can be discarded) into an extraction vial and extract according to the directions used for samples below.
4. Prepare the lab spikes using sorbent tubes (or filters) with the same lot number as the samples. Crack a tube open as above, pour the front resin bed (the glass wool is not necessary) into an extraction vial and spike with a known amount of the pesticide or group of pesticides you are likely to find. For OPs, spike with an amount that will give a final concentration in the extract of about 0.2–0.5 ng/μL. Allow to sit for at least 30 minutes. If there is no knowledge of what pesticide is present, wait to do the spikes until after the pesticide present has been identified.
5. Crack open the sample tubes. Transfer both the first glass wool plug and the front bed of resin (the larger of the two resin beds) into a labeled 6 mL sample vial with a Teflon-lined cap. As you do this step, double-check that the label on the vial matches the label on the tube. Remove the second glass wool plug and back resin bed into another labeled sample vial. Before processing any samples, don't forget to make lab blanks, and spikes if the pesticide has been identified.
6. After the tubes are cracked and the contents placed in vials for samples, blanks and spikes, use a micropipette to pipette 3.00 mL of ethyl acetate into each sample vial. Invert the samples several times and allow them to sit for 30 minutes, shaking the vials occasionally during this time period.

7. OPTIONAL: Place the tubes in the sonicator for 30 minutes (six cycles of five minutes each). Care needs to be taken when placing the samples in the sonicator so the labels don't get wet and fall off. Putting the labels on the caps is best—they should be moved to the vial after extraction.

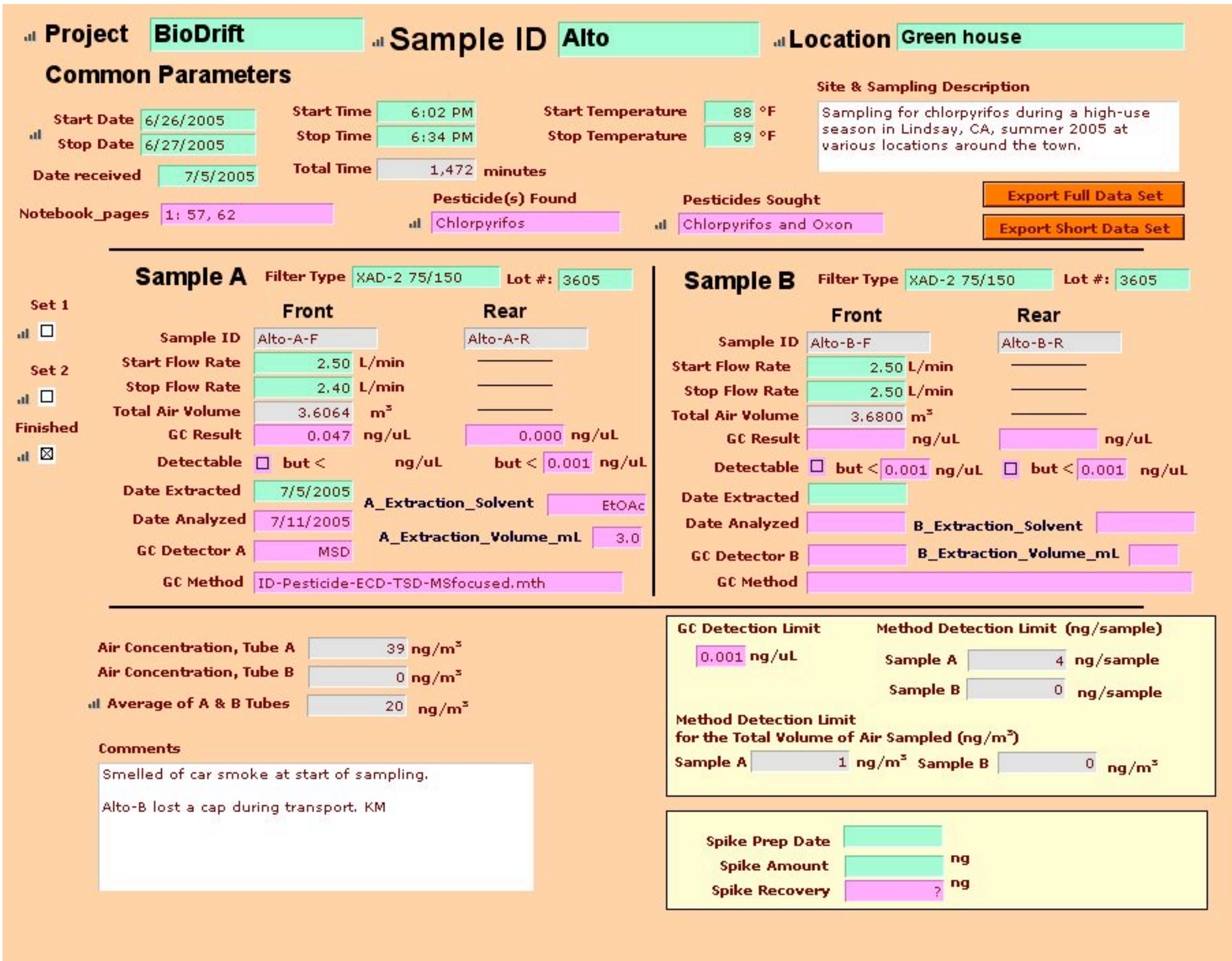
   NOTE: Some pesticide extractions do not require sonication—the extraction seems to work just as well by letting the vials sit for 30 minutes with occasional shaking. The NIOSH method explicitly says NO sonication, but the EPA method says to USE sonication. So far, we haven't found it to make a difference for OP pesticides.

8. After removal from the sonicator, the samples are pipetted as soon as possible (within the next 30 minutes), into GC autosampler vials for analysis (Restek, #21141 with caps, Restek #24670). Check the caps to be sure they are sealed tight—they should be obviously indented in the middle.

   NOTE: For every 6 mL vial of sample extract, two autosampler vials can be filled. It is recommended that two autosampler vials be filled from each extraction vial so that a backup sample is available if the first GC run fails for any reason or if the first sample needs to be used to ID the pesticide(s) present. At this point, there are FOUR autosampler vials for every resin tube (two from the front bed and two from the back).

9. Store the autosampler vials in the freezer unless the samples are to be run immediately.

Appendix 5: Sample Log Database Screen Shot



Project: BioDrift | Sample ID: Alto | Location: Green house

Common Parameters

Start Date: 6/26/2005
Stop Date: 6/27/2005
Date received: 7/5/2005
Notebook_pages: 1: 57, 62

Start Time: 6:02 PM
Stop Time: 6:34 PM
Total Time: 1,472 minutes

Start Temperature: 88 °F
Stop Temperature: 89 °F

Site & Sampling Description: Sampling for chlorpyrifos during a high-use season in Lindsay, CA, summer 2005 at various locations around the town.

Pesticide(s) Found: Chlorpyrifos
Pesticides Sought: Chlorpyrifos and Oxon

Export Full Data Set
Export Short Data Set

Set 1 ☐
Set 2 ☐
Finished ☒

Sample A Filter Type: XAD-2 75/150 Lot #: 3605

	Front		Rear	
Sample ID	Alto-A-F		Alto-A-R	
Start Flow Rate	2.50	L/min		
Stop Flow Rate	2.40	L/min		
Total Air Volume	3.6064	m³		
GC Result	0.047	ng/uL	0.000	ng/uL
Detectable	☐ but <	ng/uL	but < 0.001	ng/uL

Date Extracted: 7/5/2005
Date Analyzed: 7/11/2005
GC Detector A: MSD
GC Method: ID-Pesticide-ECD-TSD-MSfocused.mth
A_Extraction_Solvent: EtOAc
A_Extraction_Volume_mL: 3.0

Sample B Filter Type: XAD-2 75/150 Lot #: 3605

	Front		Rear	
Sample ID	Alto-B-F		Alto-B-R	
Start Flow Rate	2.50	L/min		
Stop Flow Rate	2.50	L/min		
Total Air Volume	3.6800	m³		
GC Result		ng/uL		ng/uL
Detectable	☐ but < 0.001	ng/uL	☐ but < 0.001	ng/uL

Date Extracted:
Date Analyzed:
GC Detector B:
GC Method:
B_Extraction_Solvent:
B_Extraction_Volume_mL:

Air Concentration, Tube A: 39 ng/m³
Air Concentration, Tube B: 0 ng/m³
Average of A & B Tubes: 20 ng/m³

GC Detection Limit: 0.001 ng/uL

Method Detection Limit (ng/sample)
Sample A: 4 ng/sample
Sample B: 0 ng/sample

Method Detection Limit for the Total Volume of Air Sampled (ng/m³)
Sample A: 1 ng/m³ Sample B: 0 ng/m³

Comments:
Smelled of car smoke at start of sampling.
Alto-B lost a cap during transport. KM

Spike Prep Date:
Spike Amount: ng
Spike Recovery: ? ng

Appendix 6: Instrument Parameters for Sample Analysis

All samples were analyzed using a Varian 3800 gas chromatograph equipped with two injector ports, a CP-8400 autosampler, electron capture detector (ECD) and Saturn 2200 ion trap mass selective detector (MSD). Most samples were quantified using the ECD, with the MSD primarily used to verify the identity of sample components. When both ECD and MSD were in use (2005), 2.5 μL of sample was injected sequentially into the two columns, allowing 0.5 minutes to elapse between injections. The columns used were a Varian CP SIL 8 CB-MS capillary GC column, 30 m x 0.25 mm, 0.25 μm film thickness or a VarianVF-5-MS capillary GC column, 30 m x 0.25 mm, 0.25 film thickness.

Prior to analytical runs using the MSD, the MSD was autotuned to set the electron multiplier gain, calibrate mass setpoints on PFTBA ions, and calibrate the ion trap for selected ion storage (SIS) analysis. SIS was turned on during a 1.5 minute window around the chlorpyrifos peak, using a storage mass range of m/e 195–316 to store chlorpyrifos ions at m/e 314, 258 and 197 and eject ions arising from the silicone polymers that are part of the XAD-2 resin extracts appearing at m/e 255 **xx check number here**.

Table A-3: Gas Chromatograph Parameters

	Injector Temp.	Detector Temp.	GC Column Oven Temperature Program				Flow Rates (mL/min)	
			Temp (°C)	Heating Rate (°C/min)	Hold Time (min)	Total Time (min)	Carrier Gas	Makeup Gas (N_2)
2004	250 °C (splitless)	300 °C (ECD)	180	0	1	1	1	30
			220	10	1	6		
			250	20	20	27.5		
2005	250 °C (splitless)	300 °C (ECD)	120	0	0.5	0.5	1	30
			200	10	0	8.5		
			260	20	15	26.5		
			300	20	5	33.5		

References

[1] *Chlorpyrifos Revised Risk Assessment and Agreement with Registrants,* U.S. EPA, June 2000, http://www.epa.gov/pesticides/op/chlorpyrifos/agreement.pdf.

[2] Ibid, Reference 1.

[3] *Chlorpyrifos Revised Risk Assessment and Agreement with Registrants,* U.S. EPA, June 2000, http://www.epa.gov/pesticides/op/chlorpyrifos/agreement.pdf.

[4] National Agricultural Statistics Service (NASS) database, http://www.pestmanagement.info/nass/act_dsp_usage_multiple.cfm. Viewed on on 8/22/06.

[5] *Interim Reregistration Decision for Chlorpyrifos,* US EPA, February 2002, http://cfpub.epa.gov/oppref/rereg/status.cfm?show=rereg#C

[6] United States Department of Agriculture, Agricultural Chemical Use. 2005 Fruit Summary, July 2006 at pages 35, 71, and 171.

[7] United States Department of Agriculture, Agricultural Chemical Use. 2005 Fruit Summary, July 2006 at pages 35, 71, and 171.

[8] *Monitoring Recommendation for Chlorpyrifos,* California Department of Pesticide Regulation. April 28, 1995.

[9]*Toxicology Information Briefs: Cholinesterase Inhibition,* Extension Toxicology Network, Cooperative Extension Offices of Cornell University, Oregon State University, the University of Idaho, and the University of California at Davis and the Institute for Environmental Toxicology, Michigan State University. http://extoxnet.orst.edu/tibs/cholines.htm.

[10] Reigert, JR and Roberts, JR, *Recognition and Management of Pesticide Poisoning, 5th ed.,* US EPA, 1999, http://www.epa.gov/pesticides/safety/healthcare/handbook/contents.htm.

[11] *AOEC Exposure Codes,* George Washington University, Occupational Medicine Group for the Association of Occupational and Environmental Clinics, http://www.aoec.org/aoeccode.htm.

[12] (a) Aldridge JE, Seidler FJ, Meyer A, Thillai I, Slotkin TA, Serotonergic Systems Targeted by Developmental Exposure to Chlorpyrifos: Effects during Different Critical Periods. *Envi. Health Persp.* 2003, 111(14): 1736-43.

(b) Jameson, RR, Seidler, FJ, Qiao, D, Slotkin, TA, Chlorpyrifos Affects Phenotypic Outcomes in a Model of Mammalian Neurodevelopment: Critical Stages Targeting Differentiation in PC12 Cells, *Envi. Health Persp.* 2006, 114(5): 667-72.

(c) Aldridge, JE, Meyer, A, Seidler, FJ, Slotkin, TA, Alterations in Central Nervous System Serotonergic and Dopaminergic Synaptic Activity in Adulthood after Prenatal or Neonatal Chlorpyrifos Exposure, *Envi. Health Persp.* 2005, 113(8): 1027-31.

[13] Slotkin, TA, Levin, ED, Seidler, FJ, Comparative Developmental Neurotoxicity of Organophosphate Insecticides: Effects on Brain Development Are Separable from Systemic Toxicity, *Envi. Health Persp.* 2006, 114(5): 746-51 and references cited therein.

[14] (a) Whyatt RM and Barr, DB, Measurement of organophosphate metabolites in postpartum meconium as a potential biomarker of prenatal exposure: A validation study, *Envi Health Persp*, 2001, 109(4): 417-20.

(b) Whyatt RM, Rauh V, Barr DB, *et al.* Prenatal Insecticide Exposures and Birth Weight and Length among an Urban Minority Cohort, *Envi. Health Persp.* 2004, 112(10):1125-32.

(c) Berkowitz GS, Wetmur JG, Birman-Deych E, *et al.,* In Utero Pesticide Exposure, Maternal Paraoxonase Activity, and Head Circumference, *Envi. Health Persp.* 2004, 112(3):388-91.

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[15] VA Rauh, R Garfinkel, FP Perera, HF Andrews, L Hoepner, DB Barr, R Whitehead, , D Tang, RW Whyatt, Impact of Prenatal Chlorpyrifos Exposure on Neurodevelopment in the First 3 Years of Life Among Inner-City Children, *Pediatrics*, 2006, 118:1845-1859.

[16] a) Rawlings, NC, Cook, SJ, and Waldbillig, D, Effects of the pesticides carbofuran, chlorpyrifos, dimethoate, lindane, triallate, trifluralin, 2,4-D, and pentachlorophenol on the metabolic endocrine and reproductive endocrine system in ewes, *J Tox. Envi. Health,* 1998, 54: 21–36.

b) Keith, LH, *Environmental Endocrine Disruptors: A Handbook of Property Data,* Wiley Interscience (New York, 1997).

[17] Rohlman et al, Neurobehavioral Performance in Preschool Children from Agricultural and Non-Agricultural Communities in Oregon and North Carolina, *Neurotoxicology* 26 (2005) 589-598.

[18] Rothlein et al, Organophosphate Pesticide Exposure and Neurobehavioral Performance in Agricultural and Nonagricultural Hispanic Workers, *Environmental Health Perspectives* 2006 114:5, 691-696.

[19] Kamel et al, Neurologic Symptoms in Licensed Private Pesticide Applicators in the Agricultural Health Study, Environmental Health Perspectives 113(7) July 2005, p. 877-882.

[20] Patricia Moulton, University of North Dakota School of Medicine & Health Sciences, Pesticide Exposure, Intelligence and Children: Preliminary Results, Power Point presentation at Earth Day Forum: Pesticides in Children, Winnipeg, Canada, April 22, 2006.

[21] *Interim Reregistration Decision for Chlorpyrifos,* US EPA, February 2002, http://cfpub.epa.gov/oppref/rereg/status.cfm?show=rereg#C

[22] This additional uncertainty factor was mandated by the Food Quality Protection Act of 1996, a law that updated the Federal Fungicide, Insecticide and Rodenticide Act to require greater protections from pesticide residues for children. This "FQPA" uncertainty factor is supposed to be applied to any pesticide for which data gaps exist or where toxicity studies demonstrate that developing animals are more susceptible to the toxic effects of the chemical.

[23] Furlong CE, Holland N, Richter RJ, Bradman A, Ho A, Eskenazi B, PON1 status of farmworker mothers and children as a predictor of organophosphate sensitivity. *Pharmacogenetics Genomics,* 2006, 16(3):183-190.

[24] *Cholinesterase Monitoring of Pesticide Handlers in Agriculture: Report to the Legislature*, Washington Department of Labor and Industries, January 2006.

[25] Ibid, Reference 23, p. 15.

[26] *Report for the Application and Ambient Air Monitoring of Chlorpyrifos (and the Oxon Analogue) in Tulare County during Spring/Summer 1996,* California Air Resources Board, Test Report #C96-040 and # C96-041, April 7, 1998, http://www.cdpr.ca.gov/docs/empm/pubs/tac/chlrpfs.htm.

[27] This reported concentration may be lower than the actual. The concentration of 30,950 ng/m^3 is the average of the concentrations measured by two samplers positioned in the same location, one of which measured 14,700 ng/m^3 and the other 47,200 ng/m^3. The large discrepancy led ARB to surmise that the low sampler may not have been operating properly. See reference 25.

[28] S. Lee, R. McLaughlin, M. Harnly, *et al.,* Community exposures to airborne agricultural pesticides in California: Ranking of Inhalation Risks, *Env Health Persp*, 2002, 110: 1175–84.

[29] Ibid, Reference 25 (ARB chlorpyrifos monitoring report).

[30] *NIOSH Method 5600: Organophosphorus Pesticides,* NIOSH Manual of Analytical Methods, U.S. National Institute for Occupational Safety and Health, http://www.cdc.gov/niosh/nmam/.

[31] Appendices to *Report for the Application and Ambient Air Monitoring of Chlorpyrifos (and the Oxon Analogue) in Tulare County during Spring/Summer 1996,* California Air Resources Board, Test Report #C96-040 and # C96-041, April 7, 1998, http://www.cdpr.ca.gov/docs/empm/pubs/tac/chlrpfs.htm.

[32] Ibid, Reference 29 (Appendices to ARB chlorpyrifos monitoring report).

[33] Ibid, Reference 29 (Appendices to ARB chlorpyrifos monitoring report).

[34] Ibid, Reference 20 (IRED for chlorpyrifos).

[35] Layton, D, Metabolically consistent breathing rates for use in dose assessments, *Health Physiology, 1993,* 64: 23–36.

[36] Ibid, Reference 12. **xxx check**

[37] Code of Federal Regulations 40, §136, Appendix B.

[38] Ibid, Reference 25.