Final Project Report for Kauai Air Sampling Study

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<u>Title</u>: Air sampling and analysis for pesticide residues and odorous chemicals in and around Waimea, Kauai

<u>Executive Summary</u>: This ambient air study was conducted in response to community concerns about occurrences at Kauai's Waimea Canyon Middle School during which time some students and staff exhibited symptoms such as throat irritation, tearing, and dizziness. Studies were conducted to determine (1) potential pesticide exposure and (2) if a locally common plant, stinkweed (*Cleome gynandra*), is producing odorous chemicals that may affect Waimea Canyon Middle School students and staff. The stinkweed plant was studied using multiple methodologies including plant tissue and chemical air emission analyses. A closed chamber laboratory air emission study identified 29 chemicals (some with insecticidal activities) produced by stinkweed. Those findings are consistent with the chemicals detected through the plant extraction method. The 29 chemicals were also found in a high volume ambient air sampling study within a stinkweed-infested field. Approximately half of the 29 chemicals produced by stinkweed were detected in both indoor and outdoor air samples from passive air samplers and high volume air samplers positioned at Waimea Canyon Middle School and other Kauai schools. One of the 29 natural chemicals was methyl isothiocyanate (MITC). Five pesticides were detected in the indoor and outdoor passive air samples and the high volume outdoor air samples collected at Waimea Canyon Middle School. Those pesticides were chlorpyrifos, metolachlor, bifenthrin, benzene hexachlorides (BHCs) and dichlorodiphenyltrichloroethanes (DDTs). BHCs and DDTs, likely from past uses and ubiquitous throughout the world, were detected in all air samples collected from Kauai. Concentrations of the pesticides and MITC were well below health concern exposure limits or applicable screening levels.

Objectives

The objectives of the study were:

1. To design and perform experiments to determine volatile chemicals emitted from stinkweed.
2. To design and perform experiments of passive air and high volume air sampling methods to trap pesticide residues and natural chemicals in ambient air.

3. To conduct passive air and high volume air sampling for determination of pesticide residues and natural chemicals in ambient air in and around the Waimea Canyon Middle School, where several odor incidents occurred in 2006 and 2008.
4. To conduct qualitative analyses of chemicals in ambient air (chemical identification) and quantitative analyses of the identified chemicals (concentration measurement).
5. To estimate exposure to the chemicals.

Introduction

Background Information and Problem

Several incidents of chemical odors affecting students and teachers at Waimea Canyon Middle School on Kauai occurred between November 2006 and April 2008. Unidentified odors caused students to be evacuated from the school and seek medical treatment for flu-like symptoms including dizziness, headaches and nausea. Symptoms experienced by the students could be consistent with exposure to volatile chemicals. In response, the State Department of Agriculture conducted investigations and later, with the County of Kauai, funded this study to determine what pesticides and volatile chemicals from stinkweed may be in the ambient air near the school.

We compiled a list of pesticides to study. Restricted use pesticides sales records from 2010 and 2011 were used to compile a list of pesticides currently used in the subject area. Added to this list were pesticides both known and thought to have been used historically (derived from the publication, "*Evaluation of Pesticide Problems in Hawaii*"). Based on these historical records, reports, and sales, twenty-four (24) pesticides were selected for analyses.

At the time of the incidents, fields near the school were infested with *Cleome gynandra* (Spider Plant, stinkweed). Stinkweed is used as a medicinal herb, an insecticide and a miticide in many regions of the world. For example, farmers in some countries use stinkweed leaves to eliminate chicken mites and repel livestock ticks.

Because plants are known to emit volatile chemicals and because stinkweed in particular was suspected to be a source of odors near the school, both stinkweed plant tissue and chemical air emissions from the plant were analyzed.

Project Purpose

The purpose of this study was to determine what volatile chemicals may be present in ambient air at Waimea Canyon Middle School on Kauai.

Experimental Methods

Both laboratory and field studies, including passive and high volume air sampling, were conducted to address the objectives stated above. Passive air sampling and analysis provide qualitative results (whether the chemicals are detected or not) that can offer a useful reference to perform quantitative analysis (what quantity of chemicals are present) using high volume air sampling. The project workflow is shown in Figure 1.

Laboratory chamber studies of volatile chemicals emitted from stinkweed stems, pods, leaves and flowers

Laboratory trapping experiments of volatile chemicals emitted from stinkweed (Cleome gynandra): Laboratory studies were conducted to identify chemicals emitted from stinkweed. Stinkweed stems, pods, leaves and flowers collected from Maui sampling sites were cut into small pieces. Three hundred (300) grams (g) of the cut stinkweed stems, pods, leaves and flowers were placed in a glass chamber having an inlet and outlet. A gentle flow of pure nitrogen gas (N_2) was flushed through the samples in the chamber for 5 hours. Volatile chemicals emitted from stinkweed stems, pods, leaves and flowers were trapped in 150 milliliters (mL) of dichloromethane (also called methylene chloride) (Figure 2) for analysis.

Laboratory extraction of chemicals from stinkweed stems, pods, leaves and flowers: Chemicals were extracted from the stem, pod, leaf and flower samples of stinkweed. Flower, stem, leaf, and pod samples were cut into small pieces, freeze-dried and then crushed. Tissue samples of stinkweed (10 g) were mixed with an approximately 3-fold amount of baked anhydrous sodium sulfate, and placed in a 32 mL extraction cell. The sample cell was loaded onto an accelerated solvent extractor (ASE) 300 system (Dionex, Sunnyvale, CA). The extraction was performed with a mixture of equal volumes of acetone and methylene chloride with a flush volume of 60% of the cell volume and a nitrogen gas (N_2) purge time of 5 seconds a pressure of 1500 psi at a temperature of 50 ºC for three static cycles. Each tissue sample was extracted in triplicate, and an equal weight mixture of baked anhydrous sodium sulfate and Ottawa sand was extracted as the blank control.

After the extract was dried with 30 g of baked anhydrous sodium sulfate and rinsed with 10 mL of a mixture of acetone and methylene chloride (1:1, v/v), it was concentrated to approximately 3 mL using a rotary evaporator. One mL of hexane was added and then concentrated it with a rotary evaporator to approximately 1 mL. The one mL concentrated extract was cleaned up through an 8 mm i.d. aluminum/silica column. The column was packed, from the bottom to the top, with neutral alumina (3 cm, 3% deactivated), neutral silica gel (3 cm, 3% deactivated), and baked anhydrous sodium sulfate (2 cm). The column was eluted with 15 mL of methylene chloride and hexane (1:1, v/v). The eluate was concentrated to approximately 1 mL by using a rotary evaporator and then concentrated to 200 µL under a gentle stream of high purity nitrogen after an aliquot of 200 µL of dodecane was added as trapping solvent.

Method of high volume air sampling of volatile natural chemicals in ambient air within a stinkweed-infested field on Maui

Sampling site: A stinkweed-infested sugarcane field was selected for sampling in Maui. Two high volume air samplers were set up in the stinkweed-infested field. The samplers were at least 1 meter horizontal and vertical distance from supporting structures, at least 20 meters from trees, unobstructed air flow for 270 degree, accessible to sampling personnel during time of sampling, accessible to electrical power, secure from equipment loss or tampering, and permission of property owner (1, 2).

Air sampling method and frequency: One of the most widely used air sampling equipment is high volume air samplers. It can allow more than one hundred liters of air flux per minute to pass through a columned polyurethane foam (PUF) disk to collect contaminants in air. We collected air samples in duplicate in 2, 4, 6, and 12-hour collection periods during daytime and nighttime from September 28, 2009 to October 1, 2009. At the end of the sampling period, the samples were retrieved, resealed and returned to the laboratory at the University of Hawaii, stored at -20 ºC until extraction and analysis. Detailed sampling information such as frequency and duration is listed in Table 1.

Studies were conducted in the field on Maui to determine volatile chemicals produced by stinkweed as well as the suitability of the study methods. The Maui field study included air sample collection, sample preparation and transport, and sample analyses. The flow rate for air samplers was calibrated to be 10 ft^3/min by using a standard flow meter during sampling collection. Tandem PUF disks were used to evaluate PUF disk adsorbent capacity. Three laboratory and 6 field (i.e., PUF disks sent to/from field sites unopened) blanks were extracted and analyzed in the same manner as the samples to determine possible contamination during transport, storage, and analysis.

<u>Method of passive air sampling on Kauai</u>

Passive air samples were placed at schools at the west, south, east and north of Kauai (Figure 3). These stations were set-up for three reasons: (a) to identify chemicals for high volume air sampling, (b) to compare Waimea Canyon Middle School with control sites, (c) to develop an understanding of chemical prevalence in ambient air year-round. Air monitoring was conducted during a period of over one year and samples were collected at approximately 4-month intervals to identify natural chemicals and pesticides.

Four passive samplers (two outdoor and two indoor) were set-up at Waimea Canyon Middle School, located at longitude 159°40′ 24.77″ and at latitude 21° 57′ 30.79″ on September 22, 2010 and collected on January 24, 2011. This was a preliminary study to develop the entire passive air sampling process from air sampler setup, and chemical analysis to final data presentation.

On June 6, 2011, two outdoor passive samplers were placed on the roof of Waimea Canyon Middle School buildings B and D, and two indoor samplers in rooms C101 and C102. Six (6) outdoor passive samplers were positioned on trees at Hanalei Elementary School located at longitude 159°30′12.55″ and at latitude 22° 12′ 4.44″ (2 samplers), Kalaheo Elementary School located at longitude 159°31′20.67″ and at latitude 21° 55′ 20.10″ (2 samplers), and Kapaa High School (2 samplers). West and north Kauai locations were quite windy throughout the sampling period. One sampling station set up at Kalaheo Elementary School and two stations set up at Kapaa were missing. Sampling was completed on October 12, 2011.

On October 12, 2011, the 7 disk filters in the passive air samplers were replaced with new ones. The collected samples included two outdoor and two indoor samples from the Waimea Canyon Middle School, and three outdoor samples from Hanalei Elementary School and Kalaheo Elementary School on Kauai.

The disk filters were replaced again on February 12, 2012 and a second passive air sampler was added at Kalaheo Elementary School and two samplers were set up at Kanuikapono Learning Center in Anahola (longitude 159°18′16.39″ and at latitude 22°08′15.20) to replace Kapaa High School as the East Kauai site. All sampling disk filters were collected and sampling apparatuses were removed on June 14, 2012.

All passive air disk filters (samples) were wrapped in aluminum foil pre-cleaned with acetone, placed in 7 in. by 7 ¾ in. Ziploc® bags, and then returned to the laboratory at the Department of Molecular Biosciences and Bioengineering, University of Hawaii at Manoa, where the filters were stored at -20 °C until extraction and analysis.

Method of high volume air sampling of volatile natural chemicals and pesticides in ambient air within a stinkweed-infested field on Kauai

A PUF disk filter was used to collect contaminants in air phase and a glass filtering film was used to collect contaminants in particle phase. Particles were not separated for analysis because the incidents described did not indicate that particles in the air were a probable cause of complaints (2).

Volatile natural chemicals and pesticides in the air were identified with chamber studies and passive air sampling. The period selected for high volume sampling was the month of February, when insect control may require pesticide use, especially insecticide. In addition, stinkweed is likely to be present in February, during the seasonal rainy period, because it germinates and flowers after rainfall. Furthermore, complaints about air quality in West Kauai have generally occurred from November through January; however, because rain in 2012 occurred later than usual, the sampling period was adjusted to include the likelihood of detecting volatile compounds from both natural plant chemical and pesticide sources.

During the sampling period, stinkweed bloomed and field preparation, planting, and post emergence crop management for corn occurred. Sampling with high volume air samplers was conducted from February 10, 2012 to February 18, 2012.

Two outdoor high volume air samplers were set up at Waimea Canyon Middle School, while one outdoor high volume air sampler was set up at the control site, Hanalei Elementary School. The Hanalei region was selected as a control because it is believed that less commercial, agricultural, and residential chemicals are used there.

All air sampler sites were situated considering US EPA criteria used in prior studies (1, 2, 3) for high volume ambient air sampling:

- At least 1 meter horizontal and vertical distance from supporting structure;
- Unobstructed air flow for 270 degree;
- Accessible to sampling personnel during time of sampling;

- Accessible to electrical power;
- Secure from equipment loss or tampering; and
- Permission of property owner.

Sampling frequency: Samples were collected at day (7 am – 7 pm) and night (7 pm – 7 am) intervals from February 10, 2012 to February 18, 2012. Air filters were replaced at 7:00 am and 7:00 pm to coincide with day and night conditions. Twenty-eight (28) samples were collected at Waimea (14 night and 14 day samples). Fourteen (14) samples were collected at Hanalei (7 night and 7 day samples). At the end of the sampling period, the samples were retrieved, sealed and submitted to the laboratory in the Department of Molecular Biosciences and Bioengineering, University of Hawaii at Manoa, and stored -20 °C until extraction and analysis. The air samples were analyzed for both the 29 natural chemicals emitted from stinkweed and for pesticide residues.

Flow rate, blank controls, and good field practices: The flow rate for each air sampler was calibrated using a standard flow meter before and after each sampling period. Blank samples were also collected during each sampling period as a standard used to ensure accurate analysis of the samples. Good field and laboratory practices (industry standard terms) were taken to avoid contamination during sample collection and analyses.

In the laboratory, all the apparatus were washed and then dried prior to use. Glass apparatus were baked at 450 °C for 4 hours before use.

Sample detection methods: Laboratory analyses used were similar to those developed and employed by the California Department of Pesticide Regulation during their Parlier pesticide air monitoring project (2006) as well as the scientifically accepted methods used by similar studies published in peer-reviewed journals. These processes are described below. Specific analysis was determined according to the individual samples and pollutants detected.

Air sample extraction: For air sample analysis, PUF disks were fortified with 1.5 mL Na_4EDTA aqueous solution (0.5 g/L), 0.5 mL K_2CO_3 (20%) and 0.5 mL pentafluorobenzyl bromide (PFBBr, 30%) in acetone as an on-line derivatization reagent. An appropriate amount of 2,4,5,6-tetrachloro-m-xylene (TcMX) and polychlorinated biphenyl 209 (PCB209) were also injected into the PUF disks before extraction as recovery compounds. PUF disks were placed in 32-mL accelerated solvent extraction (ASE) cells and the remaining volume of the cell was filled up with clean Ottawa sand (20–30 mesh). The sample cells were loaded into a Dionex accelerated solvent extraction (ASE) 300 system. The samples were extracted with a mixture of acetone and methylene chloride (1:1, v/v) at 1500 PSI and 100 °C for three static cycles, a flush volume of 60% of the cell volume and an nitrogen purge time of 5 seconds. A total of 53 standard compounds including the 29 odorous chemicals and 24 pesticides were fortified at 50 ng of each chemical on each of five blank PUF disks. The five fortified PUF disks were used to determine recoveries of the 53 standard compounds that were analysed in the same manner as air samples (4).

Air sample clean-up and fractionation: The extracts were concentrated and exchanged into hexane (approximately 1 mL) for cleanup. The concentrated extracts were cleaned up on a silica/aluminium column (8 mm *i.d.*), from the bottom to top, neutral alumina (3 cm, 3% deactivated), neutral silica gel (3 cm, 3% deactivated), 50% silica (2 cm), and anhydrous sodium sulphate on the top. The column was eluted with 15 mL of dichloromethane/hexane (1:1, v/v) to yield the pesticide fraction as well as odorous chemical fraction. The eluate was concentrated to approximately 1 mL by using a rotary evaporator and then concentrated to 200 μL under a gentle stream of high purity nitrogen after an aliquot of 200 μL of dodecane was added as trapping solvent. A known quantity of ^{13}C-BDE139 was added as an internal standard prior to the analysis by gas chromatography/mass spectrometry (GC/MS) (5).

GC/MS analysis of all air samples, including chamber samples, extract samples of stinkweed parts, volatile chemicals and pesticides in passive air and high volume air samples

Chemical analyses of volatile organic chemicals were performed on a Varian GC 3800 /Saturn 2000 MS system with a DB-1MS capillary column (30 m, 0.25 mm, 0.25 μm), operated under full scan mode. Each chemical was identified in selected ion mode. Helium was the carrier gas at a constant flow of 2.0 mL/min. The oven temperature started at 80 °C for 2 minute, and then increased to 300 °C at a rate of 5 °C /minute. Splitless injection of 2 μL of sample was performed with a 5 minute solvent delay time. The GC/MS ion source and transfer line temperatures were 200 and 280ºC, respectively. The injector temperature was 280 °C (5). The specific instrument operation conditions were evaluated and adjusted as necessary to assure accuracy and reliability.

Quality control/quality assurance during lab analysis (QA/QC)

All analytical procedures were operated and recorded under good laboratory practices. Records were kept in adherence to procedures. Any deviations from procedures were explained. Laboratory and field blanks (i.e., PUF disks sent to/from field sites unopened) were extracted and analyzed in the same manner as the samples. A limit of detection (LOD) was derived from the blanks and quantified as 3 times the standard deviations of the mean concentrations of the blanks. Peaks were integrated only when the signal-to-noise ratio was greater than or equal to 3; otherwise, they were considered as undetected. Recoveries between 65% and 120% were considered as acceptable.

Data analysis

Concentrations of volatile organic chemicals in air were calculated according to the equation below:

$$\text{Air concentration (ng/m}^3\text{)} = \frac{[\text{Extraction concentration (ng /μL)} \times \text{Solution volume (μL)}]}{\text{Volume of air sampled (m}^3\text{)}}$$

Abbreviations: ng, nanogram; m^3, cubic meter; μL, microliter.

Sampling Duration

1. Passive sampling on Kauai was conducted at during these times and at these intervals; September 22, 2010 – January 24, 2011; June 6, 2011 – October 12, 2011; October 12, 2011 – February 12, 2012; and February 12, 2012 – June 14, 2012.

2. High volume air sampling to establish methodology and analyze for compounds associated with stinkweed was conducted from September 28, 2009 to October 1, 2009 on Maui.

3. High volume air sampling on Kauai was conducted from February 10, 2012 to February 18, 2012.

Results and Discussion

Volatile natural chemicals emitted from stinkweed (using both laboratory chamber emission studies and flower, pod, stem, and leaf extraction studies)

Table 2 shows a list of the major 29 volatile chemicals emitted from stinkweed, as determined by the laboratory chamber studies. Table 3 shows a list of the major 29 volatile compounds extracted from the stem, pod, leaf and flower samples of stinkweed. The chemicals detected in the chamber study were determined to be the same as those extracted directly from stinkweed tissues. The 29 volatile chemicals detected in stinkweed tissues and the chamber nitrogen gas flux included methyl isothiocyanate (MITC), *trans*-2-methyl cyclopentanol, nonanal, linalool, 1-α-terpineol, carvacrol, β-caryophyllene, and *trans*-phytol. The concentrations of the 29 volatile chemicals ranged from 6 to 23 mg/g dry weight in different parts of stinkweed (Table 3).

Evaluation of high volume air sampling method and analytical procedures

Studies were conducted in the field on Maui to determine volatile chemicals produced by stinkweed as well as the suitability of air sampling methods. The Maui field study included air sample collection, sample preparation, transport, and sample analyses. Analytical results for the 2, 4, 6 and 12-hour day and night air samples showed no detection of the target compounds in the second PUF disk of the series-connected two PUF disks. Table 3 shows the average concentrations of the chemicals detected in the first PUF disks of 12-hour day and night air samples. Saturation experimental results indicated that the air sample collection design worked well. Laboratory and field blanks showed no detection of the target chemicals, demonstrating no contamination from these chemicals during transport, storage, and analysis. Recoveries of the target analytes were between 65% and 120%. The average recovery of the surrogate standard for TcMX and PCB209 was 85 ± 5% and 90 ± 10%, respectively. The experiments proved that the methods were satisfactory for the collection and analyses of volatile compounds and pesticides for the Kauai study.

Volatile natural chemicals emitted from stinkweed as collected by high volume air sampling on Maui

Ambient air samples from high volume air sampling were collected between September 28, 2009 and October 1, 2009 in a field on Maui that was heavily infested with stinkweed. The air samples were analyzed and the results showed 29 volatile chemicals. Those chemicals were the same as the ones detected in the extracts from various parts of stinkweed and from the chamber plant chemical emission study (Table 3). The results demonstrate that these 29 chemicals are emitted from stinkweed. Other plants may also emit these chemicals. Total concentrations of the 29 volatile chemicals were 30929 and 9867 ng/m^3 in the ambient air during day and night, respectively (Table 3).

Volatile natural chemicals and pesticides in ambient air samples collected by passive air sampling on Kauai

Passive air sampling was conducted at Waimea Canyon Middle School for four periods of 4-months each, which allowed for over a full year of sampling coverage, including sampling during each season. Those passive air samples were analyzed for the 24 pesticides (Table 4). These 24 pesticides were selected for analyses based on the historical and recent sales records and reports (Table 4). Pesticide residues detected in indoor and outdoor passive air samples were bifenthrin, chlorpyrifos, metolachlor, α-/γ-benzene hexachlorides (BHCs), and p,p'-dichlorodiphenyltrichloroethane (DDT)/ p,p'-dichlorodiphenyldichloroethylene (DDE)/ p,p'-dichlorodiphenyldichloroethane (DDD) (DDT, DDE and DDD are summed and called DDTs in this report).

Passive air sampling periods at Waimea Canyon Middle School specifically were September 22, 2010 – January 24, 2011, June 6, 2011 – October 12, 2011, October 12, 2011 – February 12, 2012, February 12, 2012 – June 14, 2012. A complete one year period from June 6, 2011 to June 14, 2012 was covered.

Passive air sampling period between September 22, 2010 and January 24, 2011 (Tables 5-6): This was the first passive air sampling experiment. Four passive air sampling workstations (2 indoor and 2 outdoor) were established in the Waimea Canyon Middle School on Kauai during this period. On September 22, 2010, two outdoor passive samplers were placed on the roofs of buildings B and D and two indoor samplers were placed in rooms C101 and C102. After four months, the four passive air samples were retrieved, resealed and returned to the laboratory in the Department of Molecular Biosciences and Bioengineering, University of Hawaii at Manoa for chemical analyses. Tables 5 and 6 show the results of the volatile natural chemicals and pesticides detected, respectively.

Passive air sampling period between June 6, 2011 and October 12, 2011 (Tables 7-8): A total of 7 passive air samples were collected: 2 outdoor samples on the roof of buildings B and D and 2 indoor samples in room C101 and C102, from the Waimea Canyon Middle School, and 3 outdoor samples from the control sites at Hanalei Elementary School and Kalaheo Elementary School. Fourteen (14) of the 29 volatile plant chemicals were detected in the two indoor and five outdoor passive air samples (Table 7). The samples were also analyzed for the 24 target pesticides. Pesticides residues detected in the indoor and outdoor passive air samples from the Waimea Canyon Middle School were chlorpyrifos, metolachlor, bifenthrin, BHCs and DDTs (Table 8). BHCs and DDTs were also detected at the Hanalei Elementary School and Kalaheo Elementary School control sampling sites.

Passive air sampling period between October 12, 2011 and February 12, 2012 (Tables 9-10): A total of 7 passive air samples were collected for the sampling period between October 12, 2011 and February 12, 2012. Two outdoor samples on the roof of buildings B and D and two indoor samples in room C101 and C102 were collected from the Waimea Canyon Middle School on February 12, 2012. Three outdoor samples were collected from the control sites at Hanalei Elementary School and Kalaheo Elementary School on Kauai. Fourteen (14) of the 29 volatile plant chemicals were detected in the two indoor and five outdoor passive air samples (Table 9). The samples were also analyzed for the target pesticides. Pesticide residues detected in the indoor and outdoor passive air samples from the Waimea Canyon Middle School were chlorpyrifos, metolachlor, bifenthrin, BHCs and DDTs (Table 10). BHCs and DDTs were also detected in the control sampling sites from Hanalei Elementary School and Kalaheo Elementary School on Kauai.

Passive air sampling period between February 12, 2012 and June 14, 2012 (Tables 11-12): A total of 9 passive air samples were collected for this sampling period. Two outdoor samples on the roof of buildings B and D and 2 indoor samples in room C101 and C102 were collected from the Waimea Canyon Middle School on Kauai. Five outdoor samples as control were collected from Hanalei Elementary School (2 samples), Kalaheo Elementary School (1 sample) and Kanuikapono Learning Center (2 samples) on Kauai. Fourteen (14) of the 29 volatile chemicals were detected in the 2 indoor and 7 outdoor passive air samples (Table 11). The samples were also analyzed for the target pesticides. Pesticides residues detected in the indoor and outdoor passive air samples from the Waimea Canyon Middle School included chlorpyrifos, metolachlor, bifenthrin, BHCs and DDTs (Table 12). BHCs and DDTs were also detected in the control sampling sites from Hanalei Elementary School, Kalaheo Elementary School and Kanuikapono Learning Center on Kauai.

Summary of chemicals detected in passive air samples from four sampling sites on Kauai: Passive air samples were collected from Waimea Canyon Middle School and control sites on Kauai. The control sites included Kalaheo Elementary School, Kanuikapono Learning Center, and Hanalei Elementary School for the passive air sampling periods of June 6, 2011 – June 14, 2012. Fourteen (14) of the 29 chemicals found in stinkweed and five (5) pesticides (BHCs, DDTs, chlorpyrifos, bifenthrin and metolachlor) were detected in ambient air in Waimea, Kauai. Twelve (12) of the 29 chemicals found in stinkweed and two (2) pesticides (BHCs and DDTs) were detected in ambient air in Hanalei, Kalaheo and Kanuikapono, Kauai. The two sampling sites at Kanuikapono Learning Center were added for the last passive air sampling period (between February 12, 2012 and June 14, 2012). The results of Kanuikapono Learning Center were similar to those of Kalaheo Elementary School and Hanalei Elementary School.

A total of 27 passive air samples (19 outdoor samples and 8 indoor samples) were collected at various locations on Kauai. A total of 8 indoor passive air samples and 8 outdoor samples were collected from the Waimea Canyon Middle School on Kauai from September 22, 2010 to June 14, 2012. Approximately a half of the 29 chemicals emitted from stinkweed in the chamber study and in a Maui field in the 2009 tests were also detected in the 19 outdoor and 8 indoor passive air samples. Those passive air samples were also analyzed for the 24 pesticides. Pesticide residues detected in indoor and outdoor passive air samples included chlorpyrifos, metolachlor, bifenthrin, BHCs and DDTs.

<u>Volatile natural chemicals and pesticides in ambient air samples collected by high volume air sampling on Kauai</u>

High volume sampling was conducted to determine the concentrations of volatile chemicals and pesticides in the Waimea Canyon Middle School area. Hanalei Elementary School was the control sampling site.

Fourteen (14) night samples and 14 day samples were collected from the Waimea Canyon Middle School on Kauai from February 10, 2012 to February 18, 2012. Seven (7) night samples and 7 day samples were collected from Hanalei Elementary School. Tables 13 and 14 show the chemicals detected in 42 high volume air samples. Approximately half of the 29 compounds emitted from stinkweed in a Maui field in the 2009 tests were detected in the 42 high volume air samples. Those chemicals were also detected in the 27 passive air samples.

Methyl isothiocyanate (MITC) was found in the 42 high volume air samples, as well as the 27 passive air samples conducted on Kauai. For reference, MITC was also found in ambient air in a highly stinkweed-infested field on Maui in 2009 (daytime: 262 ng/m^3; nighttime: 101 ng/m^3) (Table 3). The average concentrations of MITC in Waimea air during daytime and nighttime were 13.1 and 5.6 ng/m^3, respectively (Table 13). The average concentrations of MITC in Hanalei air during daytime and nighttime were 9.6 and 6.2 ng/m^3, respectively (Table 13). In addition to stinkweed, other plants may produce MITC. MITC is also a degradation product of metam-sodium, a pesticide that could be used to treat utility poles for wood rot and in agriculture. However, metam-sodium is classified as a restricted-use product that can only be sold in conjunction with strict recordkeeping and no sales of metam sodium were recorded on Kauai for 2012. Because we found MITC in stinkweed plant tissue, air emissions from stinkweed plants, and in passive sampling near stinkweed plants, we believe the MITC detected through high volume air sampling was from plant sources.

Twenty-four reported pesticides of current and historical uses in Waimea area, Kauai were also analyzed. Analytical results from high volume air sampling show that residues of chlorpyrifos, metolachlor, bifenthrin, BHCs, and DDTs were detected in the 14 high volume air samples collected from Waimea. The concentrations of DDTs, BHCs, chlorpyrifos, bifenthrin, and metolachlor in Waimea air during daytime were 2.5, 2.3, 35, 43, and 23 ng/m^3, respectively. The concentrations of DDTs, BHCs, chlorpyrifos, bifenthrin, and metolachlor in Waimea air during nighttime were 2.4, 1.7, 33, 29, and 19 ng/m^3, respectively. BHCs and DDTs were detected in the 14 high volume air samples from Hanalei, Kauai. The concentrations of DDTs and BHCs in Hanalei air during daytime were 2.0 and 1.1 ng/m^3, respectively. The concentrations of DDTs and BHCs in Hanalei air during nighttime were 1.8 and 1.4 ng/m^3, respectively.

The results of natural chemicals and pesticide residues in the high volume air samples from Waimea and the control site (Hanalei) agreed very well with those of the corresponding passive air samples. Residues of BHCs, chlorpyrifos, metolachlor, bifenthrin and DDTs detected in the high volume air samples from Waimea were also detected in the passive air samples from Waimea. BHCs and DDTs detected in the high volume air samples from Hanalei were also detected in the outdoor passive air samples from Hanalei and Kalaheo, Kauai.

The concentrations of the detected pesticides and MITC were compared with available health thresholds. The purpose was to get a rough idea of potential exposure and risk for the concentrations of the chemicals detected in ambient air on Kauai. Table 15 compares data and risk assessments from previous studies with the results of the high volume air samples collected on Kauai. Studies of pesticides in ambient air have previously been conducted in Lompoc, Parlier and McFarland, California. These studies established screening levels (SL) which were described as "the calculated air concentration based on a chemical's toxicity that is used to evaluate the possible health effects of exposure to the chemical" (3). When available, the California SL's have been used for the present study. For example, the Parlier study had screening levels of 3000 ng/m^3 for MITC and 850 ng/m^3 for chlorpyrifos based on 14-day exposure. Levels of MITC observed in the Parlier study were 377 ng/m^3, and the levels for chlorpyrifos were 96.1 ng/m^3. When California Screening levels were not available, the EPA No Observable Effects Level was used and then volume of air typically inhaled was used to estimate exposure. The concentrations of chlorpyrifos, metolachlor and MITC in ambient air on Kauai were approximately 24-, 650-, and 220-fold below the California subchronic screening levels.

Summary

Ambient air studies were conducted on Kauai in response to community concerns regarding potential pesticide exposure, and to determine if a locally common plant, *Cleome gynandra* (known locally as stinkweed), produces odorous chemicals that could result in health effects.

This study was conducted as a result of occurrences at Kauai's Waimea Canyon Middle School during which some students and staff exhibited symptoms such as throat irritation, tearing, and dizziness. These symptoms could be consistent with exposure to certain pesticides, but could also be caused by exposure to volatile chemicals emitted from natural sources, such as stinkweed. At the time of these occurrences, stinkweed was growing in the fields near the school and was considered by some county emergency response officials to be the potential cause of the students' symptoms.

The Hawaii Department of Agriculture (HDOA) conducted regulatory compliance investigations, including the collection of environmental samples from the school and surrounding areas, of the odor and health complaints from the school and determined that there was no evidence to indicate that pesticides had been used improperly.

In response to community concerns, HDOA and Kauai County contracted with the University of Hawaii to conduct air monitoring for chemicals in the ambient air in and near the school.

Prior to conducting air monitoring at the school and at other locations, stinkweed plants were collected, extracted and analyzed for chemical compounds in the laboratory. In a contained and controlled atmosphere (chamber), volatile chemicals from the plants were also collected and analyzed. Stinkweed was found to produce 29 chemicals during these studies. MITC was one of those 29 chemicals. MITC is a highly foul-smelling, noxious chemical at high concentrations, and is cited as a potent lachrymator and nose and throat irritant. Besides MITC, other stinkweed-derived compounds found during this study are also known potential irritants.

Because the stinkweed near the school was plowed under and managed after the incidents, researchers looked for another location infested with the plant. Unfavorable growing conditions and access issues made preliminary study sites on Kauai unavailable. An accessible and secure field of abundant stinkweed was identified on Maui and high volume sampling was conducted to collect air samples there. This sampling study also identified 29 chemicals emitted by stinkweed. Along with the laboratory chamber and plant tissue studies, this ambient air study definitively correlated the stinkweed plant with the chemicals.

Two types of air sampling were then conducted on Kauai. For over a year, passive air sampling was used to identify chemicals in ambient air around the school and at other locations on Kauai for comparison. High volume sampling was conducted at Waimea Canyon Middle School and Hanalei Elementary School to detect chemicals in the ambient air and to determine the quantity of those chemicals.

Approximately half of the 29 chemicals produced by stinkweed were detected both in indoor and outdoor air samples collected from the passive and high volume air samplers positioned at Waimea Canyon Middle School and other Kauai schools. Trace amounts of five pesticides were also detected in both the passive and high volume samples collected at Waimea Canyon Middle School. Two of the five pesticides, dichlorodiphenyltrichloroethanes (DDTs) and benzene hexachlorides (BHCs), were widely used historically for mosquito and other insect control and are no longer in use. They have no odor in low concentrations. Because these pesticides do not break down quickly, they can still be detected throughout the islands, and in fact, throughout the world. They were also detected in passive outdoor air samples collected from Hanalei Elementary School, Kalaheo Elementary School, and Kanuikapono Learning Center, as well as in high volume outdoor air samples collected from Hanalei Elementary School.

The method of chemical detection used in the study, gas chromatography-coupled mass spectrometry, is highly sensitive and can detect very low concentrations of chemicals. Harmful effects are dependent upon both the toxicity of the chemical and the amount of exposure to the chemical. The State of California has used subchronic screening levels that are considered to be protective of health and are an accepted standard for chemical analyses of air samples for pesticides. These standards were used in this study. Concentrations of chlorpyrifos, metalochlor, and MITC in ambient air at the study sites on Kauai were approximately 24-, 650-, and 220-fold below the California screening levels. Chemical levels found in the air in each of the sampling sites on Kauai were all well below health concern levels.

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Attachments

Lists of Figures and Tables

Figure 1. Project Workflow chart

Figure 2. Diagram of lab chamber experiment for analysis of volatile organic chemicals emitted from stinkweed

Figure 3. Map of air sampling sites on Kauai.

Table 1. All the sampling events and sample number of the study from September 28, 2009 to October 1, 2009 on Maui

Table 2. A list of major 29 volatile organic chemicals emitted from stinkweed, as determined by the laboratory chamber studies

Table 3. List of volatile organic chemicals extracted from different parts of stinkweed and ambient air collected during the 2009 Maui high volume air sampling

Table 4. Twenty-four (24) pesticides that are currently used, or possibly used in the Waimea area of Kauai, based on sales records and historical reports, their molecular information and qualitative and quantitative ions used for analysis

Table 5. Qualitative analytical results of target volatile natural chemicals detected in indoor and outdoor passive air samples collected at Waimea Canyon Middle School, Kauai (Sampling period of 9/22/2010-1/24/2011)

Table 6. Qualitative analytical results of target pesticides detected in indoor and outdoor passive air samples collected at Waimea Canyon Middle School, Kauai (Sampling period of 9/22/2010-1/24/2011)

Table 7. Qualitative analytical results of target volatile natural chemicals detected in indoor and outdoor passive air samples collected at Waimea Canyon Middle School, Kalaheo Elementary School and Hanalei Elementary School, Kauai (Sampling period of 6/6/2011 – 10/12/2011)

Table 8. Qualitative analytical results of target pesticides detected in indoor and outdoor passive air samples collected at Waimea Canyon Middle School, Kalaheo Elementary School and Hanalei Elementary School, Kauai (Sampling period of 6/6/2011 – 10/12/2011)

Table 9. Qualitative analytical results of target volatile natural chemicals detected in indoor and outdoor passive air samples collected at Waimea Canyon Middle School, Kalaheo Elementary School and Hanalei Elementary School, Kauai (Sampling period of 10/12/2011 – 2/12/2012)

Table 10. Qualitative analytical results of target pesticides detected in indoor and outdoor passive air samples collected at Waimea Canyon Middle School, Kalaheo Elementary School and Hanalei Elementary School, Kauai (Sampling period of 10/12/2011 – 2/12/2012)

Table 11. Qualitative analytical results of target volatile natural chemicals detected in indoor and outdoor passive air samples collected at Waimea Canyon Middle School, Kalaheo Elementary School, Hanalei Elementary School and Kanuikapono Learning Center, Kauai (Sampling period of 2/12/2012-6/14/2012)

Table 12. Qualitative analytical results of target pesticides detected in indoor and outdoor passive air samples collected at Waimea Canyon Middle School, Kalaheo Elementary School, Hanalei Elementary School, and Kanuikapono Learning Center, Kauai (Sampling period of 2/12/2012-6/14/2012)

Table 13. Concentrations of volatile chemicals in ambient air collected during the 2012 Kauai

high volume air sampling (sampling period of 2/10/2012 – 2/18/2012)
Table 14. Quantitative analytical results of target pesticides in samples collected from high volume sampling on Kauai and comparison of the results with health exposure limits
Table 15. Estimated exposure to the pesticides and MITC in ambient air at Waimea Canyon Middle School (WCMS) and Hanalei Elementary School (HES)

Figure 1. Project workflow chart.

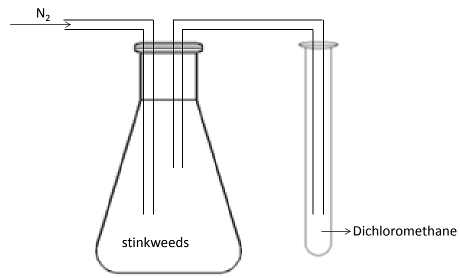

Figure 2. Diagram of laboratory chamber experiment for analysis of volatile organic chemicals emitted from stinkweed

Figure 3. Map of air sampling sites on Kauai
Waimea Canyon Middle School
Kalaheo Elementary School
Hanalei Elementary School
Kanuikapono Learning Center
Kapaa High School

Table 1. All the sampling events and sample number of the study from September 28, 2009 to October 1, 2009 on Maui

Number of Samples	Sampling Sorts	Date Start	Time Start	Date End	Time End
Air sampling					
2	2-hours night air	9/28/2009	5:30 (p.m)	9/28/2009	7:30 (pm)
2	4-hours night air	9/28/2009	7:30 (p.m)	9/28/2009	11:30 (pm)
2	6-hours night air	9/28/2009	11:30 (p.m)	9/29/2009	5:30 (am)
2	2-hours day air	9/29/2009	5:30 (a.m)	9/29/2009	7:30 (am)
2	4-hours day air	9/29/2009	7:30 (a.m)	9/29/2009	11:30 (am)
2	6-hours day air	9/29/2009	11:30 (a.m)	9/29/2009	5:30 (pm)
2	12-hours night air	9/29/2009	5:30 (p.m)	9/30/2009	5:30 (am)
2	12-hours day air	9/30/2009	5:30 (a.m)	9/30/2009	5:30 (pm)

Stinkweed tissue collection

Number of samples	Plant parts collected	Note
2	Flower	Different parts of stinkweed (flowers, stem, leaves and pods) were collected from the same field as the high volume air sampling field. The samples were collected from the sites where the high volume air samplers were located. Two samples of each plant part were collected. Those samples were collected on September 29, 2009.
2	Stem	
2	Leaf	
2	Pod	

Note: a total 16 air samples and 8 stinkweed samples

Table 2. A list of major 29 volatile organic chemicals emitted from stinkweed, as determined by the laboratory chamber studies

Chemicals	Molecular formula	Molecular weight	Quantitative ion	Qualitative ion
Methyl isothiocyanate (MITC)	C_2H_3NS	73	73	45,73
trans-2-Methyl cyclopentanol	$C_6H_{10}O$	98	98	42,55,69,98
cis-3-Hexen-1-ol	$C_6H_{12}O$	100	41	41,55,67,82
trans-2-Hexen-1-ol	$C_6H_{12}O$	100	41	41,55,67,82
Heptan-2-one	$C_7H_{14}O$	114	43	43,58
Anisole	C_7H_8O	108	108	39,65,78,108
Benzaldehyde	C_7H_6O	106	105	51,77,105
2,4,5-Trimethyl-thiazole	C_6H_9NS	127	127	71,86,127
Phenyl-acetaldehyde	C_8H_8O	120	91	65,91,120
m-Cymene	$C_{10}H_{14}$	134	119	91,119,134
δ-Limonene	$C_{10}H_{16}$	136	68	27,39,68,93
β-Ocimene	$C_{10}H_{16}$	136	93	41,53,79,93
Nonanal	$C_9H_{18}O$	142	57	41,57,70,82,98
Linalool	$C_{10}H_{18}O$	154	71	41,55,71,93
Phenyl acetonitrile	C_8H_7N	117	117	90,117
Methyl salicylate	$C_8H_8O_3$	152	120	92,120,152
1-α-terpineol	$C_{10}H_{18}O$	154	81	43,58,81,93,121,136
β-Cyclocitral	$C_{10}H_{16}O$	152	121	41,67,91,107,121,152
Nerol	$C_{10}H_{18}O$	154	69	41,69,93
trans-Geraniol	$C_{10}H_{18}O$	154	69	41,69
Carvacrol	$C_{10}H_{14}O$	150	135	135,150
α-Methyl-lonone	$C_{14}H_{22}O$	206	135	43,91,107,135,150
β-Caryophyllene	$C_{15}H_{24}$	204	93	41,69,93,105,133,161
trans-Geranyl-acetone	$C_{13}H_{22}O$	194	43	41,43,69
β-Methyl-lonone	$C_{14}H_{22}O$	206	135	43,91,107,135
Tridecanal	$C_{13}H_{26}O$	198	57	29,43,57,68,82,96
trans-Phytol	$C_{20}H_{40}O$	296	71	43,71
Cedrene	$C_{15}H_{24}$	204	119	41,69,91,119,161,204
Nerolidol	$C_{15}H_{26}O$	222	69	41,69,93

Table 3. List of volatile organic chemicals extracted from different parts of stinkweed and ambient air collected during the 2009 Maui high volume air sampling (average values of two replicates)

Chemicals	Average concentrations in different parts of stinkweed (mg/g dry weight)				Average concentrations in ambient air (ng/m^3) (12 hours collection)	
	flower	pod	stem	leaf	daytime	nighttime
Methyl isothiocyanate (MITC)	0.31	0.48	0.13	0.25	261.6	101.2
trans-2-Methyl cyclopentanol	1.07	1.66	0.43	0.85	3148.5	959.8
cis-3-Hexen-1-ol	0.15	0.23	0.06	0.12	81.8	27.3
trans-2-Hexen-1-ol	0.14	0.23	0.06	0.12	46.5	31.3
Heptan-2-one	0.04	0.07	0.02	0.04	23.3	5.3
Anisole	0.06	0.09	0.02	0.05	11.5	3.8
Benzaldehyde	0.06	0.09	0.02	0.04	12.0	2.8
2,4,5-Trimethyl-thiazole	0.06	0.10	0.02	0.05	11.8	2.6
Phenyl-acetaldehyde	0.10	0.16	0.04	0.08	456.4	5.5
m-Cymene	0.09	0.14	0.04	0.07	67.6	5.0
δ-Limonene	0.05	0.07	0.02	0.04	13.2	3.1
β-Ocimene	0.06	0.09	0.02	0.05	17.6	5.0
Nonanal	0.09	0.14	0.04	0.07	24.0	6.6
Linalool	2.00	3.07	0.80	1.58	4828	1726
Phenyl acetonitrile	0.09	0.14	0.04	0.07	15.0	5.7
Methyl salicylate	0.10	0.16	0.04	0.08	15.7	7.2
1-α-Terpineol	0.49	0.76	0.20	0.40	93.1	26.9
β-Cyclocitral	0.13	0.21	0.05	0.11	41.6	13.4
Nerol	0.15	0.23	0.06	0.12	117.2	31.8
trans-Geraniol	0.46	0.72	0.19	0.37	406.8	152.5
Carvacrol	4.35	6.74	1.75	3.46	11954	3522
α-Methyl lonone	0.16	0.25	0.07	0.13	117.8	33.7
β-Caryophyllene	0.66	1.02	0.26	0.52	1052	271.2
trans-Geranyl-acetone	0.06	0.09	0.02	0.05	13.3	3.4
β-Methyl lonone	0.36	0.55	0.14	0.28	740.9	241.0
Tridecanal	0.02	0.02	0.01	0.01	2.8	10.4
trans-Phytol	3.57	5.54	1.44	2.84	7347	2660
Cedrene	0.02	0.02	0.01	0.01	4.1	1.0
Nerolidol	0.01	0.03	0.01	0.02	3.2	1.3
total	14.90	23.09	6.01	11.87	30929.1	9866.7

Table 4. Twenty-four (24) pesticides that are currently used, or possibly used in the Waimea area of Kauai, based on sales records and historical reports, their molecular information and qualitative and quantitative ions used for analysis

Pesticides	Molecular formula	Mol. Weight	CAS	Qualitative ion	Quantitative ion
Ametryn	$C_9H_{17}N_5S$	227.3	834-12-8	227,212,170,58	227
Atrazine	$C_8H_{14}ClN_5$	215.7	1912-24-9	215,200,173,58	200
Dalapon	$C_3H_4Cl_2O_2$	142.9	75-99-0	97,62,27	62
Diuron	$C_9H_{10}Cl_2N_2O$	233.1	330-54-1	232,72	72
Pentachlorophenol	C_6H_5OH	266.3	87-86-5	266,165	266
Silvex	$C_9H_7Cl_3O_3$	269.5	93-72-1	268,196	196
TCA	$C_2HCl_3O_2$	163.3	76-03-9	82,45	82
2,4-D	$C_8H_6Cl_2O_3$	221.0	94-75-7	220,162	162
2,4,5-T	$C_8H_5Cl_3O_3$	255.4	93-76-5	254,196	196
DDTs	$C_{10}H_{14}N_2O_4$	226.2	3416-05-5	235,165	235
Malathion	$C_{10}H_{19}O_6PS_2$	330.3	121-75-5	173,158,125,93	173
BHCs	$C_6H_6Cl_6$	290.8	6108-10-7	219,181,109,51	219
Methoxychlor	$C_{16}H_{15}Cl_3O_2$	345.6	72-43-5	227	227
Naled	$C_4H_7Br_2Cl_2O_4P$	380.7	300-76-5	378,145.109,79	109
Chlorpyrifos	$C_9H_{11}Cl_3NO_3PS$	350.5	2921-88-2	314,258,197,97	197
Esfenvalerate	$C_{25}H_{22}ClNO_3$	419.9	66230-04-4	419,225,167,125	125
Permethrin	$C_{21}H_{20}Cl_2O_3$	391.2	52645-53-1	183	183
λ-Cyhalothrin	$C_{23}H_{19}ClF_3NO_3$	449.8	91465-08-6	208,181,141	181
ζ-Cypermethrin	$C_{22}H_{19}Cl_2NO_3$	416.3	67375-30-8	163,165,91,51	163
Alachlor	$C_{14}H_{20}ClNO_2$	269.7	15972-60-8	188,160,45	160
β-Cyfluthrin	$C_{22}H_{18}Cl_2FNO_3$	434.2	68359-37-5	206,163,91	163
Tefluthrin	$C_{17}H_{14}ClF_7O_2$	418.7	79538-32-2	177	177
Bifenthrin	$C_{23}H_{22}ClF_3O_2$	422	82657-04-3	181,166	181
Metolachlor	$C_{15}H_{22}ClNO_2$	283.7	51218-45-2	238,162	162

Table 5. Qualitative analytical results of target volatile natural chemicals detected in indoor and outdoor passive air samples collected at Waimea Canyon Middle School, Kauai (Sampling period of 9/22/2010-1/24/2011) (Note: The results of the two outdoor samples were the same. The results of the two indoor samples were the same.)

Compounds	Results of 9/22/2010-1/24/2011 sampling period	
	Outdoor samples	Indoor samples
Methyl isothiocyanate (MITC)	+	+
trans-2-Methyl cyclopentanol	+	+
cis-3-Hexen-1-ol	-	-
trans-2-Hexen-1-ol	-	-
Heptan-2-one	-	-
Anisole	-	-
Benzaldehyde	-	-
2,4,5-Trimethyl-thiazole	-	-
Phenyl-acetaldehyde	+	+
m-Cymene	+	+
δ-Limonene	-	-
β-Ocimene	-	-
Nonanal	+	+
Linalool	+	+
Phenyl acetonitrile	-	-
Methyl salicylate	+	+
1-α-Terpineol	-	-
β-Cyclocitral	-	-
Nerol	+	+
trans-Geraniol	+	+
Carvacrol	-	-
α-Methyl lonone	+	+
β-Caryophyllene	+	+
trans-Geranyl-acetone	-	-
β-Methyl lonone	-	-
Tridecanal	+	+
trans-Phytol	+	+
Cedrene	-	-
Nerolidol	+	+

"+" indicates "detected". "-" indicates "not detected"

Table 6. Qualitative analytical results of target pesticides detected in indoor and outdoor passive air samples collected at Waimea Canyon Middle School, Kauai (Sampling period of 9/22/2010-1/24/2011) (Note: The results of the two outdoor samples were the same. The results of the two indoor samples were the same.)

Compounds	Results of 9/22/2010-1/24/2011 sampling period	
	Outdoor samples	Indoor samples
Ametryn	-	-
Atrazine	-	-
Dalapon	-	-
Diuron	-	-
Pentachlorophenol	-	-
Silvex	-	-
TCA	-	-
2,4-D	-	-
2,4,5-T	-	-
DDTs	+	+
Malathion	-	-
BHCs	+	+
Methoxychlor	-	-
Naled	-	-
Chlorpyrifos	+	+
Esfenvalerate	-	-
Permethrin	-	-
λ-Cyhalothrin	-	-
ξ-Cypermethrin	-	-
Alachlor	-	-
β-Cyfluthrin	-	-
Tefluthrin	-	-
Bifenthrin	+	+
Metolachlor	+	+

"+" indicates "detected". "-" indicates "not detected"

Table 7. Qualitative analytical results of target volatile natural chemicals detected in indoor and outdoor passive air samples collected at Waimea Canyon Middle School, Kalaheo Elementary School and Hanalei Elementary School, Kauai (Sampling period of 6/6/2011 – 10/12/2011). Note: One sampling station set up at Kalaheo Elementary School and two stations set up at Kapaa were missing.

Compounds	Results of 6/6/2011 – 10/12/2011 sampling period						
	Waimea Canyon Middle School				Kalaheo	Hanalei	
	Indoor		Outdoor		Outdoor	Outdoor	
	IA	IB	OA	OB	OK	OH1	OH2
Methyl isothiocyanate (MITC)	+	+	+	+	+	+	+
trans-2-Methyl cyclopentanol	+	+	+	+	-	-	+
cis-3-Hexen-1-ol	-	-	-	-	-	-	-
trans-2-Hexen-1-ol	-	-	-	-	-	-	-
Heptan-2-one	-	-	-	-	-	-	-
Anisole	-	-	-	-	-	-	-
Benzaldehyde	-	-	-	-	-	-	-
2,4,5-Trimethyl-thiazole	-	-	-	-	-	-	-
Phenyl-acetaldehyde	+	+	+	+	-	+	+
m-Cymene	+	+	+	+	+	+	+
δ-Limonene	-	-	-	-	-	-	-
β-Ocimene	-	-	-	-	-	-	-
Nonanal	+	+	+	+	+	+	+
Linalool	+	+	+	+	+	+	+
Phenyl acetonitrile	-	-	-	-	-	-	-
Methyl salicylate	+	+	+	+	+	+	+
1-α-Terpineol	-	-	-	-	-	-	-
β-Cyclocitral	-	-	-	-	-	-	-
Nerol	+	+	+	+	-	+	+
trans-Geraniol	+	+	+	+	-	-	+
Carvacrol	-	-	-	-	-	-	-
α-Methyl lonone	+	+	+	+	-	-	-
β-Caryophyllene	+	+	+	+	+	+	+
trans-Geranyl-acetone	-	-	-	-	-	-	-
β-Methyl lonone	-	-	-	-	-	-	-
Tridecanal	+	+	+	+	+	+	+
trans-Phytol	+	+	+	+	-	+	+
Cedrene	-	-	-	-	-	-	-
Nerolidol	+	+	+	+	+	-	-

IA: Indoor sample from room C102 (A); IB: Indoor sample from room C102 (B); OA: Outdoor sample from room C102 (A); OB: Outdoor sample from room C102 (B) of Waimea Canyon Middle School;
OK: Outdoor sample from the Kalaheo Elementary School;
OH1: Outdoor sample from the Hanalei Elementary School; OH2: Outdoor sample from the Hanalei Elementary School.
"+" indicates "detected"; "-" indicates "un-detected"

Table 8. Qualitative analytical results of target pesticides detected in indoor and outdoor passive air samples collected at Waimea Canyon Middle School, Kalaheo Elementary School and Hanalei Elementary School, Kauai (Sampling period of 6/6/2011 – 10/12/2011). Note: One sampling station set up at Kalaheo Elementary School and two stations set up at Kapaa were missing.

Compounds	Results of 6/6/2011 – 10/12/2011 sampling period						
	Waimea Canyon school				Kalaheo	Hanalei school	
	Indoor		Outdoor		Outdoor	Outdoor	
	IA	IB	OA	OB	OK	OH1	OH2
Ametryn	-	-	-	-	-	-	-
Atrazine	-	-	-	-	-	-	-
Dalapon	-	-	-	-	-	-	-
Diuron	-	-	-	-	-	-	-
Pentachlorophenol	-	-	-	-	-	-	-
Silvex	-	-	-	-	-	-	-
TCA	-	-	-	-	-	-	-
2,4-D	-	-	-	-	-	-	-
2,4,5-T	-	-	-	-	-	-	-
DDTs	+	+	+	+	+	+	+
Malathion	-	-	-	-	-	-	-
BHCs	+	+	+	+	+	+	+
Methoxychlor	-	-	-	-	-	-	-
Naled	-	-	-	-	-	-	-
Chlorpyrifos	+	+	+	+	-	-	-
Esfenvalerate	-	-	-		-	-	-
Permethrin	-	-	-	-	-	-	-
λ-Cyhalothrin	-	-	-	-	-	-	-
ξ-Cypermethrin	-	-	-	-	-	-	-
Alachlor	-	-	-	-	-	-	-
β-Cyfluthrin	-	-	-	-	-	-	-
Tefluthrin	-	-	-	-	-	-	-
Bifenthrin	+	+	+	+	-	-	-
Metolachlor	+	+	+	+	-	-	-

IA: Indoor samples from room C102 (A); IB: Indoor samples from room C102 (B); OA: Outdoor samples from room C102 (A); OB: Outdoor samples from room C102 (B) of ;

OK: Outdoor sample from the Kalaheo Elementary School;

OH1: Outdoor sample from the Hanalei Elementary School; OH2: Outdoor sample from the Hanalei Elementary School.

"+" indicates "detected"; "-" indicates "un-detected".

Table 9. Qualitative analytical results of target volatile natural chemicals detected in indoor and outdoor passive air samples collected at Waimea Canyon Middle School, Kalaheo Elementary School and Hanalei Elementary School, Kauai (Sampling period of 10/12/2011 – 2/12/2012)

Compounds	Results of 10/12/2011 – 2/12/2012 sampling period						
	Waimea Canyon Middle School				Kalaheo	Hanalei	
	Indoor		Outdoor		Outdoor	Outdoor	
	IA	IB	OA	OB	OK	OH1	OH2
Methyl isothiocyanate (MITC)	+	+	+	+	+	+	+
trans-2-Methyl cyclopentanol	+	+	+	+	-	-	+
cis-3-Hexen-1-ol	-	-	-	-	-	-	-
trans-2-Hexen-1-ol	-	-	-	-	-	-	-
Heptan-2-one	-	-	-	-	-	-	-
Anisole	-	-	-	-	-	-	-
Benzaldehyde	-	-	-	-	-	-	-
2,4,5-Trimethyl-thiazole	-	-	-	-	-	-	-
Phenyl-acetaldehyde	+	+	+	+	-	+	+
m-Cymene	+	+	+	+	+	+	+
δ-Limonene	-	-	-	-	-	-	-
β-ocimene	-	-	-	-	-	-	-
Nonanal	+	+	+	+	+	+	+
Linalool	+	+	+	+	+	+	+
Phenyl acetonitrile	-	-	-	-	-	-	-
Methyl salicylate	+	+	+	+	+	+	+
1-α-Terpineol	-	-	-	-	-	-	-
β-Cyclocitral	-	-	-	-	-	-	-
Nerol	+	+	+	+	-	+	+
trans-Geraniol	+	+	+	+	-	-	+
Carvacrol	-	-	-	-	-	-	-
α-Methyl lonone	+	+	+	+	-	-	-
β-Caryophyllene	+	+	+	+	+	+	+
trans-Geranyl-acetone	-	-	-	-	-	-	-
β-Methyl lonone	-	-	-	-	-	-	-
Tridecanal	+	+	+	+	+	+	+
trans-Phytol	+	+	+	+	-	+	+
Cedrene	-	-	-	-	-	-	-
Nerolidol	+	+	+	+	+	-	-

IA: Indoor sample from room C102 (A); IB: Indoor sample from room C102 (B); OA: Outdoor sample from room C102 (A); OB: Outdoor sample from room C102 (B) of Waimea Canyon Middle School;
OK: Outdoor sample from the Kalaheo Elementary School;
OH1: Outdoor sample from the Hanalei Elementary School; OH2: Outdoor sample from the Hanalei Elementary School.
"+" indicates "detected"; "-" indicates "un-detected"

Table 10. Qualitative analytical results of target pesticides detected in indoor and outdoor passive air samples collected at Waimea Canyon Middle School, Kalaheo Elementary School and Hanalei Elementary School, Kauai (Sampling period of 10/12/2011 – 2/12/2012)

Compounds	Results of 10/12/2011 – 2/12/2012 sampling period						
	Waimea Canyon school				Kalaheo	Hanalei	
	Indoor		Outdoor		Outdoor	Outdoor	
	IA	IB	OA	OB	OK	OH1	OH2
Ametryn	-	-	-	-	-	-	-
Atrazine	-	-	-	-	-	-	-
Dalapon	-	-	-	-	-	-	-
Diuron	-	-	-	-	-	-	-
Pentachlorophenol	-	-	-	-	-	-	-
Silvex	-	-	-	-	-	-	-
TCA	-	-	-	-	-	-	-
2,4-D	-	-	-	-	-	-	-
2,4,5-T	-	-	-	-	-	-	-
DDTs	+	+	+	+	+	+	+
Malathion	-	-	-	-	-	-	-
BHCs	+	+	+	+	+	+	+
Methoxychlor	-	-	-	-	-	-	-
Naled	-	-	-	-	-	-	-
Chlorpyrifos	+	+	+	+	-	-	-
Esfenvalerate	-	-	-		-	-	-
Permethrin	-	-	-	-	-	-	-
λ-Cyhalothrin	-	-	-	-	-	-	-
ξ-Cypermethrin	-	-	-	-	-	-	-
Alachlor	-	-	-	-	-	-	-
β-Cyfluthrin	-	-	-	-	-	-	-
Tefluthrin	-	-	-	-	-	-	-
Bifenthrin	+	+	+	+	-	-	-
Metolachlor	+	+	+	+	-	-	-

IA: Indoor samples from room C102 (A); IB: Indoor samples from room C102 (B); OA: Outdoor samples from room C102 (A); OB: Outdoor samples from room C102 (B) of Waimea Canyon Middle School;

OK: Outdoor sample from the Kalaheo Elementary School;

OH1: Outdoor sample from the Hanalei Elementary School; OH2: Outdoor sample from the Hanalei Elementary School.

"+" indicates "detected"; "-" indicates "un-detected".

Table 11. Qualitative analytical results of target volatile natural chemicals detected in indoor and outdoor passive air samples collected at Waimea Canyon Middle School, Kalaheo Elementary School, Hanalei Elementary School and Kanuikapono Learning Center, Kauai (Sampling period of 2/12/2012-6/14/2012)

Compounds	Results of 2/12/2012-6/11/2012 sampling period								
	Waimea Canyon Middle School				Kalaheo	Hanalei		Kanuikapono Learning Center	
	Indoor		Outdoor		Outdoor	Outdoor		Outdoor	
	IA	IB	OA	OB	OK	OH1	OH2	OKLC1	OKLC2
Methyl isothiocyanate (MITC)	+	+	+	+	+	+	+	+	+
trans-2-Methyl cyclopentanol	+	+	+	+	-	-	+	-	-
cis-3-Hexen-1-ol	-	-	-	-	-	-	-	-	-
trans-2-Hexen-1-ol	-	-	-	-	-	-	-	-	-
Heptan-2-one	-	-	-	-	-	-	-	-	-
Anisole	-	-	-	-	-	-	-	-	-
Benzaldehyde	-	-	-	-	-	-	-	-	-
2,4,5-Trimethyl-thiazole	-	-	-	-	-	-	-	-	-
Phenyl-acetaldehyde	+	+	+	+	-	+	+	+	+
m-Cymene	+	+	+	+	+	+	+	+	+
δ-Limonene	-	-	-	-	-	-	-	-	-
β-Ocimene	-	-	-	-	-	-	-	-	-
Nonanal	+	+	+	+	+	+	+	+	+
Linalool	+	+	+	+	+	+	+	+	+
Phenyl acetonitrile	-	-	-	-	-	-	-	-	-
Methyl salicylate	+	+	+	+	+	+	+	+	+
1-α-Terpineol	-	-	-	-	-	-	-	-	-
β-Cyclocitral	-	-	-	-	-	-	-	-	-
Nerol	+	+	+	+	-	+	+	+	+
trans-Geraniol	+	+	+	+	-	-	+	+	+
Carvacrol	-	-	-	-	-	-	-	-	-
α-Methyl lonone	+	+	+	+	-	-	-	-	-

β-Caryophyllene	+	+	+	+	+	+	+	+	+
trans-Geranyl-acetone	-	-	-	-	-	-	-	-	-
β-Methyl lonone	-	-	-	-	-	-	-	-	-
Tridecanal	+	+	+	+	+	+	+	+	+
trans-Phytol	+	+	+	+	-	+	+	+	+
Cedrene	-	-	-	-	-	-	-	-	-
Nerolidol	+	+	+	+	+	-	-	-	-

IA: Indoor sample from room C102 (A); IB: Indoor sample from room C102 (B); OA: Outdoor sample from room C102 (A); OB: Outdoor sample from room C102 (B) of Waimea Canyon Middle School;
OK: Outdoor sample from the Kalaheo Elementary School;
OH1: Outdoor sample from the Hanalei Elementary School; OH2: Outdoor sample from the Hanalei Elementary School.
"+" indicates "detected"; "-" indicates "un-detected"
OKLC1: Outdoor sample from the Kanuikapono Learning Center; OKLC2: Outdoor sample from the Kanuikapono Learning Center.
"+" indicates "detected"; "-" indicates "un-detected"

Table 12. Qualitative analytical results of target pesticides detected in indoor and outdoor passive air samples collected at Waimea Canyon Middle School, Kalaheo Elementary School, Hanalei Elementary School, and Kanuikapono Learning Center, Kauai (Sampling period of 2/12/2012-6/14/2012)

Compounds	Results of 2/12/2012-6/11/2012 sampling period								
	Waimea Canyon Middle School				Kalaheo	Hanalei		Kanuikapono Learning Center	
	Indoor		Outdoor		Outdoor	Outdoor		Outdoor	
	IA	IB	OA	OB	OK	OH1	OH2	OKLC1	OKLC2
Ametryn	-	-	-	-	-	-	-	-	-
Atrazine	-	-	-	-	-	-	-	-	-
Dalapon	-	-	-	-	-	-	-	-	-
Diuron	-	-	-	-	-	-	-	-	-
Pentachlorophenol	-	-	-	-	-	-	-	-	-
Silvex	-	-	-	-	-	-	-	-	-
TCA	-	-	-	-	-	-	-	-	-
2,4-D	-	-	-	-	-	-	-	-	-
2,4,5-T	-	-	-	-	-	-	-	-	-
DDTs	+	+	+	+	+	+	+	+	+
Malathion	-	-	-	-	-	-	-	-	-
BHCs	+	+	+	+	+	+	+	+	+
Methoxychlor	-	-	-	-	-	-	-	-	-
Naled	-	-	-	-	-	-	-	-	-
Chlorpyrifos	+	+	+	+	-	-	-	-	-
Esfenvalerate	-	-	-		-	-	-	-	-
Permethrin	-	-	-	-	-	-	-	-	-
λ-Cyhalothrin	-	-	-	-	-	-	-	-	-
ξ-Cypermethrin	-	-	-	-	-	-	-	-	-
Alachlor	-	-	-	-	-	-	-	-	-
β-Cyfluthrin	-	-	-	-	-	-	-	-	-
Tefluthrin	-	-	-	-	-	-	-	-	-
Bifenthrin	+	+	+	+	-	-	-	-	-
Metolachlor	+	+	+	+	-	-	-	-	-

IA: Indoor samples from room C102 (A); IB: Indoor samples from room C102 (B); OA: Outdoor samples from room C102 (A); OB: Outdoor samples from room C102 (B) of Waimea Canyon Middle School;
OK: Outdoor sample from the Kalaheo Elementary School;
OH1: Outdoor sample from the Hanalei Elementary School; OH2: Outdoor sample from the Hanalei Elementary School.
"+" indicates "detected"; "-" indicates "un-detected".
OKLC1: Outdoor sample from the Kanuikapono Learning Center; OKLC2: Outdoor sample from the Kanuikapono Learning Center.
"+" indicates "detected"; "-" indicates "un-detected"

Table 13. Concentrations of volatile chemicals in ambient air collected during the 2012 Kauai high volume air sampling (sampling period of 2/10/2012 – 2/18/2012)

Chemicals	Concentrations (± standard deviations) of chemical in the air (ng/m^3)					
	WCS (day)	WCS (night)	Average	Hanalei (day)	Hanalei (night)	Average
Methyl isothiocyanate (Screening level: 3000)	13.1 ± 3.5	5.6 ± 1.7	9.4	9.6 ± 2.5	6.2 ± 1.6	7.9
trans-2-Methyl cyclopentanol	15.7±3.6	5.3±1.4	10.5	10.6±2.5	6.7±1.2	8.7
cis-3-Hexen-1-ol	-	-	-	-	-	-
trans-2-Hexen-1-ol	-	-	-	-	-	-
Heptan-2-one	-	-	-	-	-	-
Anisole	-	-	-	-	-	-
Benzaldehyde	-	-	-	-	-	-
2,4,5-Trimethyl-thiazole	-	-	-	-	-	-
Phenyl-acetaldehyde	2.3±0.7	1.3±0.6	1.8	3.2±1.1	2.0±0.7	2.6
m-Cymene	3.4±1.2	1.8±0.5	2.6	2.8±0.9	1.8±0.6	2.3
δ-Limonene	-	-	-	-	-	-
β-Ocimene	-	-	-	-	-	-
Nonanal	1.2±0.8	0.4±0.5	0.8	2.8±1.9	1.8±0.7	2.3
Linalool	24.1±4.5	9.6±2.3	16.8	20.2±3.5	15.7±3.5	18
Phenyl acetonitrile	-	-	-	-	-	-
Methyl salicylate	0.8±0.7	0.4±0.3	0.6	3.2±1.4	2.0±0.8	2.6
1-α-Terpineol	-	-	-	-	-	-
β-Cyclocitral	-	-	-	-	-	-
Nerol	5.9±1.2	1.8±1.1	3.8	4.6±0.9	3.0±0.8	3.8
trans-Geraniol	20.3±4.6	8.5±2.4	14.4	14.4±3.2	9.2±1.9	11.8
Carvacrol	-	-	-	-	-	-
α-Methyl lonone	5.9±1.3	1.9±0.6	3.9	-	-	-
β-Caryophyllene	5.3±0.9	5.1±1.1	5.2	19.2±2.5	13.2±2.6	16.2
trans-Geranyl-acetone	-	-	-	-	-	-
β-Methyl lonone	-	-	-	-	-	-
Tridecanal	0.1±0.3	0.6±0.4	0.4	0.4±0.6	0.4±0.3	0.4
trans-Phytol	36.7±3.3	14.8±2.4	25.8	11.8±2.7	7.4±1.3	9.6

Cedrene	-	-	-	-	-	-
Nerolidol	0.2±0.2	0.1±0.3	0.2	-	-	-
total	135.0±20.4	57.2±15.6	96.1	102.8±23.7	69.4±16.0	86.1

WCS, Waimea Canyon Middle School
Hanalei, Hanalei Elementary School
"-" indicates "not detected"

Table 14. Quantitative analytical results of target pesticides in samples collected from high volume air sampling on Kauai and comparison of the results with health exposure limits

Chemicals	Results of 2/10/2012 – 2/18/2012 sampling period					
	Limit of quantitation (ng/m^3)	Exposure limits or screening level[a] (ng/m^3)	WCS[b] (day) (ng/m^3)	WCS[b] (night) (ng/m^3)	HES[c] (day) (ng/m^3)	HES[c] (night) (ng/m^3)
Ametryn	1.5	-	-	-	-	-
Atrazine	0.9	-	-	-	-	-
Dalapon	1.2	-	-	-	-	-
Diuron	0.8	-	-	-	-	-
Pentachlorophenol	1.2	-	-	-	-	-
Silvex	1.5	-	-	-	-	-
TCA	1.5	-	-	-	-	-
2,4-D	1.2	-	-	-	-	-
2,4,5-T	1.5	-	-	-	-	-
DDTs	0.6	500x10^3 [d]	2.5 ± 0.5	2.4 ± 0.7	2.0 ± 0.4	1.8 ± 0.3
Malathion	0.9	-	-	-	-	-
BHCs	0.6	45x10^3 [e]	2.3±0.4	1.7±0.3	1.1±0.2	1.4±0.2
Methoxychlor	1.2	-	-	-	-	-
Naled	1.5	-	-	-	-	-
Chlorpyrifos	0.6	850 [f]	35±3	33±2	-	-
Esfenvalerate	0.9	-	-	-	-	-
Permethrin	0.9	-	-	-	-	-
λ-Cyhalothrin	1.2	-	-	-	-	-
ξ-Cypermethrin	0.6	-	-	-	-	-
Alachlor	0.6	-	-	-	-	-
β-Cyfluthrin	0.9	-	-	-	-	-
Tefluthrin	1.5	-	-	-	-	-
Bifenthrin	0.6	328 [g]	43±4	29±3	-	-
Metolachlor	0.3	36x10^6 [h]	23±3	19±2	-	-

[a] Some screening levels are based on California pesticides air monitoring studies, the others are derived from the sources referred to in the superscript (a No Observed Effects Level, or Reference Dose expressed in mg/kg bodyweight/day. A weight of 40 kilograms or about 88 pounds was used for calculating exposure in terms of milligrams per kilogram, and the 11,000 liters or 11 m^3 was the estimated amount of air

breathed in per day.
[b] WCS, Waimea Canyon Middle School
[c] HES, Hanalei Elementary School
[d] WHO 1979. http://www.inchem.org/documents/ehc/ehc/ehc009.htm#SubSectionNumber:1.1.6
[e]FAO and WHO 1969. http://www.inchem.org/documents/jmpr/jmpmono/v068pr03.htm
[f] DPR. 2005. Environmental Justice Pilot Project-Project Objectives, Pesticide, and Community for Monitoring. State of California Department of Pesticide Regulation. June 2005 (2)
[g] The acute reference dose (RfD) µg /kg bodyweight/day
[h] EPA Reregistration Eligibility Decision (RED) Metolachlor, EPA 738-R-95-006, April 1995, http://www.epa.gov/oppsrrd1/REDs/0001.pdf (7)
"-" indicates "not detected".

Table 15. Estimated exposure to the pesticides and MITC in ambient air at Waimea Canyon Middle School (WCS) and Hanalei Elementary School (HES)

	DDTs[a]	BHCs	Chlorpyrifos	Bifenthrin[b]	Metolachlor[c]	MITC	Total daily exposure
LOQ (ng/m^3)	0.6	0.6	0.6	0.6	0.3	6	
WCS daytime (ng/m^3)	2.5	2.3	35	43	23	13.1	
WCS nighttime (ng/m^3)	2.4	1.7	33	29	19	5.6	
HES daytime (ng/m^3)	2	1.1	ND	ND	ND	9.6	
HES nighttime (ng/m^3)	1.8	1.4	ND	ND	ND	6.2	
CA subchronic screening level (ng/m^3)	Not applicable	Not applicable	850	Not applicable	15000	3000	
No observable adverse effect level	1.5×10^6 (ng/kg/day)	6×10^5 (ng/m^3)	3×10^4 (ng/kg/day)	1.3×10^4 (ng/kg/day)	9.7×10^6 (ng/kg/day)	3×10^2 (ng/m^3)	
Daily exposure at WCS (ng/day)[d]	42.3	34.6	587.5	622	363	162	1811
Daily exposure at HES (ng/day)[d]	32.8	21.6				137	191.4

[a] "http://www.inchem.org/documents/ehc/ehc/ehc009.htm" \l "SubSectionNumber:1.1.6" (6)

[b] Bifenthrin: Revised Human-Health Risk Assessment for a Section 3 Registration Request for Application of Bifenthrin and Establishment of Tolerances for Residues in/on Bushberries (Crop Subgroup 13B), Juneberry, Lingonberry, Salal, Aronia Berry, Lowbush Blueberry, Buffalo Currant, Chilean Guava, European Barberry, Highbush Cranberry, Honeysuckle, Jostaberry, Native Currant, Sea Buckthorn, and Leaf Petioles (Crop Subgroup 4B); U.S. Environmental Protection Agency, Office of Prevention, Pesticides, and Toxic Substances, Office of Pesticides Programs, U.S. Government Printing Office; Washington, DC, 2008

[c] EPA Registration Eligibility Document (RED) Metolachlor, EPA 738-R-95-006, April 1995 (7)

[d] Daily Exposure was estimated as follows: A person was present on the school campus for 24 hours and was breathing 12 liters of air per minute.