Air Monitoring in Hastings, Florida December 6–14, 2006:

Technical Report

Pesticide Action Network

Pesticide Action Network North America

April 2007

Air Monitoring in Hastings, Florida, December 6–14, 2006

List of Abbreviations

ARB	Air Resources Board, the California agency in charge of regulating air pollution in the state.
ATSDR	Agency for Toxic Substances and Disease Registry, the agency within the US Department of Health and Human Services that "performs specific functions concerning the effect on public health of hazardous substances in the environment."
DPR	Department of Pesticide Regulation, the California agency in charge of regulating pesticides in the state.
FQPA	The Federal Food Quality Protection Act. Passed in 1996, this law substantially revised the way US EPA evaluates pesticides for registration, requiring them to account for the special vulnerability of children and women of child-bearing age.
LD_{50}	A dose that is lethal to 50% of test animals of a given species. Commonly expressed in units of mg/kg, LD_{50} values are used to rank the acute toxicity of chemicals.
LOQ	Limit of Quantitation, the lowest concentration at which a laboratory can reliably measure the amounts of a pesticide present in a sample. See **Calculations** section for details.
MDL	Method Detection Limit, the lowest concentration that can reliably be detected for a sample collected and analyzed according to a specific method. See **Calculations** section for details.
NIOSH	National Institute for Occupational Safety and Health, the federal agency that oversees worker safety.
NOAEL	No Observable Adverse Effect Level, the toxicological dose of a chemical below which no adverse effects are anticipated from exposure to that chemical alone, usually in units of mg/kg-day.
OP	Organophosphorus compound, usually insecticides. Most OPs are neurotoxic, inhibiting the uptake of cholinesterase, an enzyme necessary for the proper functioning of the nervous system.
REL	Reference Exposure Level, the concentration of a chemical in air, derived from the US EPA-selected NOAEL, below which no adverse effects are anticipated from exposure to that chemical alone, given in units of ng/m^3. See **Calculations** section for details. A REL represents a level of concern for inhalation exposure analogous to the Reference Dose US EPA uses to assess levels of concern for dietary exposure.
SOP	Standard Operating Procedure, a written method for conducting sampling, analysis and other laboratory protocols. See Appendix 3 for an example.
US EPA	United States Environmental Protection Agency, the federal agency charged with regulating pesticides, air, water, hazardous waste sites, and more.
USDA-ARS	United States Department of Agriculture-Agricultural Research Service, the research arm of the USDA. One part of their work is to evaluate the fate and transport of pesticides in the environment.
USGS	United States Geological Survey, a federal agency that, among other activities, evaluates airborne pesticides as a source of water pollution.

Air Monitoring in Hastings, Florida, December 2006

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Executive Summary

This report presents the results of air monitoring in an agricultural area near South Woods Elementary School located adjacent to fields of Chinese cabbage in Hastings, Florida during December 2006. Monitoring was conducted for eight days, from December 6–14, and three pesticides were identified in the samples; the insecticides endosulfan and diazinon, and the herbicide trifluralin. The fact that pesticides were detected on most days indicates that volatilization of the pesticides is the primary source of the drift, although application-related drift may have contributed on the day(s) applications took place.

Endosulfan is an organochlorine insecticide that is applied in the US in greatest quantities to cotton, potatoes, and apples, and used in lesser amounts on a variety of vegetable and fruit crops. Residential uses of endosulfan were terminated in 2000. Endosulfan is acutely neurotoxic to both insects and mammals and a suspected endocrine disruptor. Symptoms of acute poisoning include hyperactivity, tremors, convulsions, lack of coordination, staggering, difficulty breathing, nausea/vomiting, and diarrhea. Studies have found associations between chronic exposure and delayed sexual maturity (in males) and increased incidence of birth defects of the male reproductive system. Skin irritation and brain damage have been noted among adults exposed to endosulfan occupationally. Nationwide from 1987–1997, US EPA estimated that average annual use of endosulfan was 1.38 million pounds.

Diazinon is an organophosphorus insecticide applied in the US to a wide variety of fruits, nuts, and vegetables. Diazinon is neurotoxic to both insects and mammals, inhibiting cholinesterase, an enzyme essential for the proper transmission of nerve impulses. Citing unacceptable risks to children and the environment, the US EPA banned all residential uses of diazinon effective 2004; however, agricultural use continues. Symptoms of acute poisoning range from headache, nausea and vomiting, dizziness, weakness, drowsiness, and agitation to difficulty breathing, twitching, excessive salvation and sweating, watery eyes, pinpoint pupils, confusion, inability to concentrate, and memory loss. Asthma, gestational diabetes, and certain types of cancer have been linked to chronic exposure to diazinon. Nationwide in 2001, US EPA estimated that 4-7 million pounds of diazinon were used, third behind malathion and chlorpyrifos for US organophosphorus insecticide use.

Trifluralin is a dinitroaniline herbicide used as a preemergent weed control agent to control annual grasses and broadleaf weeds on cotton, soybeans, peanuts, leafy greens, cole crops, peppers, tomatoes, and fruit trees in the US. It is also currently permitted for residential use on lawns and for use on golf courses. It is not acutely toxic, but it is listed by the EPA as a “Possible”

carcinogen. Epidemiological studies of farm workers and pesticide applicators have linked trifluralin exposure to increased incidence of stomach cancer and birth defects, and animals studies show increases in urinary bladder tumors, renal pelvis carcinomas, and thyroid gland tumors. Nationwide in 2001, US EPA estimated that 12-16 million pounds of trifluralin were used.

Sample results from air monitoring in Hastings, FL are reported below and summarized in Table 2 on page 19. The data presented here should be viewed as exposure estimates that may or may not represent worst-case exposure scenarios, and do not necessarily represent the precise exposure individuals may experience. Variability in actual exposures and the effects that may be experienced by individuals are governed by breathing rates and activity levels, time spent in areas where pesticide exposure can occur, and individuals' ability to detoxify chemicals. Inhalation may not be the sole exposure source, and total exposures from all routes (air, skin, diet) may be higher.

Of the eight samples collected (spikes and blanks excluded) between December 6th and 14th, 100% were found to be above the limit of quantitation (LOQ) of 26 nanograms (ng) of α–endosulfan per sample (equivalent to an air concentration of 8.9 ng/m^3 for a 24-hour sample at a 2.00 L/min flow rate and using a 2.00 mL solvent extraction volume). Eighty-eight percent were found to be above the LOQ of 40 ng of β–endosulfan per sample (equivalent to an air concentration of 14 ng/m^3 for a 24-hour sample at a 2.00 L/min flow rate and using a 2.00 mL solvent extraction volume). Thirty eight percent of the samples were above the 24-hour acute and sub-chronic 1-year-old child Reference Exposure Level (REL) of 340 ng/m^3, calculated from the US Environmental Protection Agency's inhalation No Observed Adverse Effect Level (NOAEL), as shown in the **Calculations** section of this report. A REL represents a level of concern for inhalation exposure analogous to the Reference Dose US EPA uses to assess levels of concern for dietary exposure. Twenty-five percent of the samples were above the 7-year-old REL of 500 ng/m^3. The highest concentration of total endosulfan observed for a 24-hour period was 626 ng/m^3 (1.8 times the 24-hour acute 1-year-old REL and 1.2 times the 7-year-old REL) on December 6, 2006, and the average concentration for the sampling period was 278 ng/m^3. Endosulfan sulfate was not detected in any of the samples.

For the insecticide diazinon, 88% of the eight samples were found to be above the LOQ of 51 ng per sample (equivalent to an air concentration of 18 ng/m^3 for a 24-hour sample at a 2.00 L/min flow rate and using a 2.00 mL solvent extraction volume). Sixty-three percent of the samples were above the 24-hour acute and sub-chronic 1-year-old child REL of 145 ng/m^3, and 50% were above the 7-year-old REL of 220 ng/m^3, calculated from the US EPA's inhalation NOAEL, as shown in the **Calculations** section of this report. The highest concentration of diazinon observed for a 24-hour period was 897 ng/m^3 (6.1 times the 24-hour acute 1-year-old REL and 4.1 times the 7-year-old REL) on December 12, 2006, and the average concentration for the sampling period was 311 ng/m^3. The diazinon oxon degradation product was not detected in any of the samples.

For the herbicide trifluralin, 50% of the eight samples were found to be above the LOQ of 129 ng per sample (equivalent to an air concentration of 45 ng/m^3 for a 24-hour sample at a 2.00 L/min flow rate and using a 2.00 mL solvent extraction volume). The highest concentration of trifluralin observed for a 24-hour period was 376 ng/m^3 on December 6, 2006, and the average concentration for the sampling period was 84 ng/m^3. Because this herbicide has relatively low

acute toxicity to mammals, the US EPA has not determined an acute or sub-chronic NOAEL, and therefore a REL could not be calculated. Trifluralin is ranked by the US EPA as a "Possible" carcinogen, and concerns with exposure center around the carcinogenicity of the compound, not its acute or sub-chronic toxicity. For trifluralin, potential lifetime cancer risk estimates were developed for a range of hypothetical exposure scenarios to bracket the potential lifetime cancer risk from potential exposures. The lifetime cancer risk is defined as the estimated number of cancer cases above the number the medical community considers the norm for a population. Lifetime cancer risks exceeding one in one million represent risks of concern. Table 3 on page 22 shows the results for trifluralin, none of which exceed levels of concern for even the highest hypothetical exposures. See the **Calculations** section for full details.

Exceedances of the RELs for diazinon and endosulfan are not necessarily anticipated to cause the symptoms of acute poisoning described above; however, the REL does represent a level of concern for inhalation exposure analogous to US EPA's Reference Dose for dietary exposure. It is unknown what exposure levels would produce the chronic effects noted above. Concentrations below the REL do not necessarily indicate that the air is "safe" to breathe. In particular, a number of recent studies evaluating the capacity of different people to metabolize toxic substances show that the variability among different people can be substantially greater than the variability assumed by US EPA in its toxicological analysis. In addition, on all but one day, all three pesticides were found in samples above detection limits. No "acceptable" levels have been established for exposures to multiple pesticides simultaneously. It is possible that additive or synergistic effects may increase the toxicity of one pesticide in the presence of others.

About Air Monitoring Results

What is a Reference Exposure Level?

In this air monitoring study, we compare measured air concentrations of pesticides found in 24-hour air samples to available 24-hour Reference Exposure Levels (RELs) for two subpopulations for each pesticide found: 1-year-old children and 7-year-old children. A REL represents a level of concern for inhalation exposure analogous to the Reference Dose US EPA uses to assess levels of concern for dietary exposure. The REL is an air concentration in nanograms of pesticide per cubic meter of air (ng/m^3) equivalent to a dose in milligrams of pesticide per kilogram of body weight (mg/kg) below which no adverse effects are anticipated from exposure to a *single pesticide*.[1] The REL is calculated from a NOAEL determined by US EPA from toxicology studies conducted by the pesticide manufacturer.

We evaluate whether the measured levels of pesticide in air exceed the REL for two sensitive populations—1-year-olds and 7-year olds—by taking into account the body weight and breathing rate of the average child in each category (see the **Calculations** section of this report for the detailed calculation). Exceedances of the REL are not necessarily anticipated to cause the symptoms of acute poisoning described in this report but do represent a potential health concern—the larger the exceedance, the higher the probability of adverse effects from pesticide exposure. It is unknown what exposure levels would produce the chronic effects noted above.

The REL is not an enforceable standard like a water quality standard or a worker protection standard, but in dietary assessments, EPA designates the dose of a pesticide at this level as a Level of Concern (LOC) and typically takes action to reduce dietary exposures of the 99.9th percentile person below the LOC to decrease exposure risk. This means that if even one-tenth of one percent of the people were exposed to a pesticide in their diet at this level, US EPA would take action to reduce risk. Unfortunately, there are regulatory gaps for inhalation exposure—US EPA does not currently assess bystander inhalation exposures for most pesticides, including those found in this study, instead assuming inhalation is not a significant contributor to total exposure. This Hastings study and others cited in this report indicate that this assumption is flawed.

Are Levels Below the REL "Safe"?

Concentrations below the REL do not necessarily indicate that the air is "safe" to breathe. In particular, a number of recent studies evaluating the capacity of different people to metabolize toxic substances show that the variability among different people can be substantially greater than the variability assumed by US EPA in its toxicological analysis.[2] Additionally, as in this study, people are often exposed to multiple pesticides simultaneously, or are taking a prescription or non-prescription drug, or are exposed to other chemicals, thus reducing their capacity to detoxify the pesticides to which they are exposed. Finally, the pesticide industry's definition of an "adverse" effect doesn't include symptoms like headache, nausea, or malaise because these are not observable symptoms in laboratory animals. These effects are nevertheless uncomfortable and often debilitating for humans, interfering with people's ability to earn a living, perform well in school, take care of their children, or simply be comfortable in their homes.

What Do Air Monitoring Results Tell Us About Exposure?

The data presented here should be viewed as exposure estimates that may or may not represent worst-case exposure scenarios, and do not necessarily represent the precise exposure individuals may experience. Variables that affect an individual's exposure to airborne pesticides include the amount of time spent in areas with high concentrations of airborne pesticides, body weight and breathing rate. Exposures to the pesticides may also occur through other routes, especially for children. Pesticide drift can contaminate house dust, lawns, playground equipment, pets and toys that children may touch and eventually they may ingest these residues.

The breathing rates used to derive the RELs in this study (see Table 6 on page 33, and the **Calculations** section) represent the breathing rates of individuals *averaged over the course of 24 hours*. An individual child's breathing rate will, of course, vary substantially over the course of 24 hours. For example, the typical breathing rate of a 10-year child during resting activity (e.g. sleeping, reading or watching television) is 0.4 m^3/hr, while during moderate activity (e.g. climbing stairs) it is 2.0 m^3/hr, and during heavy activity (e.g. playing sports) is almost ten times greater at 3.9 m^3/hr.[3] The breathing rate of a child at play during recess or exercising during a gym class is best approximated by the moderate or heavy activity breathing rate. Thus, children are outside and maximally exposed to air contaminants precisely when their breathing rates are expected to be highest. The RELs used this report are calculated using lower than moderate breathing rates—the daily averages—and assuming 24 hour exposure. But even though a child is at school for less than 24 hours, during the time she spends there—particularly the time spent playing outside—her breathing rate is higher than the daily average, and thus she may still inhale enough pesticide to exceed the reference dose.

For most pesticides, only a limited number of monitoring studies are available for comparison, and most of the available studies only provide results for applications conducted according to label instructions and for exposure estimates to a single pesticide. The Drift Catcher project is providing additional monitoring data for comparison, and as we gather more data, a clearer picture of pesticide levels in air near homes, schools, parks and workplaces will emerge.

Notwithstanding that available monitoring data are not comprehensive, the data indicate that many people are routinely exposed to levels of airborne pesticides that exceed both acute and sub-chronic levels of concern.

About Endosulfan

Endosulfan Use and History

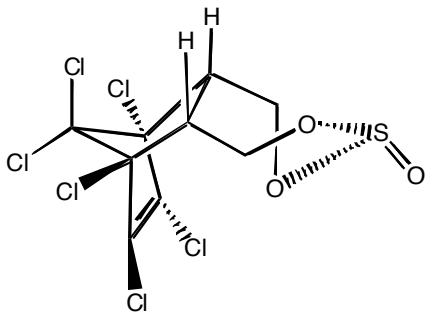
First registered for use in 1954, endosulfan is a broad-spectrum organochlorine insecticide and acaricide. In the 2002 Reregistration Eligibility Decision, US EPA determined that children's dietary exposure to endosulfan was above the agency's level of concern, and required the deletion of certain US crop uses from endosulfan product labels as a mitigation measure.[4] Residential uses of endosulfan were voluntarily withdrawn by the registrant in 2000, but this insecticide continues to be registered for use on a wide variety of field, orchard, and vegetable crops. The agency also announced it was concerned about drinking water contamination and worker exposure and therefore required several additional label amendments, including reductions in application rates and increases in restricted entry intervals for workers.

US EPA estimates that for the period from 1987 to 1997, the average annual use of endosulfan was 1.38 million lbs active ingredient. The crops with the highest total endosulfan use were cotton (286,000 lbs/yr), potatoes (120,000 lbs/yr), and apples (110,000 lbs/yr). The crops with the highest average percent acreage treated were eggplant (41%), squash (40%), cantaloupe (31%), and sweet potatoes (31%).[4] US EPA claims that endosulfan usage is declining, and this trend can be observed in Pesticide Use Reporting data from California.[5] From 1990 to 1999, the average annual use of endosulfan in the state was 268,000 lbs/yr, while from 2000 to 2005 the average declined to 135,000 lbs/yr. Bayer CropScience, Makhteshim-Agan, and Drexel Company produce the endosulfan products that are currently registered in the US. Common product names include Thionex, Thiodan, and Phaser.

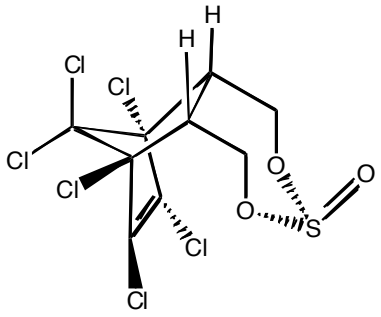
Endosulfan is banned in Germany, Norway, the Netherlands, the Philippines, and other countries.[6] In some countries—but not in the US—it is a restricted use pesticide.[7] In March of 2007, the Chemical Review Committee of the Rotterdam Convention on Prior Informed Consent recommended endosulfan for inclusion in the convention. If approved by the parties to the convention when they meet in 2008, restrictions would be placed on the import and export of endosulfan containing products.[8]

Physical Properties of Endosulfan

Endosulfan [6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepine-3-oxide] is a cyclodiene insecticide derived from hexachlorocyclopentadiene. Technical grade endosulfan exists as a mixture of two stereoisomers, α-endosulfan and β-endosulfan, in a ratio of approximately 7:3, with up to 8% endosulfan sulfate and related compounds. It is a brownish crystalline material with a turpentine or slight sulfur dioxide odor. β-endosulfan slowly converts to α-endosulfan. The chemical structures of the two isomers are shown below.[9]



α-Endosulfan



β-Endosulfan

Physical properties of endosulfan are shown in Table 1 below.

Endosulfan is a semi-volatile chemical that 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. Endosulfan sulfate is the major biodegradation product in soils under aerobic, anaerobic and flooded conditions.[10]

Health Effects of Endosulfan

Like other organochlorine pesticides, the toxicity of endosulfan to both insects and humans arises from overstimulation of the nervous system. Specifically, endosulfan interferes with the transmission of nerve impulses by inhibiting Ca^{2+}, Mg^{2+}-ATPase and acting as a GABA-gated chloride channel antagonist.[11] There is some evidence that endosulfan is also a weak inhibitor of acetyl cholinesterase, the same enzyme that is targeted by the organophosphate and carbamate insecticides.[11]

US EPA classifies endosulfan as highly acutely toxic (Toxicity Category I) by oral exposure, based on oral LD_{50} values in rats of 82 mg/kg (males) and 30 mg/kg (females).[4] The α-isomer is reported to be three times as acutely toxic as the β–isomer.[11] In humans, death from endosulfan intoxication has been documented at doses as low as 35 mg/kg.[12] Symptoms of acute poisoning include hyperactivity, tremors, convulsions, lack of coordination, staggering, difficulty breathing, nausea/vomiting, diarrhea, and in severe cases, unconsciousness. In one case, a man suffered permanent brain damage after ingesting endosulfan in an attempted suicide.[11]

Less is known about the effects of chronic endosulfan exposure. According to the US EPA, data on farm workers handling foliage treated with endosulfan "show a consistent risk of skin rash or irritation,"[4] and long-term brain damage has resulted from occupational endosulfan intoxication.[13] Impairment of learning and memory was observed in studies of rats exposed to low doses of endosulfan.[11]

A growing body of evidence suggests that endosulfan has estrogenic activity and can disrupt hormonally mediated biological processes. US EPA considers it to be a potential human endocrine disruptor,[4] and ATSDR concluded that "endosulfan may potentially cause reproductive toxicity in humans."[11] Studies of children from areas with high endosulfan contamination have demonstrated a link between the insecticide and abnormal male reproductive development. One study compared male schoolchildren from an isolated Indian village with a 20-year history of endosulfan pollution to a control group of children from a demographically similar village with no history of endosulfan contamination. The study found that relative to the control group, the exposed boys had statistically significant delays in reaching sexual maturity, depressed testosterone levels, and high levels of endosulfan and its metabolites in their bodies. There was also an increased incidence of birth defects of the reproductive organs including cryptorchidism (undescended testicles), although because of the small sample size this increase did not reach statistical significance.[14] An increase in the rate of cryptorchidism was also observed in the Granada region of Spain, where endosulfan or its metabolites were detected in 40% of children hospitalized for various reasons.[11] Finally, a study of Scandinavian births found that the content of organochlorine pesticides including endosulfan in breast milk is higher in mothers giving birth to boys with cryptorchidism.[15] In addition to these studies of human populations, there are numerous studies demonstrating that endosulfan can act as a reproductive and developmental toxicant and as an endocrine disruptor in animals.[11, 14]

A variety of studies in young animals suggest that children are likely to be more susceptible to the toxic effects of endosulfan than adults. The US EPA has therefore included an additional 10-fold safety into its calculation of the level of exposure it considers to be "acceptable" to

children.[4, 11] Animal studies also indicate that people with seizure disorders may be more susceptible to endosulfan.[11]

About Diazinon

Diazinon Use and History

Diazinon is an organophosphate insecticide, acaricide, and nematicide. It is marketed by several companies including Makhteshim-Agan and Drexel Chemical Company and sold under the trade names Diazol, Spectracide and Knox-Out. In the US, diazinon is registered for use on a variety of fruit, vegetable, and fields crops and in cattle ear-tags, but it is no longer registered for residential use. It is not a restricted use pesticide.

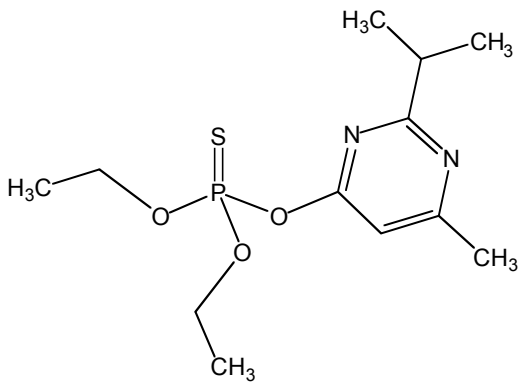
Diazinon was developed by Ciba-Geigy in the 1950s and first registered in the US in 1956.[16] As many organochlorine insecticides were phased out in the 1970s and 80s, the use of diazinon increased.[17] US EPA estimates that between 1987 and 1997, the average annual use of diazinon in the US was greater than 13 million pounds of active ingredient, with about 70% being used in residential, non-agricultural settings. The crops with the highest total diazinon use during this period were almonds (170,000 lbs/yr), prunes and plums (130,000 lbs/yr), and peaches (63,000 lbs/yr). The crops with the highest average percent acreage treated were Brussels spouts (90%), hops (63%), and nectarines (54%).[18]

In 2000, US EPA concluded that the residential uses of diazinon posed an unacceptable risk to children.[18] To protect children from exposure, the agency negotiated phase-outs and cancellations that ended all residential uses of diazinon in 2004; however, most agriculture uses were allowed to continue. Prior to the phase-out, diazinon was the most widely used insecticide in the home and garden sector.[19]

In 2002, the US EPA recognized that farm workers also faced unreasonable risks when handling diazinon and proposed several measures to protect them.[18] A fact sheet published by the US EPA in 2004 admitted that the proposed worker protection measures were inadequate: "Even with the recommended mitigation measures, diazinon's worker and ecological risks will still be above levels of concern, but these risks are offset by strong benefits of diazinon use in fruit and vegetable production."[20]

Physical Properties of Diazinon

When pure, diazinon [*O*,*O*-diethyl *O*-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate] is a colorless oil with a slight ester odor. The technical material is about 90% pure, and exists as an amber to brown liquid. It is moderately volatile, with a vapor pressure of 1.40×10^{-4} mm Hg at 20 °C, and can readily drift from areas where it has been applied. The chemical structure of diazinon is shown below and the physical properties of diazinon are summarized in Table 1 below.



Diazinon

Health Effects of Diazinon

In both insects and other animals, including humans, the immediate effect of diazinon is overstimulation of the nervous system caused by inhibition of acetyl cholinesterase, an enzyme involved in the transmission of nerve impulses. This mode of action is common to all organophosphate and carbamate insecticides, and therefore exposure to several different pesticides from these classes has additive effects.[21] It can take weeks for cholinesterase activity to return to normal after exposure to diazinon, and therefore repeated exposure can have a cumulative effect. In a controlled experiment with healthy volunteers, plasma cholinesterase activity was measured 15 days after a single dose of diazinon and found to have recovered to only 70% of baseline activity.[17]

Diazinon is considered to be of moderate acute toxicity based on the World Health Organization's rating of diazinon as "moderately hazardous" (Category II),[31] and on the oral LD_{50} values in rats ranging from 76 to 600 mg/kg that are listed in the Draft Toxicological Profile for Diazinon published in September 2006 by ATSDR.[17] The US EPA regards diazinon as "slightly toxic," (Category III) based on an unpublished study reporting a rat oral LD_{50} of 1,250 mg/kg.[18] Symptoms of mild acute poisoning include headache, nausea and vomiting, dizziness, weakness and drowsiness, and agitation. Difficulty breathing, twitching, excessive salvation and sweating, watery eyes, and pinpoint pupils are signs of more serious poisoning, and can be accompanied by confusion, an inability to concentrate, and memory loss. Severely poisoned individuals can experience loss of consciousness, seizures, and death if not treated.[22] These symptoms are for single exposures to relatively large amounts of diazinon, but many of these effects have also been observed in people who have been chronically exposed to lower levels of diazinon.[17] Cases of farm worker diazinon poisonings are many, and there are also cases of infants hospitalized for diazinon poisoning resulting from residential use. In one case, twins showed signs of poisoning one day after a *neighboring* apartment was spot-treated with a 1% diazinon formulation.[23]

The Association of Occupational and Environmental Clinics (AOEC) lists organophosphate pesticides in general—and diazinon specifically—as capable of causing asthma in previously unaffected individuals. Exposure can also exacerbate asthmatic symptoms in individuals who already have the disease.[24]

Diazinon exposure is also a risk factor for gestational diabetes mellitus (GDM). A recent of study of pesticide applicators and their spouses found that among women who reported working with pesticides on the farm during pregnancy, incidence of GDM was increased by 200 to 300% for women who had ever used diazinon.[25]

There is little evidence to suggest that diazinon is an endocrine disruptor or reproductive toxin. There is, however, evidence of developmental neurotoxicity from studies of laboratory animals and accidentally exposed humans.[17] A recent study in neonatal rats demonstrated developmental neurotoxicity at doses lower than those that cause inhibition of acetyl cholinesterase.[26] Diazinon is not considered to be carcinogenic by either the US EPA or the National Toxicological Program (NTP); however, ATSDR notes that there are several studies showing "weak associations" and "possible links" between diazinon and lung cancer, multiple myeloma, non-Hodgkin's lymphoma, and childhood brain cancer. Participants in these studies were also exposed to other pesticides, making it difficult to draw direct links to diazinon specifically.[17] Diazinon did not cause cancer in rats and mice in controlled experiments.

Experiments with young animals and studies of accidentally exposed children suggest that children are particularly susceptible to the effects of diazinon,[17] and recent research has shown that there is a 65-fold range of variability in sensitivity to the effects of diazoxon—a metabolite of diazinon that is more toxic than diazinon itself—among a cohort of Latina mothers and their children.[2] This study concluded that, "These data predict that most, if not all, newborns, as well as a subpopulation of adults, will exhibit significantly increased sensitivity to organophosphate exposure." Ignoring these studies, US EPA has instead focused on studies provided by Ciba-Giegy, a major manufacturer of diazinon, which found no evidence of increased sensitivity among young animals. The agency has therefore reduced the 10-fold child protection safety factor to one in their calculation of the maximum "acceptable" acute dose of diazinon for children.[18] However, for repeated exposures and when considering cumulative exposures to all organophosphorus pesticides, US EPA selected a child protection factor of 10.[21] We calculated diazinon RELs *without* the additional factor of 10 because it is not precisely clear how EPA intends this "repeated exposure" uncertainty factor to be interpreted. If the exposure of children at the school fits the "repeated exposure" scenario, the 1-year-old child REL for diazinon would be 14.5 ng/m^3, a factor of 10 *lower* than the 145 ng/m^3 level used for comparison in this study.

About Trifluralin

Trifluralin Use and History

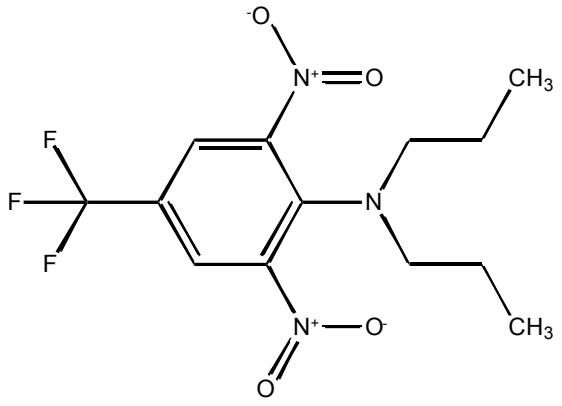
Trifluralin is a selective pre-emergent herbicide that is registered for use in both agricultural and residential settings. Patented by Eli Lilly, it has been registered for use in the US since 1963. In 1979 US EPA considered a cancellation of registration because trifluralin products were found to contain high levels of NDPA (N-nitroso-di-*n*-propylamine), a possible human carcinogen. Cancellation was averted when manufacturers agreed to reformulate their trifluralin products and certify that the new formulations contained no more than 0.5 ppm of NPDA.[27] In 1990, trifluralin was classified under the Clean Air Act as a hazardous air pollutant.[28] The European Community recently announced a plan to phase out trifluralin by March 2009 because of safety concerns.[29]

Patented by Eli Lilly, trifluralin products are currently manufactured by a number of companies including Dow Agrosciences, Makhteshim-Agan, Drexel Chemical Company, and Gowan Company, and sold under a variety of trade names including Treflan and Trifluro. Formulations that are marketed to homeowners often contain trifluralin in combination with other pesticides, especially benfluralin.

The US EPA estimates that between 1987 and 1993, average annual US use of trifluralin in agriculture totaled 28 million lbs a.i. The crops with the highest total trifluralin use during this period were soybeans (17,985,000 lbs/yr), cotton (5,379,000 lbs/yr), and wheat (945,000 lbs/yr). The crops with the highest average percent acreage treated were green beans (93%), broccoli (85%), tomatoes (63%), and cotton (62%).[27] Agricultural use declined to 18 million lbs/yr for the period from 1997 to 2001, with cotton and soybeans still accounting for the majority (75%) of total use.[30] Estimates of the volume of residential use are not available, but it is not included in US EPA's top 10 list of pesticides sold for home and garden use.[19]

Physical Properties of Trifluralin

Trifluralin [α,α,α-trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine] is a dinitroaniline herbicide, similar in structure to benfluralin, prodiamine, and oryzalin. It is a yellow-orange crystalline solid with an aromatic odor. Trifluralin is a semi-volatile chemical that can readily volatilize from leaf and soil surfaces and become airborne. Trifluralin can be decomposed by sunlight. The physical properties of trifluralin are summarized in Table 1 below and the chemical structure of trifluralin is shown below.



Trifluralin

Health Effects of Trifluralin

Based on high oral LD_{50} values in rats (>5000 mg/kg), the US EPA has classified trifluralin as acute Toxicity Category IV, "practically non-toxic," for oral exposure.[27] Likewise, the World Health Organization classifies trifluralin as "unlikely to present an acute hazard in normal use."[31] Some individuals may develop an allergic reaction to trifluralin after dermal exposure, and tests in lab animals show that trifluralin is a mild eye irritant.[32]

Increases in liver weight and changes in the levels of some blood components were noted in laboratory animals fed moderate amounts of trifluralin (≥3.75 mg/kg/day) daily over the course of a year. In animal studies, reproductive and developmental effects where observed only at dose

levels that were also toxic to adult animals;[27] however, there is some of evidence of developmental effects in humans. Researchers examining Minnesota birth registries have observed a small but statistically significant increase in the incidence of birth defects in the children of pesticide applicators who use trifluralin.[33] The US EPA has stated that "trifluralin does not appear to be an endocrine disruptor,"[27] although experts on endocrine disruption including Theo Colborn and Lawrence Keith as well as other environmental agencies such as the UK Environment Agency, and the Illinois Environmental Protection Agency have included it on their lists of suspected endocrine disruptors.[34]

US EPA classifies trifluralin as a "Possible" human carcinogen based on increased incidence of benign and malignant tumors in rats fed trifluralin for 2 years. Types of tumors included urinary bladder tumors in females, renal pelvis carcinomas in male rats, and thyroid gland follicular cell tumors (adenomas plus carcinomas combined) in males. Purified trifluralin did not cause cancer in mice; however, when trifluralin contaminated with NDPA was tested, female mice did develop cancer.[27] A recently published study of California farm workers found that those who had likely been exposed to trifluralin were 69% more likely to be diagnosed with stomach cancer than unexposed workers.[35]

Young animals do not appear to be more sensitive to the effects of trifluralin than adults, so the US EPA has used a child protection factor of one in their calculation of maximum acceptable dose for children.[27]

Table 1: Physical Properties of Endosulfan, Diazinon and Trifluralin

Property or Identifier	Endosulfan			Diazinon	Trifluralin
	α–	β–	Technical		
CAS Number	959-98-9	33213-65-9	115-29-7	333-41-5	1582-09-8
Chemical Formula	$C_9H_6Cl_6O_3S$	$C_9H_6Cl_6O_3S$	$C_9H_6Cl_6O_3S$[a]	$C_{12}H_{21}N_2O_3PS$	$C_{13}H_{16}F_3N_3O_3$
Molecular Weight (g/mol)	406.95	406.95	[b]	304.36	335.32
Melting Point (°C)	108-110	208-210	70-100	dec. > 120	42-49
Water Solubility (µg/L)	330 @ 25°C	320 @ 25°C	NA	60 @ 22°C	300 @ 25°C
Octanol-Water Partition Coefficient (Log K_{ow})	3.55	3.62	4.45–5.67	3.81	5.07
Vapor Pressure (mm Hg)	3.0×10^{-6} @ 25 °C	7.2×10^{-7} @ 25 °C	1×10^{-5} @ 25 °C	1.40×10^{-4} @ 20 °C	1.03×10^{-4} @ 27 °C
Henry's Law Constant (atm-m^3/mol)	1×10^{-5} @ 25 °C	1.91×10^{-5} @ 25 °C	1.01×10^{-4} @ 25 °C	1.17×10^{-7} @ 25 °C	1.51×10^{-4} @ 25 °C
Avg. Hydrolysis Half-life	218 hours	187 hours	94 days	138 days	>32 days
Avg. Aerobic Soil Half-life	NA	NA	26 days (pH 6.4)	40 days	169 days
Avg. Anaerobic Soil Half-life	NA	NA	152 days (pH 6.4)	16 days	37 days

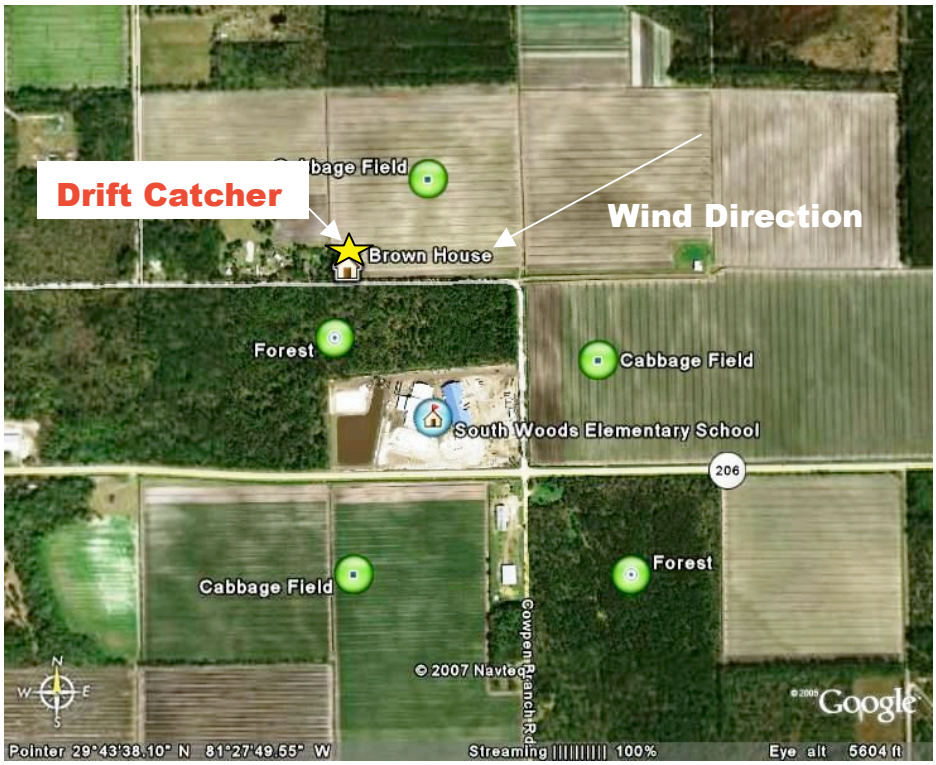
NA = not available.
[a]Technical grade endosulfan also contains some endosulfan sulfate and other impurities from the production process.
Data source: CA Department of Pesticide Regulation Physical Properties database (Reference 36) and the ARB monitoring studies for endosulfan and diazinon (References 10 and 38).

Siting the South Woods Study

The original intent of the study was to monitor pesticides in air on the school grounds; however, repeated requests to locate the Drift Catcher at the school were denied. Instead, the Drift Catcher was placed in the northeast corner of the back yard of a house (the "Brown House" on the map) on Cowpen Branch Road, 0.3 miles north of the school. The Drift Catcher was located approximately 65 ft to the west and 65 ft to the south of fields where Chinese cabbage was cultivated, midway between a row of mature trees to the east and a tool shed to the west, approximately three feet from both the trees and the shed (see photos below).

The Drift Catcher was placed in this location because it equaled the distance between the playground at South Woods Elementary School and the field where Chinese cabbage was cultivated directly east of the school. The location of the sampling site relative to cabbage fields and that of the school relative to cabbage fields were similar with respect to prevailing winds. A potentially significant difference between the two sites is the row of trees between the field and the Drift Catcher at the sampling site that does not exist at the school. It is possible that this row of trees might have blocked some of the airborne pesticides from reaching the sample tubes. If so, the concentrations found at the sampling site might be lower than what would have been found at the school.

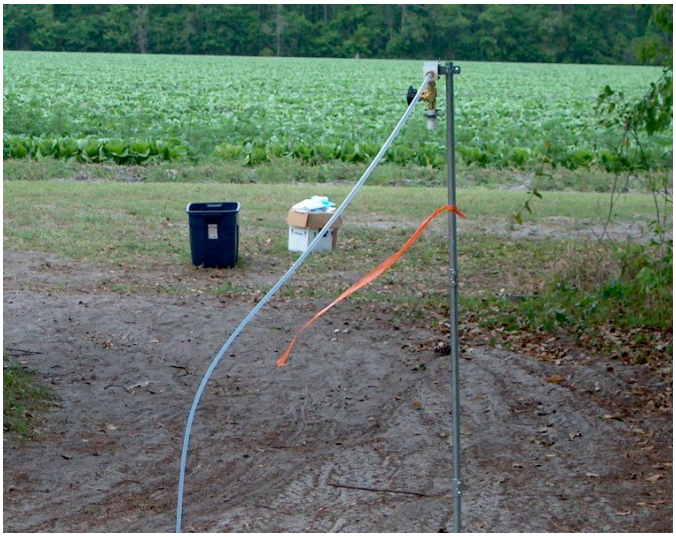
Prevailing winds were primarily from the northeast during the course of the eight days of sampling, December 6–14, 2006. Pesticide applications were observed on December 6 and 13, and a field worker indicated that the pesticides applied on the 13th were "diazinon" and "thionex". Thionex is a trade name for endosulfan.



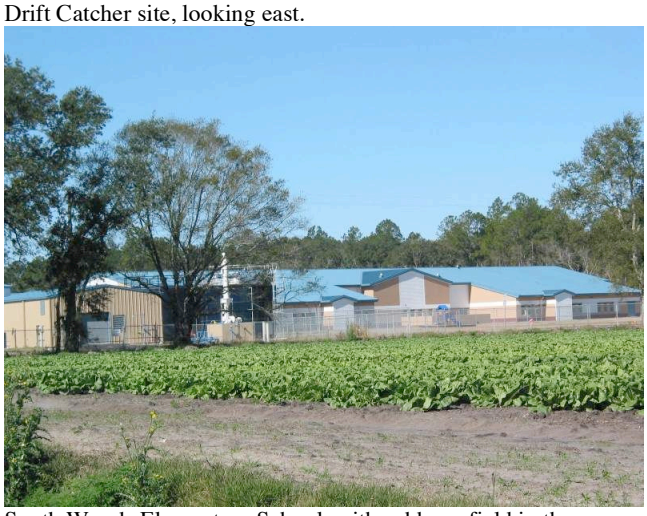
Google satellite map showing prevailing wind direction, Drift Catcher site and South Woods Elementary School.

Drift Catcher site, looking south.

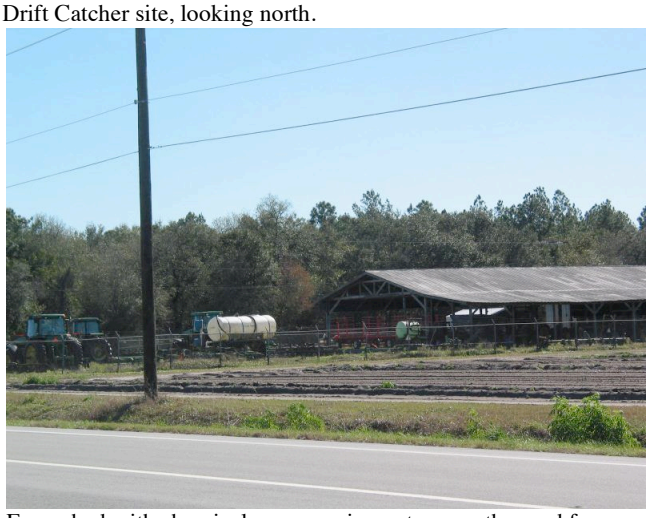
Drift Catcher site, looking east.



Drift Catcher site, looking north.



South Woods Elementary School, with cabbage field in the foreground.



Farm shed with chemical spray equipment across the road from South Woods Elementary School.

Results

Monitoring was conducted near the school for eight days, from December 6–14, and three pesticides were identified in most of the samples; the insecticides endosulfan and diazinon, and the herbicide trifluralin. The fact that pesticides were detected on most days indicates that volatilization of the pesticides is the primary source of the drift, although application-related drift may have contributed on the day(s) applications took place. Complete results for all pesticides are provided in Table 2, and plots of the daily pesticide concentrations for each pesticide are presented in Figures 1, 2 and 3. No diazinon or trifluralin was detected in any of the rear beds of the XAD-2 resin tubes, indicating that there was no breakthrough of these pesticide compounds from the front resin bed to the rear, i.e. no overloading of the sampling tubes. Trace amounts (less than the LOQ but greater than the MDL) of α- and β-endosulfan were detected on the rear beds of some samples. The calculation of the total endosulfan concentration does not include the trace amounts of endosulfan detected in rear beds. 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.[10]

Table 2: Pesticide Concentrations in Hastings, FL, December 6–14, 2006

Sample Name	Start Date	Start Time (p.m.)	Total Time (min)	Total Volume (m^3)	Total Endosulfan[c] (ng/m^3)	Diazinon (ng/m^3)	Trifluralin (ng/m^3)	Comment
Red[a]	12/6/06	4:24	N/A	N/A	0	0	0	α- & β-Endosulfan, Diazinon & Trifluralin < MDL
Sky	12/6/06	4:36	1355	2.98	626	162	376	Minimum values.[b]
Bird	12/7/06	3:20	1428	3.08	45	116	21	β–Endosulfan & trifluralin < LOQ
Banana	12/8/06	3:18	1759	3.69	92	129	18	Trifluralin < LOQ
Bread	12/9/06	8:44	1237	2.69	204	0	0	Trifluralin & Diazinon < MDL
House	12/10/06	5:28	1511	3.32	244	233	54	
---	12/11/06	ND	ND	ND	ND	ND	ND	No sample taken on this day
Salt	12/12/06	5:24	1547	3.40	511	897	79	
Apple	12/13/06	3:19	1470	3.23	340	684	89	Minimum values.[b]
Mom	12/14/06	3:58	1303	1.82	160	271	35	Trifluralin < LOQ. Minimum values.[b]
Average					**278**	**311**	**84**	

ND = no data
MDLs: α-endosulfan, 1.8 ng/m^3; β-endosulfan, 2.8 ng/m^3; diazinon, 3.5 ng/m^3; trifluralin, 9.0 ng/m^3.
LOQs: α-endosulfan, 8.9 ng/m^3; β-endosulfan, 14 ng/m^3; diazinon, 18 ng/m^3; trifluralin, 45 ng/m^3.
[a] Red was a trip blank sample. The tube was cracked on the day and time indicated at the site, transported along with the samples, and analyzed as though it were a sample. It was never attached to the Drift Catcher.
[b] Flow rate changed by >10% during sampling, so the maximum flow rate was used to calculate sample air volume. This will give a conservative estimate of concentration.
[c] Total endosulfan includes the sum of the α and β isomers of endosulfan.

Endosulfan

Of the eight samples collected (spikes and blanks excluded) between December 6th and 14th, 100% were found to be above the limit of quantitation (LOQ) of 26 nanograms (ng) of α–endosulfan per sample (equivalent to an air concentration of 8.9 ng/m^3 for a 24-hour sample at

a 2.00 L/min flow rate and using a 2.00 mL solvent extraction volume). Eighty-eight percent were found to be above the LOQ of 40 ng of β–endosulfan per sample (equivalent to an air concentration of 14 ng/m^3 for a 24-hour sample at a 2.00 L/min flow rate and using a 2.00 mL solvent extraction volume). Thirty eight percent of the samples were above the 24-hour acute and sub-chronic 1-year-old child Reference Exposure Level (REL) of 340 ng/m^3, calculated from the US Environmental Protection Agency's inhalation No Observed Adverse Effect Level (NOAEL), as shown in the **Calculations** section of this report. Twenty-five percent of the samples were above the 7-year-old REL of 500 ng/m^3. The highest concentration of total endosulfan observed for a 24-hour period was 626 ng/m^3 (1.8 times the 24-hour acute 1-year-old REL and 1.2 times the 7-year-old REL) on December 6, 2006, and the average concentration for the sampling period was 278 ng/m^3. Endosulfan sulfate was not detected in any of the samples. The Method Detection Limit (MDL) for α-endosulfan was 1.8 ng/m^3 and β-endosulfan was 2.8 ng/m^3 and the LOQ was estimated at five times the MDL or 8.9 ng/m^3 (α) and 14 ng/m^3 (β). Results are summarized in Figure 1.

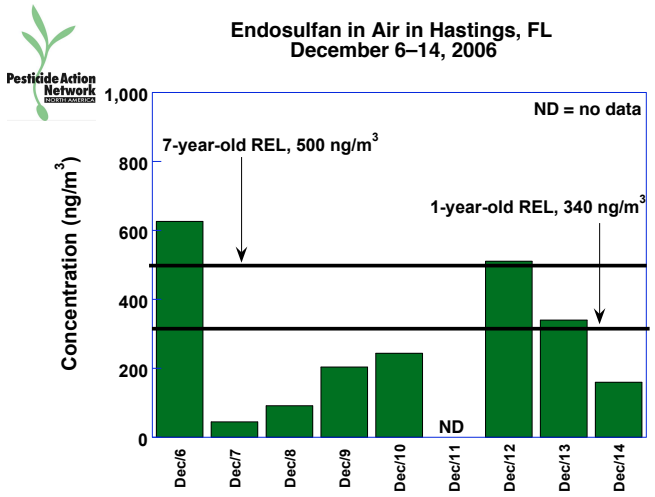


Figure 1: Endosulfan concentrations in Hastings, FL December 6–14, 2006. REL = 24-hour Reference Exposure Level calculated from US EPA's "acceptable" daily dose for acute and sub-chronic exposures.

Diazinon

For the insecticide diazinon, 88% of the eight samples were found to be above the LOQ of 51 ng per sample (equivalent to an air concentration of 18 ng/m^3 for a 24-hour sample at a 2.00 L/min flow rate and using a 2.00 mL solvent extraction volume). Sixty-three percent of the samples were above the 24-hour acute and sub-chronic 1-year-old child REL of 145 ng/m^3, and 50% were above the 7-year-old REL of 220 ng/m^3, calculated from the US EPA's inhalation NOAEL, as shown in the **Calculations** section of this report. Twenty-five percent even exceeded the adult REL of 335 ng/m^3. The highest concentration of diazinon observed for a 24-hour period was 897 ng/m^3 (6.1 times the 24-hour acute 1-year-old REL and 4.1 times the 7-year-old REL) on December 12, 2006, and the average concentration for the sampling period was 311 ng/m^3. The diazinon oxon degradation product was not detected in any of the samples. The MDL for diazinon was 3.5 ng/m^3, and the LOQ was estimated at five times the MDL or 18 ng/m^3. Results are summarized in Figure 2.

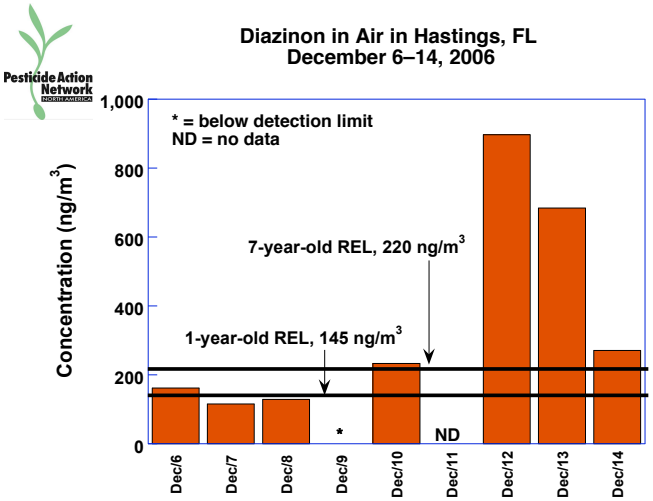


Figure 2: Diazinon concentrations in Hastings, FL December 6–14, 2006. REL = 24-hour Reference Exposure Level calculated from US EPA's "acceptable" daily dose for acute and sub-chronic exposures.

Trifluralin

For the herbicide trifluralin, 50% of the eight samples were found to be above the LOQ of 129 ng per sample (equivalent to an air concentration of 45 ng/m^3 for a 24-hour sample at a 2.00 L/min flow rate and using a 2.00 mL solvent extraction volume). The highest concentration of trifluralin observed for a 24-hour period was 376 ng/m^3 on December 6, 2006, and the average concentration for the sampling period was 84 ng/m^3. Because this herbicide has relatively low acute toxicity to mammals, the US EPA has not determined an acute or sub-chronic NOAEL, and therefore a REL could not be calculated. The MDL for trifluralin was 9.0 ng/m^3 and the LOQ was estimated at five times the MDL or 45 ng/m^3. Results are summarized in Figure 3.

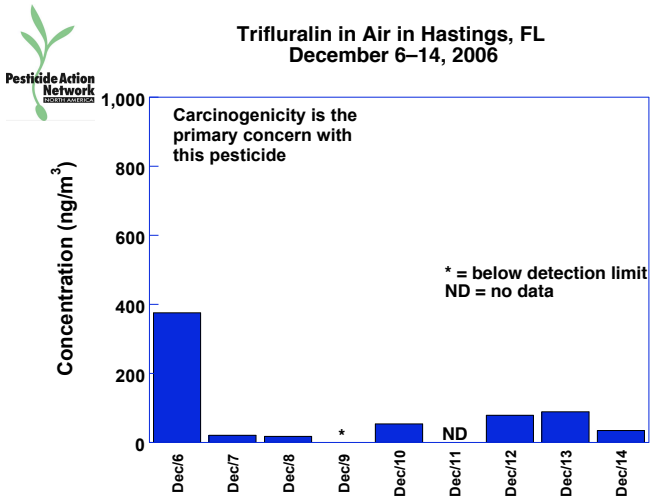


Figure 3: Trifluralin concentrations in Hastings, FL December 6–14, 2006. No acute or sub-chronic REL has been determined for this pesticide.

Trifluralin is ranked by the US EPA as a "Possible" carcinogen, and concerns with exposure center around the carcinogenicity of the compound, not its acute or sub-chronic toxicity.[27] For trifluralin, potential lifetime cancer risk estimates were developed for a range of hypothetical exposure scenarios to bracket the potential lifetime cancer risk from potential exposures. The lifetime cancer risk is defined as the estimated number of cancer cases above the number the medical community considers the norm for a population. Lifetime cancer risks exceeding one in one million represent risks of concern. Table 3 shows the results for trifluralin, none of which exceed levels of concern for even the highest estimated exposures. See the **Calculations** section for full details.

Table 3: Cancer Estimates for Various Trifluralin Exposure Scenarios

Parameter	Lowest dose scenario	Low dose scenario	Medium dose scenario 1[b]	Medium dose scenario 2	High dose scenario	Highest dose scenario
Average concentration during monitoring period (ng/m^3)	1	10	84[b]	84	1000	10,000
Exposure frequency as percent of a year	3.80%	3.8%	3.8%	10.0%	25.0%	3.8%
Average annual concentration (ng/m^3)	0.038	0.38	3.2	8.4	250	380
Annual exposure to trifluralin[a] (mg/kg-day)	0.011	0.11	0.89	2.4	70	106
Cancer potency factor, Q* (mg/kg-day)$^{-1}$	0.0077	0.0077	0.0077	0.0077	0.0077	0.0077
Lifetime Cancer Risk (excess cancers per million people)	**0.000082**	**0.00082**	**0.0069**	**0.0184**	**0.54**	**0.82**

[a]For an adult breathing rate of 0.28 m^3 per kilogram per day, representing the predominant breathing rate for a 70-year life span.
[b]This scenario is the one that most closely matches data obtained in this study, assuming exposure was only for the eight days of sampling.

Other Air Monitoring Results for Endosulfan, Diazinon, and Trifluralin

As part of the implementation of the California Toxic Air Contaminant Act, the California Air Resources Board (ARB) has conducted air monitoring for a number of different pesticides adjacent to pesticide application sites, which provides information on acute (short-term) exposures in these settings.[37] In these application site monitoring studies, air sampling stations are generally set up between 25 and 500 feet from the borders of the field on all sides. Additionally, for a subset of pesticides, ARB has conducted air monitoring in regions of high pesticide use, but some distance from application sites to provide information on longer-term, seasonal exposures. In these seasonal air monitoring studies, sampling stations are generally located atop government buildings such as schools, firehouses, and offices. All pesticide applications monitored by the ARB were carried out under legal conditions and according to label instructions. Therefore, their monitoring results represent a best-case scenario in terms of applicator compliance with best practices to reduce drift.

The US Geological Survey, US Department of Agriculture, and several academic groups have also conducted seasonal air monitoring for the pesticides observed in this study in a variety of different locations in the US and Canada. The St. Johns County School District conducted air monitoring at the South Woods Elementary School subsequent to the work described in this report.

Application Site Monitoring Studies

Endosulfan

In April of 1997, ARB conducted an endosulfan application site monitoring study at an apple orchard in San Joaquin County, California.[10] The results of this study indicate the potential for high exposures immediately adjacent to application sites.

Figure 4 shows the results of the study in terms of measured air concentrations of endosulfan over time for sampling sites on each edge of the field. Air concentrations of endosulfan (sum of α and β isomers) peaked at 4,000 ng/m^3 at the east downwind site 21 feet from the field boundary during the 4-hour sampling period starting three hours after the end of the application. The time-weighted-average concentration for the first 24-hour sampling period ranged from 50 to 1326 ng/m^3, 15% to 390% of the 1-year-old acute REL of 340 ng/m^3 (depending on the location of the monitoring station). Concentrations exceeded the 1-year-old acute REL in 54% of samples, and the three-day, time-weighted averages ranged from 25 to 778 ng/m^3. Concentrations of endosulfan were still above the child REL at the downwind site during the last monitoring period, at 418 ng/m^3 (1.2 times the 1-year-old REL). These data indicate that those who live, work, or go to school near application sites are potentially at risk of acute nervous system toxicity from airborne exposure to this pesticide.

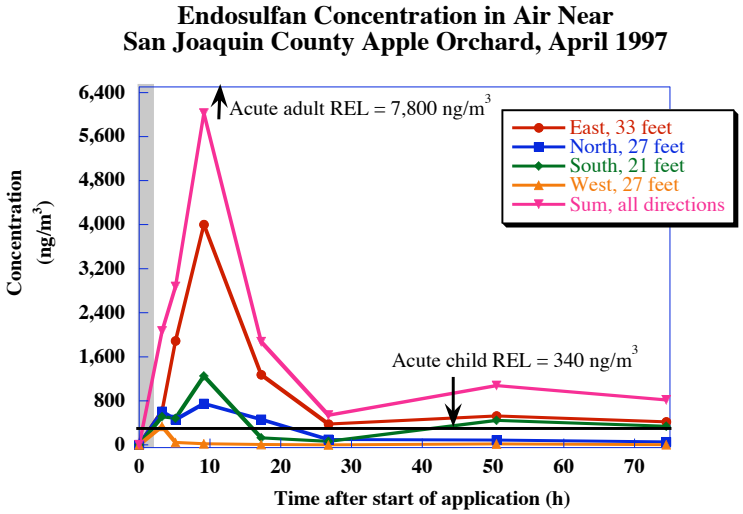


Figure 4: Endosulfan air concentrations peaked approximately eight hours after the end of the application, with 24-hour time-weighted-average concentrations on the downwind side of the orchard 3.9 times the 24-h acute REL for a 1-year-old child. Off-gassing continued for several days after application and exceeded child acute RELs in the downwind directions for much of the sampling period. (Data source: California Air Resources Board, Reference 10.)

ARB only conducted a single application site monitoring study for endosulfan; however, the concentrations measured do not represent a worst-case exposure scenario. Winds were somewhat variable during the sampling period, so drift was distributed to the east, south and north of the field. If the winds were blowing steadily from one direction, concentrations at the downwind site would be higher than any of those measured in this study, with concentrations closer to that described by the sum of all directions (Figure 4). Additionally, the study was conducted in April,

with temperatures ranging from a minimum of 40°F to a maximum 73°F. The rate of volatilization will be higher at warmer temperatures, leading to higher concentrations.

Diazinon

In California, the peak season for agricultural use of diazinon is January and early February to kill overwintering insects in dormant almond and stonefruit orchards in the Central Valley. In February 1998, ARB conducted an air monitoring study of a winter application to a Kings County peach orchard.[38] The results of this study indicated the potential for high exposures immediately adjacent to application sites.

Figure 5 shows the results of the study in terms of measured air concentrations of diazinon over time for sampling sites on each edge of the orchard. Air concentrations of diazinon peaked at 5,500 ng/m^3 at the west site 72 feet from the field boundary during the 4-hour sampling period starting two hours after the end of the application. The time-weighted-average concentration for the first 24-hour sampling period ranged from 1,219 to 3,220 ng/m^3, 8.4 to 22.2 times the 1-year-old child acute REL of 145 ng/m^3 and 3.6 to 9.6 times the adult acute REL of 335 ng/m^3 (depending on the location of the monitoring station). Concentrations exceeded both the 1-year-old acute REL and the adult acute REL in 82% and 71% of the samples taken throughout the monitoring period, respectively. The three-day, time-weighted averages ranged from 513 to 2,123 ng/m^3 (depending on the monitoring station location). Concentrations of diazinon were still above the RELs for both adults and children at the downwind site during the last sampling period, at 600 ng/m^3, or 4.1 times the 1-year-old REL and 1.8 times the adult REL. These data indicate that those who spend time near application sites are potentially at risk of nervous system toxicity from airborne exposure. Infants and children are especially at risk because their nervous systems are still developing.

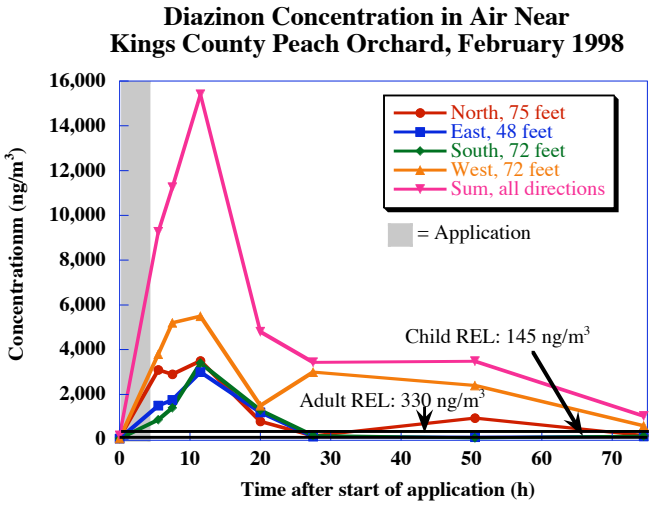


Figure 5: Diazinon air concentrations peaked approximately seven hours after the end of the application, with 24-hour time-weighted-average concentrations for the first day of sampling 22.2 times the 24-h acute REL for a 1-year-old child on the downwind side of the field. Off-gassing continued for several days after application, with 82% of the samples exceeding the child acute REL. (Data source: California Air Resources Board, Reference 38.)

This is the only application site monitoring study available for diazinon; however, it does not represent a worst-case exposure scenario. Because winds were light and variable during the sampling period, drift was fairly evenly distributed to all sides of the field. If the wind were blowing steadily from one direction, concentrations at the downwind site would be higher than those measured, with a peak concentration closer to that described by the sum of all directions (Figure 5). The study also occurred in February, when temperatures are low. Concentrations will be higher at warmer temperatures due to the increased vapor pressure of the pesticide at higher temperatures.

Trifluralin

There are no application site monitoring studies available for comparison for trifluralin.

Seasonal Air Monitoring Studies

Endosulfan

ARB also sampled seasonal concentrations of endosulfan in ambient air by placing monitoring stations on several schools somewhat distant from application sites but in regions of high use of the pesticide, primarily in cotton-growing areas of Fresno County.[10] Monitoring occurred four days per week for five consecutive weeks, which serves as an estimate of sub-chronic exposure (see Figure 6). For endosulfan, acute and sub-chronic RELs are the same. Average concentrations of all samples taken at each site (four days per week for five weeks) were below both adult and child RELs over the time frame of the monitoring study, ranging from less than 1% of the 1-year-old child REL at the control site at the ARB office in downtown Fresno to 9% of the REL for the San Joaquin Elementary School in San Joaquin, where cotton fields were ½ to ¾ mile from the monitoring station. The maximum measured 24-hour concentrations ranged from 1% of the child REL at the ARB office to 49% of the REL in San Joaquin.

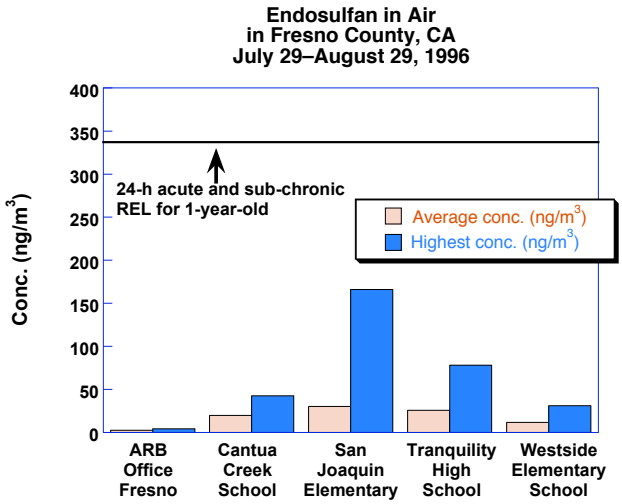


Figure 6: Average endosulfan concentrations in ambient air in Fresno County ranged from 1% to 9% of sub-chronic RELs for a one-year-old child. Maximum measured 24-hour concentrations at each site ranged from 1% to 49% of the acute REL. (Data source: Reference 10.)

The US Department of Agriculture-Agricultural Research Services (USDA-ARS) has also conducted air monitoring for ambient levels of endosulfan and other pesticides in three locations

in South Florida: Homestead (an agricultural area with substantial use of endosulfan), Adam's Key in Biscayne Bay (the control site) and in the Everglades National Park some distance from agricultural areas.[39] At the Homestead site, endosulfan was found in 91% of samples, with a median concentration of 8.5 ng/m^3 ($\alpha + \beta$) and a maximum concentration of 84 ng/m^3. At the Everglades site, endosulfan was found in 100% of the samples with a maximum concentration of 11 ng/m^3. Trace levels of endosulfan were even found at the control site in Biscayne Bay. Concentrations were found to be highest during the growing season, October through March.

Diazinon

The California ARB sampled seasonal concentrations of diazinon in ambient air by placing monitoring stations on several schools somewhat distant from direct applications but in regions of high use, primarily in almond- and stonefruit-growing areas of Fresno County during the dormant spray season of January and February.[38] Monitoring occurred 3–4 days per week for three consecutive weeks, which serves as an estimate of sub-chronic exposure (see Figure 7). For diazinon, acute and sub-chronic RELs are the same. Average concentrations were below the 1-year-old child REL during the study, averaging 15% of the REL over all sites. Maximum measured 24-hour concentrations exceeded the REL at one site, ranging from 20–110%.

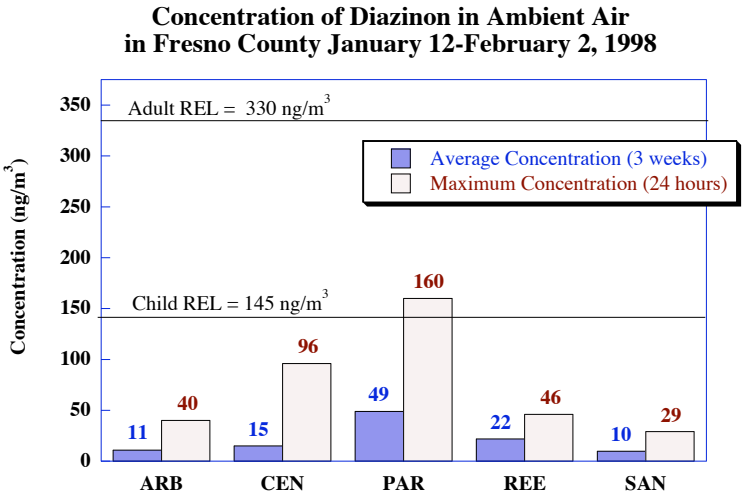


Figure 7: Three-week average diazinon ambient air concentrations in Fresno County remained below RELs for both adults and children. The child REL was exceeded at one site for one 24-hour sample. Monitoring sites included ARB, the ARB office in downtown Fresno; CEN, Centerville School; PAR, Parlier High School; REE, Kings Canyon Unified District Office in Reedley; SAN, Fairmont Elementary School in Sanger. (Data source: Reference 38).

The US Geological Survey (USGS) and others have conducted a number of air monitoring studies for diazinon in air, and in water and frogs in the Sierra Nevada mountains in California.[40] Concentrations and frequency of detections for the pesticide in amphibian tissue follow north-south and west-east patterns consistent with intensified agriculture upwind of the areas with the most serious declines in amphibian populations. Pesticide residue concentrations also decrease with increasing elevation.

A recent USGS study found residues of organophosphorus pesticides, including diazinon, in Pacific tree frog adults and tadpoles in the Sierra Nevada in areas downwind of high pesticide use, and found further that that activity of an enzyme involved in nerve impulse transmission, cholinesterase (ChE), in these individuals was depressed, indicating that exposure was significant enough to exceed the NOAEL for amphibians.[41]

In 2003, the USGS released a study on the occurrence of diazinon in rainwater in California's Central Valley.[42] The bulk of the pesticide loading to a watershed was attributed to volatilization drift from applications to dormant almond and stonefruit orchards that take place in the winter. Concentrations of diazinon in rainwater were high enough to exceed the proposed California Department of Fish and Game water quality criteria for diazinon.

The studies above indicate that diazinon is long-lived and volatile enough to be transported in air far from application sites, with higher concentrations observed closer to application sites. For people living close to applications, inhalation exposure can contribute a substantial amount to the aggregate dose that is a combination of residues on foods and in drinking water and airborne diazinon.

Trifluralin

The California ARB has not conducted air monitoring for trifluralin; however, a number of other ambient air studies have routinely found trifluralin in a high percentage of samples taken, demonstrating the volatility of this herbicide and its potential for transport far from application sites.[43] The US Geological Survey included trifluralin as one of the pesticides analyzed for in a 2-year-long study of airborne pesticides in the Sacramento area in 1996–1997,[44] as well as in a 10-day study of airborne pesticides near the Mississippi River in early June 1994.[45] Researchers in Saskatchewan sampled for pesticides in an agricultural area near the city of Regina[46] and an Environment Canada program monitored in the Yamaska Valley in Quebec.[47] In all cases, a high-volume air sampler was used (>100 L/min sampling rate), which permitted detections of much lower levels of pesticides in air than the Drift Catcher method does. Data are summarized in Table 4.

Table 4: Results for Trifluralin Detections in Air from Other Studies

Location	Percent of samples with detections[a]	Mean conc. and (Std. Deviation) (ng/m^3)	Maximum conc. (ng/m^3)	Minimum conc. (ng/m^3)	Sampling period	Reference
Sacramento International Airport	82 (South) 66 (North)	4.78 (3.88) 2.49 (2.34)	19.18 12.87	0.02 0.13	7 day 24 h/day	44
Franklin Field Airport	71 (South) 40 (North)	2.88 (2.85) 2.53 (3.66)	14.58 19.50	0.09 0.10	7 days 24 h/day	44
Downtown Sacramento	68 (South) 39 (North)	2.29 (1.97) 3.63 (8.14)	10.28 43.01	0.08 0.17	7 days 24 h/day	44
Mississippi River Valley	90	2.4 (median)	80	NR[b]	24 hours	45
Regina, Saskatchewan	79	0.68	3.13	NR[b]	7 days 12 h/day	46
Yamaska Valley, Quebec	100	1.60	NR[b]	NR[b]	30 days 24 h/day	47

[a]The Sacramento study collected two samples each week, where airflow was directed to one tube when winds were blowing from the north and to the other tube when winds were blowing from the south to distinguish the geographical sources of the different chemicals found in the study. [b]NR = not reported.

MACTEC Air Monitoring, South Woods Elementary School, Spring 2007

At the request of the St. Johns County School District, MACTEC, an environmental consulting and remediation firm, tested the air and soil at South Woods Elementary School for the same three pesticides found in the study described in this report.[48] One outdoor and one indoor air sample were collected on each of three days (for a total of 6 samples) and three soil samples were collected from the playground and softball field. Each was analyzed for diazinon, α- and β-endosulfan, endosulfan sulfate, and trifluralin.

It is unclear from the published report whether the analytical methodology employed by MACTEC would have detected pesticides other those targeted. A total of 65 pesticide active ingredients are legally allowed to be used on cabbage; MACTEC tested for only three. Pesticide applications were observed in adjacent fields on two of the days when air samples were collected; however, it not known if endosulfan, diazinon, or trifluralin were applied, or whether the wind was blowing in a direction that would have carried pesticide drift into the area where the air samples were collected.

The MACTEC study did not detect the target pesticides in any of their air samples; however, as shown in Table 5, the detection limits of the methodology employed were approximately 1,000 times higher than ours, which means that the target pesticides could not have been detected at the levels observed our study. In other words, the methodology used by MACTEC was not sensitive enough to detect the quantities of pesticides in described in the **Results** section of this report. Therefore, the results of the MACTEC air testing in no way contradict results reported in this study: MACTEC did not detect endosulfan, diazinon, or trifluralin in concentrations greater than 3,300, 2,100, and 8,300 ng/m^3, respectively, nor did this study.

Table 5: Detection Limits of PANNA and MACTEC Methodology

Analyte	Maximum Observed Concentration in PANNA Study (ng/m^3)	8-Day Average Observed Concentration in PANNA Study (ng/m^3)	PANNA Detection Limit (ng/m^3)	MACTEC Detection Limit (ng/m^3)
Endosulfan (total)	626	278	4.6[a]	3,300
Diazinon	897	311	3.5	2,100
Trifluralin	376	84	9.0	8,300

[a] Sum of MDLs of α- and β-Endosulfan.

Not detecting pesticides on 3 days of sampling—even if appropriately sensitive methodology had been used—would not necessarily indicate that the air at the school is always free of pesticide contamination. As the MACTEC report correctly concedes "[t]he results of the testing of the three chemicals performed may not be representative of the concentrations at other times." Likewise, the pesticide levels detected in this study from Dec 6–14 are not necessarily representative of pesticide levels for the rest of the year. The levels of pesticides in the air after an application can vary dramatically based on factors such as: the physical properties of pesticide itself, the application method and rate, the length of time between the application and sampling, wind direction and speed, temperature, humidity, and more difficult to quantify factors such as how carefully the application was conducted.

The "Applicable Standards" that MACTEC cites in their report are the Occupational Safety and Health Administration (OSHA) Permissible Exposure Limits and the NIOSH Recommended

Exposure Limits. These standards are intended to protect an *adult* worker who is being paid to accept some degree of risk, and are not intended to protect the health of children and pregnant women from involuntary environmental exposure to toxic chemicals. Children breathe more air per unit body weight than adults, and therefore their exposures are proportionately higher than those of adults. Furthermore, children are not simply small adults. They can be—and frequently are—more susceptible to effects of toxic chemicals than adults, since their bodies are still developing. This is especially true of the developing fetus (see the **Health Effects** sections for each individual pesticide, above).

The US EPA is required by the Federal Food Quality Protection Act of 1996 to accommodate the special sensitivity of these subpopulations, and accordingly treats them differently in their risk assessment methodology. For example, when calculating "acceptable" dietary exposures to pesticides for children and women of childbearing age, the EPA often incorporates additional uncertainty factors that are not used for adult men. For these reasons, RELs derived from studies selected by the US EPA are the appropriate benchmarks to which the air levels observed in this study should be compared, although because of the simultaneous occurrence of multiple pesticides, even these RELs (which were developed based on animal exposure to a single chemical) may not be sufficiently protective. See the **Calculations** section for a discussion of the derivation of the RELs used in this study.

MACTEC was given a file containing a preliminary version of our results, which are officially released in this report, and asked to provide comments. The MACTEC report made four comments about these results, summarized below:

(1) All of the MACTEC samples were attended during collection, while the sampling conducted by PANNA/the Pedro Menendez High School students was not. "This reflects a loss in the chain-of-custody of the samples."

(2) Field and laboratory blanks were not mentioned in the report provided to MACTEC, therefore "there was no way to assess if samples had been previously contaminated prior to testing."

(3) The RELs used for comparison in the project are for infants and are "not applicable to adults or children."

(4) The "lower [detection] limits [cited in the project] were achieved by deviating from the laboratory methodology and collecting samples over a longer period of time [than allowed by the methods, NIOSH 5600 and OSHA 2023]."

The implication of Comment 1 is that since our sampling was not attended over the duration of the study, we cannot guarantee that the samples were not tampered with and contaminated with pesticides. While we admit that we cannot rule out this possibility, we also believe that it is highly unlikely that a saboteur would trespass onto the sample site and spike the sample tubes with all three pesticides. It is also common practice to leave samplers unattended if they are in a secure location, as ours was. The California Air Resources Board, California Department of Pesticide Regulation, and the US Geological Survey all do this routinely. Environmental consulting firms sampling for longer than a few hours will also secure their samplers and leave

the site; otherwise, it would be prohibitively expensive (and hazardous to personnel) to conduct any kind of long-term air monitoring with a full-time "watch-person" on duty.

In response to Comment 2, field blanks were indeed collected, one was analyzed in the same batch as the samples, and no pesticides were detected (see results in Table 2). Solvent blanks were also analyzed and no pesticides were detected (see **Quality Assurance-Quality Control**). Prior contamination of the sample tubes, the extraction solvent, and all other components of the analytical equipment can therefore be confidently ruled out.

Regarding Comment 3, we use a 1-year-old child as one of the more sensitive (but not the most sensitive) groups to compare our results to. The unborn child is the most sensitive and can be exposed if there are pregnant women working at the school. Infants and the fetus are among the most sensitive members of any population, and any benchmark used as a level of concern should be protective of all members of the population, hence our selection of RELs for 1-year-old children, as opposed to RELs for adults or older children, although we have included these levels in the report for comparison. The RELs for other ages are easily calculated (see the **Calculations** section). If the breathing rate and body weight of an average 7-year-old are used to derive RELs, then the acute and subchronic REL for endosulfan for a 7-year-old would be 500 ng/m^3 and that for diazinon would be 220 ng/m^3. The observed pesticides air levels are also above these 7-year-old child RELs on several days during the study; in fact, the observed diazinon levels even exceeded the adult REL of 335 ng/m^3 on two days. Note that average breathing rates were employed in the calculation of RELs used in this report. Had breathing rates corresponding moderate or heavy activity, been employed (such as might occur with children playing on the school grounds), the calculated RELs would be lower.

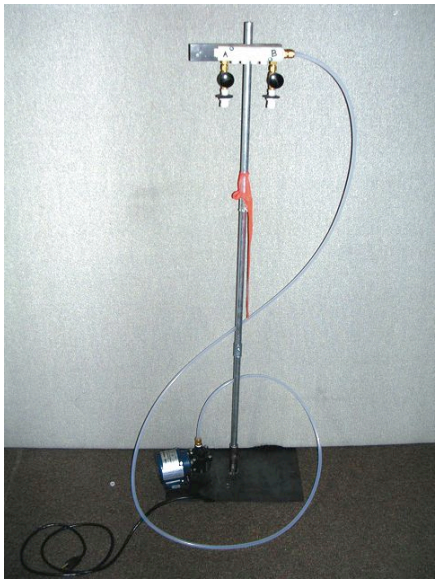
Finally, in regard to Comment 4, we note that using sampling periods longer than those recommended by NIOSH 5600 in order to attain more sensitive detection limits is not a violation of the method. Instead, it is a standard practice employed by many air pollution researchers in academia and government. For example, Table 4 on page 27 shows results from trifluralin studies where a single sample was collected over periods of 24-hours, seven days, and even 30 days to enhance the sensitivity of the method.

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.[49]

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 8).

(a) 

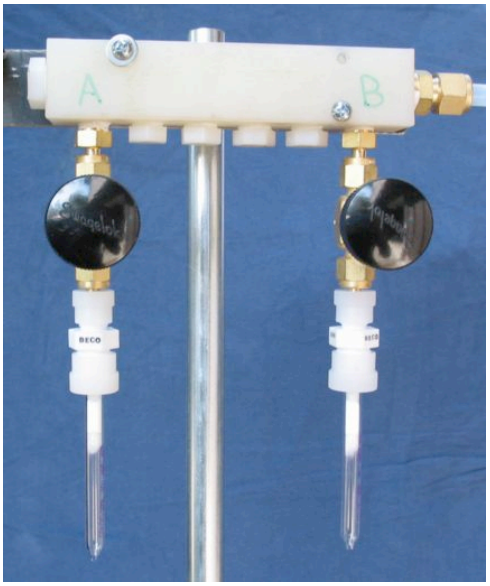
(b) 

Figure 8: (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 2.00 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 more than 10% from the starting flow rate, the greater flow rate was used, giving a conservative value for the final pesticide concentration.

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 (Appendix 1). 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 log sheet.

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 2) 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, which occurred within four weeks of receipt in the laboratory. Prior sample storage stability assessments conducted by the California ARB indicate no decomposition in samples held at -20°C for as long as 20 days for endosulfan (stability study

concluded at 20 days)[50] and 120 days for diazinon (stability study terminated at 120 days).[38] No comparable data exist for trifluralin.

Sample Analysis

Detailed Standard Operating Procedures (SOPs) for processing of sorbent tubes containing organophosphorus pesticides such as diazinon and organochlorine pesticides like endosulfan were developed from NIOSH method 5600[49] and the methods used by CA ARB[50] and are attached as Appendix 3. Briefly, the front and rear XAD-2 resin beds were each extracted with 2.00 mL of pesticide-grade ethyl acetate using sonication, and the extracts were analyzed using a Varian 3800 gas chromatograph equipped with an 8400 autosampler using both split and splitless injection, depending on detection limits desired. Samples were quantified using an electron capture detector (ECD). Confirmation of peak identity was made by mass spectrometry. The details of instrumental conditions can be found in Appendix 5.

Concentrated stock standards of α–endosulfan, β-endosulfan, diazinon and trifluralin for use in analysis were obtained directly from Accustandard (Catalog numbers P-091S and P-092S, P-033S and P-197S respectively), at a concentration of 100 μg/mL in Methanol. Five to 7 dilute analytical standards were prepared from the stock solution using pesticide-grade ethyl acetate as diluent. Standards spanned the anticipated concentration range for the samples in the linear response range for the detector. Samples that were initially determined to contain analyte in amounts less than the LOQ for the initial method were reanalyzed using a more sensitive method with a lower LOQ. Samples that were above the range of the calibration curve were diluted and reanalyzed.

Calculations

Air Concentrations

Pesticide concentrations in air were calculated from the GC results as shown in equation (1):

$$\text{Air concentration, ng/m}^3 = \frac{\text{Extract concentration, ng/}\mu\text{L} \times \text{Solvent volume, } \mu\text{L}}{\text{volume of air sampled, m}^3} \quad (1)$$

Conversion of Dose Levels into Air Concentrations

The dose levels used by US EPA in their risk assessments come from animal studies conducted by the manufacturer and are reported in milligrams of pesticide per kilogram of body weight per day (mg/kg-day), for both oral (dietary) exposure and inhalation exposure. Inhalation doses were converted to air concentrations in ng/m^3 using equation (2), where BW and BR are the average body weight and breathing rate of the population in question (70 kg adult male, 7-year-old child, and 1-year-old child). For this conversion, absorption of the compound via inhalation was assumed to be equivalent to absorption via ingestion, thus the factor of 100%, according to standard US EPA methodology.[51] We chose a single point estimate of exposure using exposure parameters previously developed for the three populations (see Table 6).[52] The Dose Level in ng/m^3 determined in equation (2) can be thought of as the answer to the following question: For a human to inhale, over the course of 24 hours, a dose equivalent (in mg/kg-day) to the animal dose in question, what would the concentration of the pesticide in the air have to be?

$$\text{Dose Level (ng/m}^3) = \frac{\text{Dose Level (mg/kg - day)} \times \text{BW(kg)} \times 10^6 \text{ ng/mg}}{\text{BR (m}^3\text{/day)}} \times 100\% \quad (2)$$

Table 6: Exposure Parameters

	Body Weight (BW) in kg	Daily Breathing Rate (BR) in m^3/day
Adult male	70	18
7-year old child	25	10
1-year old child	7.6	4.5

Source: Reference 52.

Calculation of Reference Exposure Levels (RELs) from Dose Levels

The US EPA estimates the "acceptable" dietary exposure to a chemical for a human by dividing the test-animal oral No Observed Adverse Effect Level (NOAEL, in mg/kg-day) by two or more uncertainty factors. Analogously, calculation of the "acceptable" air concentration of a chemical for a human requires modifying the test-animal inhalation NOAEL (in ng/m^3) with the same uncertainty factors:

- An interspecies factor (UF_{inter}) of 10 to allow for the differences between laboratory animals and humans. For example, if the dose that results in no observed effect (the NOAEL) in a rat study were 3 mg/kg-day and no human studies on acute toxicity were available, the "acceptable" dose for a human would be lowered to 0.3 mg/kg-day. In practice, the relative sensitivity of laboratory animals compared to humans is different for each chemical. In cases where both human data and rat data are available, this factor ranges from humans being 1,000 times more sensitive than rats to one tenth as sensitive.[53] The factor of ten—to allow for ten times greater human vulnerability—is the most commonly chosen, but is not sufficiently protective for all chemicals.
- An intraspecies factor (UF_{intra}) of 10 to allow for the differences between different human individuals. Genetic differences exist in humans' ability to detoxify and eliminate toxic substances. A good example is the 80-year-old who has smoked two packs of cigarettes a day for 60 years and escapes lung cancer compared to the 25-year-old who acquires multiple chemical sensitivity after a single exposure to a toxic substance. The intraspecies uncertainty factor attempts to take these differences into account. However, the genetic variability in humans' ability to detoxify pesticides is known to exceed a factor of 10 in at least one situation.[2]
- Other uncertainty factors (UF_{other}) may also apply. This is the case when an inhalation NOAEL is not available because the pesticide is toxic to the test-animals at all dose levels tested. In such a case, the lowest dose tested—the Lowest Observed Adverse Effect Level (LOAEL)—can be used in place of a NOAEL, but an additional uncertainty factor is required. This additional factor can range from 2 to 10. In the case of diazinon, toxicity was observed at all dose levels in the inhalation study, therefore the US EPA used the LOAEL and an additional uncertainty factor of 3 when evaluating inhalation exposure of workers.[18]
- For children, the Federal Food Quality Protection Act (FQPA) requires US EPA to use an additional child uncertainty factor (FQPAF) of 10 to allow for the fact that infants and children are particularly susceptible to toxicants. If additional information is available

indicating that children are *not* especially susceptible to toxic effects from the chemical, this uncertainty factor might be reduced to less than 10 and can even be reduced to one. If no data are available on toxic effects that might be specific to children (e.g., developmental neurotoxicity), the law requires the factor of 10 to be used. For endosulfan, US EPA used an FQPA factor or 10, while for diazinon a factor of one was employed.

Table 7: Summary of Toxicity Information Used To Calculate RELs

Parameter	Endosulfan	Diazinon
Uncertainty factors[a] FQPA factor	10, 10 10	10, 10, 3[b] 1
Relevant Dose Level: Acute NOAEL or LOAEL (mg/kg-day) Acute adult REL (ng/m^3) Acute 7-year-old child REL (ng/m^3) Acute 1-year-old child REL (ng/m^3) Toxic endpoint	0.20 (NOAEL) 7,800 500 340 Neurotoxicity—increased incidence of convulsions. Decreased body-weight gain and decreased leukocyte counts in males and increased creatinine values in females.	0.026 (LOAEL) 335 220 145 Neurotoxicity: Plasma cholinesterase inhibition
Relevant Dose Level: Sub-chronic NOAEL or LOAEL (mg/kg-day) Sub-chronic adult REL (ng/m^3) Sub-chronic child REL (ng/m^3) Toxic endpoint	0.20 (NOAEL) 7,800 340 Neurotoxicity—increased incidence of convulsions. Decreased body-weight gain and decreased leukocyte counts in males and increased creatinine values in females.	0.026 (LOAEL) 335 145 Neurotoxicity: Plasma cholinesterase inhibition
Data source	US EPA RED, Reference 4	US EPA IRED, Reference 18

a. Given in the order: Intraspecies, interspecies, and other modifying factors.
b. No NOAEL was available, with toxic effects observed at all doses tested. EPA used the LOAEL with an additional uncertainty factor of three.

Acute and sub-chronic RELs for a 70 kg adult male were obtained by dividing the relevant NOAEL or LOAEL (in ng/m^3, converted from the value in mg/kg-day listed in Table 7 using equation (2), and the appropriate body weight and breathing rate from Table 6), by the intraspecies and interspecies uncertainty factors, as well as any other modifying factors used by the EPA, as shown in equation (3). The FQPAF was not used, as it only applies to children.

$$\text{Adult REL (ng/m}^3\text{)} = \frac{\text{NOAEL or LOAEL (ng/m}^3\text{)}}{\text{UF}_{\text{intra}} \times \text{UF}_{\text{inter}} \times \text{UF}_{\text{other}}} \quad (3)$$

Acute and sub-chronic RELs for children were obtained by dividing the NOAEL or LOAEL (in ng/m^3, converted from the value in mg/kg-day listed in Table 7 using equation (2) and the appropriate BW and BR from Table 6) by the intraspecies, interspecies, and any other relevant uncertainty factors, as well as the child uncertainty factor (FQPAF), as shown in equation (4).

$$\text{Child REL (ng/m}^3\text{)} = \frac{\text{NOAEL or LOAEL (ng/m}^3\text{)}}{UF_{intra} \times UF_{inter} \times UF_{other} \times \text{FQPAF}} \quad (4)$$

Table 7 provides toxicity endpoints developed by US EPA for endosulfan and diazinon. Trifluralin is not included because US EPA has not developed acute and sub-chronic NOAELs because of the chemical's low acute toxicity.

No "acceptable" levels have been established for exposures to multiple pesticides. It is possible that additive or synergistic effects may increase the toxicity of one pesticide in the presence of others.

Estimation of Lifetime Cancer Risk from Seasonal Exposures to Trifluralin

To estimate the risk of cancer from exposure to a substance over a 70-year lifetime, one must know the following:

- The **average concentration** of the substance in air during the monitoring period.
- The **exposure frequency**, or the fraction of a year in which concentrations are estimated to equal the average concentration measured during the monitoring period.
- The **average annual concentration** of the substance in air, determined from the exposure frequency and the average concentrations observed during the monitoring period.
- The **cancer potency factor, Q***, determined from toxicity studies. For trifluralin, US EPA determined that Q*= 0.0077 (mg/kg-day)$^{-1}$.[27]

Details for each calculation are shown below.

Estimation of Average Air Concentrations of Trifluralin during the Application Season

The eight-day time-weighted average concentration of trifluralin measured in this study was used as an estimate of the average air concentration during the application season, a value of 84 ng/m^3. Because it was not known how representative this concentration is, we estimated cancer risks for five different hypothetical air concentrations to estimate low, moderate and high exposure scenarios: 1 ng/m^3, 10 ng/m^3, 84 ng/m^3 (the eight-day average found in this study), 1,000 ng/m^3, and 10,00 ng/m^3.

Estimation of Exposure Frequency

The length of the application season (and hence exposure frequency) for trifluralin in the Hastings area of Florida is not precisely known. Because this herbicide is applied both pre-plant and during the growing season, there may be from one to four applications to an individual field

during the year.[54] Assuming different fields in the same vicinity might be treated at different times during the growing season and contribute to overall exposure, and noting that trifluralin was detected in the samples collected on seven of the eight days of sampling, we estimated the length of the trifluralin application season to be approximately two weeks to three months, using values of 3.8%, 10% and 25% of the year as estimates of low, moderate and high exposure scenarios.

Estimation of Average Annual Trifluralin Air Concentration and Exposure

Average annual air concentrations were calculated by multiplying estimated seasonal average air concentrations by the exposure frequency, according to equation (5).

$$\text{Avg. annual conc. (ng/m}^3\text{)} = \text{(Avg. conc. during monitoring period)} \times \text{(Exposure frequency)} \quad (5)$$

Annual exposure to trifluralin was calculated by multiplying the average annual air concentration by the adult inhalation rate of 0.28 m^3/kg-day,[52] according to equation (6). This calculation assumes the annual average air concentrations remain at the same level from year to year.

$$\text{Annual exposure (mg/kg - day)} = \text{(Avg. annual conc. (ng/m}^3\text{)} \times 10^{-6}\text{ mg/ng)} \times \text{(0.28 m}^3\text{/kg - day)} \quad (6)$$

Determination of Lifetime Cancer Risk from Trifluralin Exposures

To obtain the lifetime (70-year) cancer risk, the average annual exposure to triflurain in mg/kg-day is multiplied by the potency factor (Q*) of 0.0077 $(mg/kg/day)^{-1}$, according to equation (7).

$$\text{Lifetime cancer risk} = \left(\text{Annual exposure (mg/kg - day)}\right) \times \left(0.0077\ \text{(mg/kg - day)}^{-1}\right) \quad (7)$$

For trifluralin, potential lifetime cancer risk estimates were developed for a range of exposure scenarios to bracket the potential lifetime cancer risk from potential exposures. The lifetime cancer risk is defined as the estimated number of cancer cases above the number the medical community considers the norm for a population. Lifetime cancer risks exceeding one in one million represent risks of concern. Table 3 on page 22 shows the results for trifluralin, none of which exceed levels of concern for even the highest estimated exposures.

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."[55] 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 2.00 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 a low-level solution of the analyte of interest (0.01 ng/µL for α- and β-endosulfan, 0.025 ng/µL for diazinon, and 0.05 ng/µL for trifluralin) and multiplying this value times 3.14, the student T value at the 99% confidence interval for seven replicates, as shown in equation (8).

$$\text{IDL (ng/}\mu\text{L)} = 3.14 * \sigma \tag{8}$$

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 equation for the MDL calculation is shown in equation (9).

$$\text{MDL (ng/m}^3\text{)} = \frac{(\text{IDL ng}/\mu\text{L}) \times (2{,}000\ \mu\text{L})}{(2.0\ \text{L/min}) \times (60\ \text{min/h}) \times (24\ \text{h}) \times (1\ \text{m}^3/1000\ \text{L})} \tag{9}$$

The IDL depends strongly on the injector split ratio employed in the analysis. As indicated in Appendix 5, a variety of split ratios were employed in order to bring the analytes and calibration standards into the linear range of the ECD. The LOQs, IDLs, and MDLs quoted in the body of this text reflect the detection limits of the most sensitive method (lowest split ratio) for each analyte.

The Limit of Quantitation (LOQ) was estimated at five times the MDL.

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. Participants 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 4 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 diazinon and endosulfan sampling indicated that there was no significant loss of sample under similar field sampling conditions.[38, 50]

Lab Spikes

In order to test extraction efficiency of the method for each pesticide, ten lab spikes were prepared at two different concentrations, with known quantities of pesticides 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 Tables 8–11. Recoveries were: α-endosulfan 70%–108%, average 86%; β-endosulfan 86%-113%, average 93%; diazinon, 97%–109%, average 103%; trifluralin, 25%–103%, average 75%. The pesticide concentrations for the field samples reported in Table 2 were not corrected for the recoveries reported below.

Lab spike recoveries obtained for diazinon and endosulfan compare favorably to those obtained by ARB:[38, 50] ARB recoveries were: α-endosulfan 87%–89%, average 88%; β-endosulfan 66%-71%, average 68%; diazinon, 72%–81%, average 75%. No comparable studies were available for trifluralin.

Table 8: α-Endosulfan Lab Spike Recoveries

Sample ID	Fortification (ng)	Recovery (ng)	Recovery (%)
LS-High-1	3,000	3,242	108
LS-High-2	3,000	2,718	91
LS-High-3	3,000	2,770	92
LS-High-4	3,000	2,566	86
LS-High-5	3,000	2,606	87
LS-Low-1	300	268	89
LS-Low-2	300	234	78
LS-Low-3	300	228	76
LS-Low-4	300	244	81
LS-Low-5	300	210	70
		Average	**86**
		Standard deviation	**10.6**

Table 9: β-Endosulfan Lab Spike Recoveries

Sample ID	Fortification (ng)	Recovery (ng)	Recovery (%)
LS-High-1	3,000	3,394	113
LS-High-2	3,000	2,636	88
LS-High-3	3,000	2,894	96
LS-High-4	3,000	2,642	88
LS-High-5	3,000	2,582	86
LS-Low-1	300	270	90
LS-Low-2	300	282	94
LS-Low-3	300	280	93
LS-Low-4	300	272	91
LS-Low-5	300	262	87
		Average	**93**
		Standard deviation	**7.9**

Table 10:Diazinon Lab Spike Recoveries

Sample ID	Fortification (ng)	Recovery (ng)	Recovery (%)
LS-High-1	3,000	3,212	107
LS-High-2	3,000	3,054	102
LS-High-3	3,000	3,148	105
LS-High-4	3,000	2,902	97
LS-High-5	3,000	2,952	98
LS-Low-1	300	304	101
LS-Low-2	300	316	105
LS-Low-3	300	306	102
LS-Low-4	300	322	107
LS-Low-5	300	328	109
		Average	**103**
		Standard deviation	**4.0**

Table 11: Trifluralin Lab Spike Recoveries

Sample ID	Fortification (ng)	Recovery (ng)	Recovery (%)
LS-High-1	1,500	1,538	103
LS-High-2	1,500	1,370	91
LS-High-3	1,500	1,334	89
LS-High-4	1,500	1,392	93
LS-High-5	1,500	1,276	85
LS-Low-1	150	130	87
LS-Low-2	150	68	45
LS-Low-3	150	112	75
LS-Low-4	150	38	25
LS-Low-5	150	90	60
		Average	**75**
		Standard deviation	**24.4**

Trip Blanks

Two trip blank tubes were prepared at the end of the first 24-hour sampling period. These tubes were stored and transported with the batch of samples from that location, and one (sample "Red" in Table 2) was chosen at random to be processed and analyzed as part of the batch on arrival in the lab. No pesticide residues were detected in the trip blank.

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.

Instrumental QA/QC

Quantification was conducted using an electron capture detector (ECD) calibrated with a set of at least five standards bracketing the anticipated concentrations of the samples. Positive identification of each pesticide was established by mass spectrometry, as well as by comparison of retention times between two different columns. 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 5 for detailed instrument parameters.

Appendices

Appendix 1: 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 2: 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

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				

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

Appendix 3: Standard Operating Procedures for Organophosphate Pesticides (NIOSH Method 5600)

QuickView

- ❑ Label extraction vials for samples and lab blanks
- ❑ 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

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. Spike with an amount that will give a final concentration in that falls within the expected range of the samples. 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 2.00 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 4: 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 m^3	———
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

A_Extraction_Solvent: EtOAc | A_Extraction_Volume_mL: 3.0

GC Method: ID-Pesticide-ECD-TSD-MSfocused.mth

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 m^3	———
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/m^3

Air Concentration, Tube B: 0 ng/m^3

Average of A & B Tubes: 20 ng/m^3

Comments:

Smelled of car smoke at start of sampling.

Alto-B lost a cap during transport. KM

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/m^3): Sample A: 1 ng/m^3 | Sample B: 0 ng/m^3

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

Appendix 5: 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). Samples were quantified using the ECD, with the MSD used to verify the identity of sample components. 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 Varian CP SIL 5 CB capillary GC column, 30 m x 0.32 mm, 1.0 µm film thickness. Split injection was employed using a variety of split ratios to bring the analytes and calibration standards into the linear range of the ECD. The LOQs, IDLs, and MDLs quoted in the body of this text reflect the detection limits of the most sensitive method (lowest split ratio) for each analyte.

Prior to analytical runs using the MSD, the MSD was autotuned to set the electron multiplier gain and calibrate mass setpoints on PFTBA ions.

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 (He)	Makeup Gas (N_2)
Endosulfan and Trfluralin	250 °C	300 °C (ECD)	120	0	0.5	0.5	1	30
			200	4	0	20.5		
			260	10	9.0	32.5		
			300	20	5.0	42.5		
Diazinon	250 °C	300 °C (ECD)	120	0	0.5	0.5	1	30
			200	5	0	16.5		
			260	10	9.0	31.5		
			300	20	0	33.5		

References

[1] This terminology is currently used by the California Office of Environmental Health Hazard Assessment in its evaluation of air toxics. See *Air*, California Office of Environmental Health Hazard Assessment, http://www.oehha.ca.gov/air.html.

[2] 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, *Pharmacogen. Genom.,* 2006, 16(3):183-190.

[3] *Exposure Factor Handbook,* Table 5-16, US EPA, August 1997, http://www.epa.gov/ncea/efh/.

[4] *Reregistration Eligibility Decision for Endosulfan*, US EPA, November 2002, http://www.epa.gov/oppsrrd1/REDs/endosulfan_red.pdf.

[5] *California Pesticide Use Reporting Data, 1990-2005,* California Department of Pesticide Regulation, http://www.cdpr.ca.gov/docs/pur/purmain.htm.

[6] *International Pesticide Registration for Endosulfan*, PAN Pesticides Database, Pesticide Action Network, http://www.pesticideinfo.org/Detail_ChemReg.jsp?Rec_Id=PC35085#ChemReg.

[7] *Endosulfan: Fact sheet & Answers to common questions*, Thanal, January 2004, http://thanaluser.web.aplus.net/sitebuildercontent/sitebuilderfiles/endofinal.pdf.

[8] *Chemical Review Committee 3 Press Release*, United Nations Environment Programme and the Food and Agriculture Organization of the United Nations, March 26, 2007, http://www.pic.int/home.php?type=t&id=170&sid=1.

[9] (a) Schmidt WF, Hapeman CJ, Fettinger JC, Rice CP, and Bilboulian S, Structure and Asymmetry in the Isomeric Conversion of α– to β–Endosulfan, *J. Ag. Food Chem.,* 1997, 45(4): 1023–1026.

(b) Schmidt WF, Bilboulian S, Rice CP, Fettinger JC, McConnell LL, and Hapeman CJ, Thermodynamic, Spectroscopic, and Computational Evidence for the Irreversible Conversion of β– to α–Endosulfan, *J. Ag. Food Chem.,* 2001, 49(11): 5372–5376.

[10] *Report for the Air Monitoring of Endosulfan in Fresno County (Ambient) and in San Joaquin County (Application),* California Air Resources Board, Project No. #C96-034, April 17, 1998, http://www.cdpr.ca.gov/docs/empm/pubs/tac/endoslfn.htm.

[11] (a) *Toxicological Profile for Endosulfan*, Agency for Toxic Substances and Disease Registry, September 2000, http://www.atsdr.cdc.gov/toxprofiles/tp41.html.

(b) *EPA Memorandum: Endosulfan 079401; Toxicology Chapter for the Reregistration Eligibility Decision,* U.S. EPA, November 22, 1999, http://www.epa.gov/oppsrrd1/reregistration/endosulfan/toxendosul_1.pdf.

(c) Dutta, MD and Arends, DA, Effects of endosulfan on brain acetylcholinesterase activity in juvenile bluegill sunfish, *Environ. Res.* 2003 91(3):157-62.

(d) *Monograph 792. Endosulfan, Pesticide Residues in Food: 1989 Evaluations Part II Toxicology,* World Health Organization (WHO) and Food and Agriculture Organization of the United Nations (FAO) Joint Meeting on Pesticide Residues (JMPR), 1989, http://www.inchem.org/documents/jmpr/jmpmono/v89pr08.htm.

[12] *Endosulfan (Poison Information Monograph 576)*, International Programme on Chemical Safety, World Health Organization, July 2000, http://www.inchem.org/documents/pims/chemical/pim576.htm.

[13] Aleksandrowicz DR, Endosulfan Poisoning and Chronic Brain Syndrome, *Arch. Toxicol.*, 1979, 43:65-68.

[14] Saiyed H, Dewan A, Bhatnagar V, *et al.*, Effect of Endosulfan on Male Reproductive Development, *Environ. Health Perspect.*, 2003, 111:1958-1962.

[15] Damgaard IN, Skakkebæk NE, Toppari J, *et al.*, Persistent Pesticides in Human Breast Milk and Cryptorchidism, *Environ. Health Perspect.,* 2006, 114:1133-1138.

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[16] *ChemWATCH Factsheet: Diazinon*, Beyond Pesticides, July 2000, http://www.beyondpesticides.org/pesticides/factsheets/Diazinon.pdf.

[17] *Toxicological Profile for Diazion, Draft for Public Comment*, Agency for Toxic Substances and Disease Registry, September 2006, http://www.atsdr.cdc.gov/toxprofiles/tp86.html.

[18] *Interim Reregistration Eligibility Decision for Diazinon*, US EPA, May 2004, http://www.epa.gov/oppsrrd1/REDs/diazinon_ired.pdf.

[19] (a) *Pesticide Industry Sales and Usage: 2000 and 2001 Market Estimates*, US EPA, May 2004, http://www.epa.gov/oppbead1/pestsales/01pestsales/market_estimates2001.pdf.

(b) *Pesticide Industry Sales and Usage: 1998 and 1999 Market Estimates*, US EPA, August 2002, http://www.epa.gov/oppbead1/pestsales/99pestsales/market_estimates1999.pdf.

(c) Pesticide Industry Sales and Usage: 1996 and 1997 Market Estimates, US EPA, November 1999, http://www.epa.gov/oppbead1/pestsales/97pestsales/market_estimates1997.pdf.

(d) Pesticide Industry Sales and Usage: 1994 and 1995 Market Estimates, US EPA, August 1997, http://www.epa.gov/oppbead1/pestsales/95pestsales/market_estimates1995.pdf

[20] *I.R.E.D. Facts: Diazinon*, US EPA, May 2004, http://www.epa.gov/oppsrrd1/REDs/diazinon_ired.pdf.

[21] *Organophosphorus Cumulative Risk Assessment: 2006 Update,* US EPA, July 31, 2006, http://www.epa.gov/pesticides/cumulative/2006-op/index.htm.

[22] *EPA Memorandum: Review of Diazinon Incident Reports DP Barcode D245285, Chemical #057801, Reregistration Case #0238*, US EPA, July 2, 1998, http://www.epa.gov/pesticides/op/diazinon/incident.pdf.

[23] *Environmental Health Criteria 198: Diazinon*, International Programme on Chemical Safety, World Health Organization, 1998, http://www.inchem.org/documents/ehc/ehc/ehc198.htm.

[24] *AOEC Exposure Codes*, George Washington University, Occupational Medicine Group for the Association of Occupational and Environmental Clinics, http://www.aoec.org/content/tools_1_2.htm.

[25] Saldana TN, Basso O, Hoppin JA, *et al*., Pesticide Exposure and Self-Reported Gestational Diabetes Mellitus in the Agricultural Health Study, *Diabetes Care*, 2007, 30(3):529-534.

[26] Slotkin TA, Levin ED, and Seidler FJ, Comparative Developmental Neurotoxicity of Organophosphate Insecticides: Effects on Brain Development are Separable from Systemic Toxicity, *Environ. Health Perspect*., 2006, 114:746-751.

[27] *Reregistration Eligibility Decision Trifluralin*, US EPA, April 1996, http://www.epa.gov/REDs/0179.pdf.

[28] *Hazardous Air Pollutants,* 42 USC § 7412.

[29] *Information Update - Products to be withdrawn from the market – trifluralin and benfuracarb,* UK Pesticides Safety Directorate, March 4, 2007, http://www.pesticides.gov.uk/approvals.asp?id=2104.

[30] *Report of the Food Quality Protection Act (FQPA) Tolerance Reassessment Progress and Risk Management Decision (TRED) for Trifluralin*, US EPA, August 31, 2004, http://www.epa.gov/oppsrrd1/REDs/trifluralin_tred.pdf.

[31] *The WHO Recommended Classification of Pesticides by Hazard,* International Programme on Chemical Safety, World Health Organization, 2005, http://www.who.int/ipcs/publications/pesticides_hazard_rev_3.pdf.

[32] *Pesticide Information Profile: Trifluralin*, Extension Toxicology Network, Cooperative Extension Offices of Cornell University, Oregon State University, the University of Idaho, the University of California at Davis, and the Institute for Environmental Toxicology, Michigan State University, June 1996, http://extoxnet.orst.edu/pips/triflura.htm.

[33] Garry VF, Schreinemachers D, Harkins ME, and Griffith J, Pesticide Appliers, Biocides, and Birth Defects in Rural Minnesota, *Environ. Health Perspect*., 1996, 104(4):394-399.

[34] (a) Pesticide Action Network United Kingdom, Trifluralin – Fact Sheet, *Pesticide News*, 2001, (50):20-21.

(b) *Trifluralin: Identification, toxicity, use, water pollution potential, ecological toxicity and regulatory information,* PAN Pesticide Database, Pesticide Action Network, http://www.pesticideinfo.org/Detail_Chemical.jsp?Rec_Id=PC35146.

[35] Mills PK and Yang RC, Agricultural exposures and gastric cancer risk in Hispanic farm workers in California, *Environ. Res.*, In press, 2007.

[36] Physical Properties database, CA Department of Pesticide Regulation, obtained by request from the ground water protection staff.

[37] *Toxic Air Contaminant Program: Monitoring Reports,* CA Department of Pesticide Regulation and CA Air Resources Board, http://www.cdpr.ca.gov/docs/empm/pubs/tac/tacstdys.htm.

[38] *Report for the Application (Kings County) and Ambient (Fresno County) Air Monitoring of Diazinon during Winter, 1998*, California Air Resources Board, Test Reports #C97-070 and # C97-069, November 6, 1998, http://www.cdpr.ca.gov/docs/empm/pubs/tac/diazinon.htm.

[39] (a) Hapeman C, Harman-Fetcho JA, Potter TL, *et al.,* Atmospheric transport and deposition of pesticides in South Florida, American Chemical Society Meeting, Agrochemical Division, #231, San Francisco, September 2006, http://oasys2.confex.com/acs/232nm/techprogram/P1013594.htm.

(b) Schaffer B, Hapeman C, Rice C, McConnell L, *Determining Atmospheric Loadings of Agrochemicals and Other Organic Pollutants to the Everglades and the Greater South Florida Basin*, Project No. 1265-12220-003-05, USDA-ARS, http://www.ars.usda.gov/research/projects/projects.htm?ACCN_NO=407716.

[40] (a) McConnell L, LeNoir J, Datta S, Seiber J, "Wet Deposition of Current-use Pesticides in the Sierra Nevada Mountain Range, California, USA," *Environ. Toxicol. Chem,* 1998, 17(10):1908–1916.

(b) Aston, L, Seiber, J, "Fate of Summertime Airborne Organophosphate Pesticide Residues in the Sierra Nevada Mountains," *J. Envi. Qual.,* 1997, 26:1483–1492.

(c) Zabik J, Seiber J, Atmospheric Transport of Organophosphate Pesticides from California's Central Valley to the Sierra Nevada Mountains, *J. Environ. Qual.,* 1993*,* 22:80–90.

[41] (a) Sparling DW, Fellers GM, McConnell LL, Pesticides and Amphibian Population Declines in California, USA. *Environ. Toxicol. Chem.*, 2001, 20:1591-1595.

(b) McConnell L, LeNoir J, Datta S, Seiber J, Wet Deposition of Current-use Pesticides in the Sierra Nevada Mountain Range, California, USA, *Environ. Toxicol. Chem.*, 1998*,* 17(10):1908–1916.

[42] Zamora C, Kratzer CR, Majewski MS, Knifong DL, *Diazinon and Chlorpyrifos Loads in Precipitation and Urban and Agricultural Storm Runoff during January and February 2001 in the San Joaquin River Basin, California,* US Geological Survey, Water–Resources Investigations Report 03–4091, 2003, http://pubs.usgs.gov/wri/wri034091/.

[43] Grover R, Wolt JD, Cessna AJ, Schiefer HB, Environmental Fate of Trifluralin, *Rev. Environ. Contam. and Toxicol.*, 1997, 153:1–64.

[44] Majewski MS, Baston DS, *Atmospheric Transport of Pesticides in the Sacramento, California, Metropolitan Area, 1996–1997,* Water Resources Investigation Report 02–4100, US Geological Survey, 2002, http://water.usgs.gov/pubs/wri/wri024100.

[45] Majewski MS, Foreman WT, Goolsby DA, *et al.*, Airborne pesticide residues along the Mississippi River, *Environ. Sci. Technol.,* 1998, 32,:3689–98.

[46] Waite DT, Cessna AJ, Grover R, Kerr LA, Snihura AD, Environmental Concentrations of Agricultural Herbicides in Saskatchewan, Canada: Bromoxynil, Dicamba, Diclofop, MCPA, and Trifluralin, *J. Environ. Qual.*, 2004, 33:1616-1628.

[47] Poissant L, Past and currently used pesticides in the air and precipitation in Québec, Canada, American Chemical Society Meeting, Agrochemical Division, #206, San Francisco, September 2006, http://oasys2.confex.com/acs/232nm/techprogram/P1008411.htm.

[48] *Report of Pesticide Testing Services South Woods Elementary School*, MACTEC Engineering and Consulting, Inc., Project No. 6741-07-3343, March 30, 2007, http://www.stjohns.k12.fl.us/about/press/South_Woods_Report.pdf.

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

[50] *Appendices to Report for the Air Monitoring of Endosulfan in Fresno County (Ambient) and in San Joaquin County (Application),* California Air Resources Board, Project No. #C96-034, April 17, 1998, http://www.cdpr.ca.gov/docs/empm/pubs/tac/tacpdfs/endosapa.pdf.

[51] For an example of US EPA use of this methodology, see *Occupational/Residential Handler and Postapplication Residential/Non-Occupational Risk Assessment for Chlorpyrifos,* US EPA, June 20, 2000, p. 6, http://www.epa.gov/oppsrrd1/op/chlorpyrifos.htm.

[52] a) Layton D, Metabolically consistent breathing rates for use in dose assessments, *Health Phys.,* 1993, 64:23–36.

b) *Air Toxics Hot Spots Program Risk Assessment Guidelines, Part IV: Technical Support Document for Exposure Assessment and Stochastic Analysis*, California Office of Environmental Health Hazard Assessment, September 2000, Chap. 3, http://www.oehha.ca.gov/air/exposure_assess/index.html.

[53] Vermeire TH, Stevenson MN, Pieters M, *et al.*, Probabilistic assessment factors for human health risk assessement, Rijksinstitut voor Volksgesondheien Milieu (RIVM) report #601516005, TNO report V3489, March 2001, http://www.rivm.nl/bibliotheek/rapporten/601516005.html.

[54] *Specimen Label Treflan 4ec Herbicide*, Helena Chemical Co., 2005, http://www.cdms.net/LabelsMsds/LMDefault.aspx?pd=8305.

[55] *Definition and Procedure for the Determination of the Method Detection Limit—Revision 1.11*, 40 CFR §136 Appendix B.