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A case study of air quality - Pesticides and odorous phytochemicals on Kauai, Hawaii, USA

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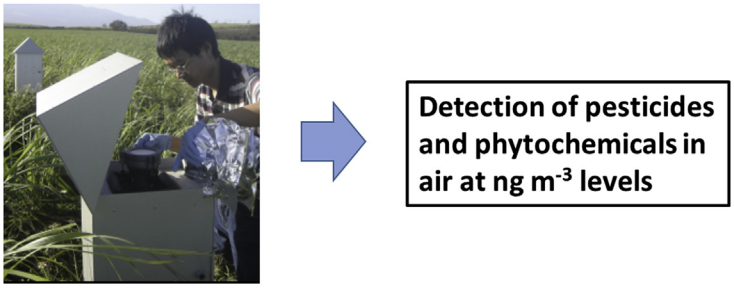
HIGHLIGHTS

- This study was prompted by incidences occurred at a school on Kauai, Hawaii.
- After the incidences, phytochemicals and pesticides were monitored for one year.
- Five pesticides and many phytochemicals were detected, most at ng m^{-3} ranges.
- Methyl isothiocyanate in outdoor air averaged 13.1 ng m^{-3} daytime.

GRAPHICAL ABSTRACT



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ABSTRACT

This study was conducted after a series of incidences occurred at Waimea Canyon Middle School on Kauai, Hawaii. Some students and staff members exhibited symptoms such as throat irritation, tearing, and dizziness. These symptoms could be associated with natural causes or human activities, which include exposures to pesticides and odorous phytochemicals. At the time of the occurrences, *Cleome gynandra* (known locally as stinkweed) was growing in the fields near the school and might be a potential cause of the reported symptoms. This work was designed to study pesticides and phytochemicals in ambient air around Waimea Canyon Middle School in comparison with other locations on Kauai. Among many chemicals, top 29 were selected for the analysis of stinkweed-emitted chemicals in a chamber study. One out of the 29 chemicals was methyl isothiocyanate (MITC) that is a highly foul-smelling, noxious chemical at high concentrations. Approximately half of the 29 chemicals produced by stinkweed and trace amounts of five pesticides were detected in indoor and outdoor air samples collected from the passive and high volume air samplers. The average concentrations of MITC in Waimea outdoor air during daytime and nighttime were 13.1 and 5.6 ng m^{-3}, respectively. The average concentrations of the five pesticides DDTs, HCHs, chlorpyrifos, bifenthrin, and metolachlor in Waimea outdoor air were respectively 2.5, 2.3, 35, 43, and 23 ng m^{-3}during daytime and 2.4, 1.7, 33, 29, and 19 ng m^{-3} during nighttime. The concentrations of the pesticide and phytochemicals found in air on Kauai were below health concern levels.

1. Introduction

Several incidents of chemical odors affecting students and teachers at Waimea Canyon Middle School on Kauai occurred

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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 possibly associated with exposure to volatile chemicals including pesticides and volatile phytochemicals from plants.

Cleome gynandra, locally called stinkweed, is an annual wildflower plant native to Africa but has become widespread in many tropical and sub-tropical parts of the world. Stinkweed was considered as an invasive weed in many places in the USA and elsewhere in the Pacific. Nutritional analysis has found it to be high in certain nutrients including amino acids, vitamins and minerals in the leaves. Stinkweed is used as a medical herb, an insecticide and a miticide in many regions in the world. For example, farmers use extracts of stinkweed leaves to eliminate mites from chicken plumage and to repel effectively all stages of the livestock ticks. The repellent and miticide properties are attributed to volatile oils emanating from the leaves (Samuel and Brian, 2007; Choi et al., 2004; Isman, 2000).

Target chemicals in ambient air on Kauai were sampled with passive air sampling (Cheng et al., 2004; Jaward et al., 2004a, 2005; Harner et al., 2006; Jaward et al., 2004b; Wang et al., 2007) and high volume air sampling (Chakraborty et al., 2010; Ji et al., 2015). For over a year, passive air sampling was used to identify the types of chemicals in ambient air around the school and at other locations on Kauai for comparison. High volume sampling was conducted at these locations to detect chemicals in the ambient air and to determine the quantity of those chemicals. The project workflow was shown in Fig. 1. The objectives of this study were to (1) design and perform experiments to determine volatile chemicals emitted from stinkweed, (2) design and perform experiments of passive air and high volume air sampling methods to trap pesticide residues and natural chemicals in ambient air, (3) 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 odorous incidents occurred in 2006 and 2008, (4) conduct qualitative analyses of chemicals in ambient air (chemical identification) and quantitative analyses of the identified chemicals, and (5) estimate exposure risk to the chemicals.

2. Experimental methods

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

Stinkweed stems, pods, leaves and flowers collected from Maui Island, Hawaii as a control site were cut into small pieces. An amount of 300 g of the cut stinkweed stems, pods, leaves and flowers was placed in a glass chamber having an inlet and outlet. A gentle flow of pure N_2 gas was flushed through the samples in the chamber for 5 h at a flow rate of 5 mL min^{-1}. Volatile chemicals emitted from stinkweed stems, pods, leaves and flowers were trapped in 150 mL of dichloromethane for analysis.

2.2. 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 N_2 gas purge time of 5 s at 1500 psi and 50 °C for three static cycles. Each tissue sample was extracted in triplicate. 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 N_2 after an aliquot of 200 μL of isooctane was added as trapping solvent.

2.3. High volume air sampling of volatile natural chemicals in ambient air within a stinkweed-infested field on Maui, Hawaii

A stinkweed-infested sugarcane field was selected for sampling in Maui. The studies in the field on Maui were 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. Two high volume air samplers were set up in the stinkweed-infested field. The samplers were at least 1 m horizontal and vertical distance from supporting structures, at least 20 m from trees, unobstructed air flow for 270°, accessible to sampling personnel during time of sampling, accessible to electrical power, secure from equipment loss or tampering, and permission of property owner (DPR, 2005; ARB, 2005).

High volume air samplers allow greater than 100 L of air flux per minute to pass through columned polyurethane foam (PUF) disks to collect contaminants in air. Air samples were collected in duplicate in 2, 4, 6, and 12-h 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 °C until extraction and analysis. Detailed sampling information such as frequency and duration is listed in Table S1.

The flow rate for air samplers was calibrated to be 10 ft^3 min^{-1} (10 $ft^3 = 3.048$ m^3) 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.

2.4. Method of passive air sampling on Kauai, Hawaii

Passive air samples were placed at schools at the west, south, east and north of Kauai (Fig. 2). 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, and (c) to learn 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

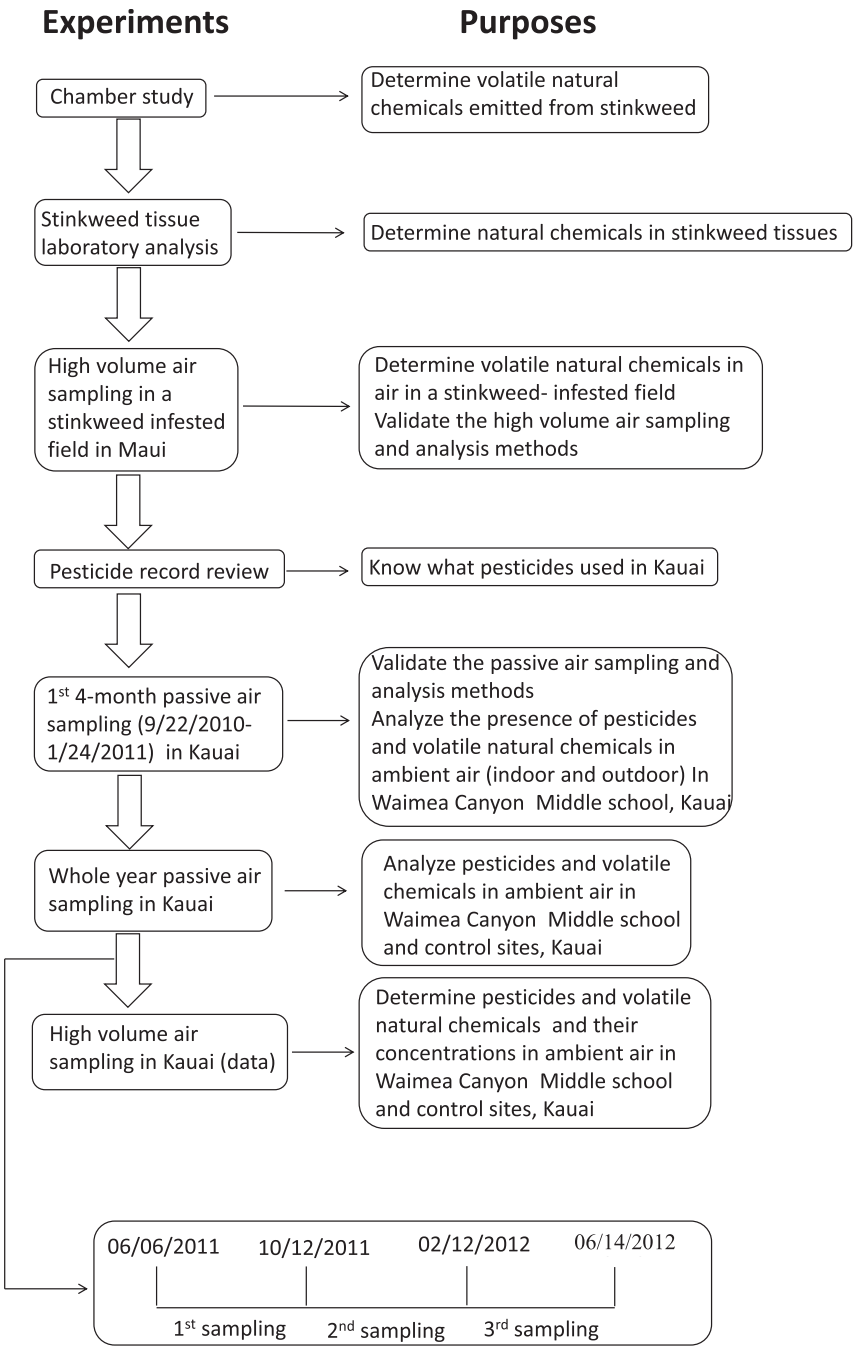

Fig. 1. Study workflow chart.

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, and two indoor samplers in rooms. Six 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 2 outdoor and 2 indoor samples from the Waimea Canyon Middle School, and 3 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

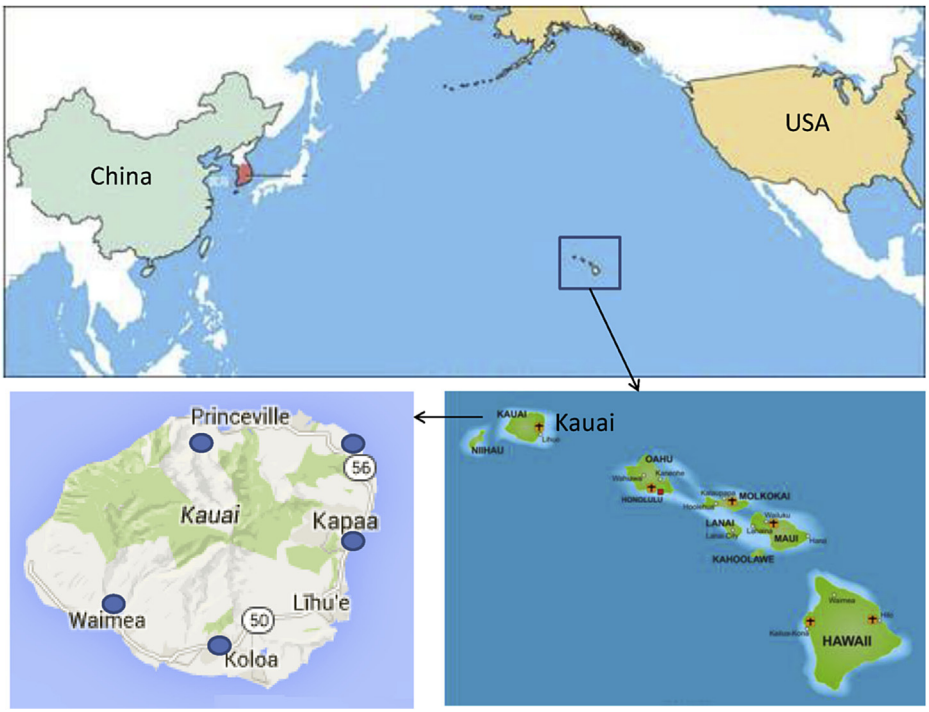

Fig. 2. Map of air sampling sites on Kauai, Hawaii.

foil pre-cleaned with acetone, placed in Ziploc® bags (18 × 20 cm), and then returned to the laboratory at the University of Hawaii at Manoa, where the filters were stored at −20 °C until extraction and analysis.

2.5. High volume air sampling of volatile natural chemicals and pesticides in ambient air within a stinkweed-infested field on Kauai, Hawaii

A PUF disk filter was used to collect chemicals in air phase and a glass filtering film was used to collect chemicals 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 (Wofford et al., 2009).

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 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 was believed that less commercial, agricultural, and residential chemicals were used there. All air sampler sites were situated considering US EPA criteria used in prior studies (DPR, 2005; ARB, 2005; Wofford et al., 2009) for high volume ambient air sampling.

2.6. High volume sampling frequency, flow rate, blank controls, and good field practices

Samples were collected at day (7 a.m.–7 p.m.) and night (7 p.m.–7 a.m.) intervals from February 10, 2012 to February 18, 2012. Air filters were replaced at 7:00 a.m. and 7:00 p.m. to coincide with day and night conditions. Twenty-eight samples were collected at Waimea (14 night and 14 day samples). Fourteen samples were collected at Hanalei (7 night and 7 day samples). At the end of the sampling period, the samples were retrieved, sealed, 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.

The flow rate for each air sampler was calibrated with 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. In the laboratory, all the apparatus were washed and then dried prior to use. Glass apparatus were baked at 450 °C for 4 h prior to use.

2.7. Air sample detection, extraction, clean-up and fractionation

Laboratory analyses were similar to those developed and employed by the California Department of Pesticide Regulation during their Parlier pesticide air monitoring project (2006). Specific analysis was determined according to the individual samples and pollutants detected.

For air sample analysis, PUF disks were fortified with 1.5 mL Na_4EDTA aqueous solution (0.5 g L^{-1}), 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 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 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 3 static cycles, a flush volume of 60% of the cell volume and an N_2 purge time of 5 s. 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 analyzed in the same manner as air samples (Campbell and Li, 2001).

The extracts were concentrated and exchanged into hexane (approximately 1 mL) for cleanup. The concentrated extracts were cleaned up on a silica/alumina 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 sulfate 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) (Wang et al., 2007, 2011).

2.8. GC/MS analysis of 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^{-1}. The oven temperature started at 80 °C for 2 min, and then increased to 300 °C at a rate of 5 °C min^{-1}. Splitless injection of 2 μL of sample was performed with a 5 min solvent delay time. The GC/MS ion trap and transfer line temperatures were 200 and 280 °C, respectively. The injector temperature was 280 °C (Wang et al., 2007). The individual compound was identified with retention time correlation to their standards and qualitative and quantitative ion (Tables S2 and S3) matches. Concentrations of each compound were calculated from external standards with confirmed with the MS.

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

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.

2.10. Data analysis

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

$$\text{Air concentration}\left(\text{ng m}^{-3}\right) = \frac{[\text{Extraction concentration}\ \left(\text{ng }\mu\text{L}^{-1}\right) \times \text{Solution volume}\ (\mu\text{L})]}{\text{Volume of air sampled}\ (\text{m}^3)}$$

3. Results

3.1. Volatile phytochemicals emitted from stinkweed

Table 1 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 (Table S2). The 29 volatile chemicals detected in stinkweed tissues and the chamber N_2 gas flux included 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^{-1} dry weight in different parts of stinkweed.

3.2. Evaluation of high volume air sampling method and analytical procedures

Studies were conducted in the field on Maui to determine volatile phytochemicals 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-h 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 1 shows the average concentrations of the phytochemicals detected in the first PUF disks of 12-h 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 recoveries of the surrogate standard for TcMX and PCB209 was 85 ± 5% and 90 ± 10%, respectively. The methods were satisfactory for the collection and analyses of volatile phytochemicals and pesticides for the Kauai study.

3.3. Volatile phytochemicals 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 phytochemicals. Those chemicals were the same as the ones detected in the extracts from various parts of stinkweed and from the chamber phytochemical emission study (Table 1). The results demonstrate that those 29 chemicals are emitted from stinkweed. Other plants may also emit these chemicals. Total concentrations of the 29 volatile chemicals were 30,929 and 9867 ng/m^3 in the ambient air during day and night, respectively (Table 1).

3.4. Volatile phytochemicals 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

Table 1
List of volatile organic chemicals extracted from different parts of stinkweed and ambient air collected during the 2009 Maui high volume air sampling.

Chemicals	Concentrations in different parts of stinkweed (mg g^{-1} dry weight)				Concentrations in ambient air (ng m^{-3})	
	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-Terpeneol	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	11,954	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	30,929.1	9866.7

season. Those passive air samples were analyzed for the 24 pesticides (Table S3). These 24 pesticides were selected for analyses based on the historical and recent sales records and reports (Table S3). Pesticide residues detected in indoor and outdoor passive air samples were bifenthrin, chlorpyrifos, metolachlor, α/γ-hexachlorobenzenes (HCHs), and p,p'- dichlorodiphenyltrichloroethane (DDT)/p,p'-dichlorodiphenyldichloroethylene (DDE)/p,p'-dichlorodiphenyldichloroethane (DDD) (Sum of DDT, DDE and DDD is referred to as DDTs).

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.

3.5. Passive air sampling period between September 22, 2010 and January 24, 2011

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 for the analyses of volatile natural chemicals and pesticides (Tables S4 and S5).

3.6. Passive air sampling period between June 6, 2011 and October 12, 2011

A total of 7 passive air samples was 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 S6). 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, HCHs and DDTs (Table S7). HCHs and DDTs were also detected at the Hanalei Elementary School and Kalaheo Elementary School control sampling sites.

3.7. Passive air sampling period between October 12, 2011 and February 12, 2012

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 and two indoor samples in room 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 out of the 29 volatile phytochemicals were detected in the two indoor and five outdoor passive air samples (Table S8). 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, HCHs and DDTs (Table S9). HCHs and DDTs were also detected in the control sampling sites from Hanalei Elementary School and Kalaheo Elementary School on Kauai.

3.8. Passive air sampling period between February 12, 2012 and June 14, 2012

A total of 9 passive air samples were collected for this sampling period. Two outdoor samples on the roof of buildings and 2 indoor samples 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 10S). 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, HCHs and DDTs (Table 11S). HCHs and DDTs were also detected in the control sampling sites from Hanalei Elementary School, Kalaheo Elementary School and Kanuikapono Learning Center on Kauai.

3.9. Volatile phytochemicals and pesticides in ambient air samples collected by high volume air sampling on Kauai

Tables 2 and 3 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. MITC was found in the 42 high volume air samples, as well as the 27 passive air samples conducted on Kauai. Being a 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 1). The average concentrations of MITC in Waimea air during daytime and nighttime were 13.1 and 5.6 ng m^{-3}, respectively (Table 2). The average concentrations of MITC in Hanalei air during daytime and nighttime were 9.6 and 6.2 ng m^{-3}, respectively (Table 2). In addition to stinkweed, other plants may produce MITC. MITC is also a degradation product of the pesticide metam-sodium 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 record keeping and no sales of metam sodium were recorded on Kauai for 2012. Because we found MITC in stinkweed plant tissues, 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, HCHs, and DDTs were detected in the 14 high volume air samples collected from Waimea. The concentrations of DDTs, HCHs, 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, HCHs, chlorpyrifos, bifenthrin, and metolachlor in Waimea air during nighttime were 2.4, 1.7, 33, 29, and 19 ng m^{-3}, respectively. HCHs and DDTs were detected in the 14 high volume air samples from Hanalei, Kauai. The concentrations of DDTs and HCHs in Hanalei air during daytime were 2.0 and 1.1 ng m^{-3}, respectively. The concentrations of DDTs and HCHs 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

Table 2
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 3
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	500×10^3 [d]	2.5 ± 0.5	2.4 ± 0.7	2.0 ± 0.4	1.8 ± 0.3
Malathion	0.9	–	–	–	–	–
HCHs	0.6	45×10^3 [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	36×10^6 [h]	23 ± 3	19 ± 2	–	–

"-" indicates "not detected".
[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 kg or about 88 pounds was used for calculating exposure in terms of milligrams per kilogram, and the 11,000 L 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.
[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.

air samples. Residues of HCHs, chlorpyrifos, metolachlor, bifenthrin and DDTs detected in the high volume air samples from Waimea were also detected in the passive air samples from Waimea. HCHs 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 an idea of potential exposure and risk for the concentrations of the chemicals detected in ambient air on Kauai. Table 4 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" (WHO, 1979; FAO and WHO, 1969; EPA, 1995). 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.

4. Discussion

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. The symptoms could be associated with exposure to toxicants in the air. This investigation was conducted in response to the incidences and community concerns regarding potential exposure to pesticides and toxic odorous chemicals emitted from *Cleome gynandra* (known locally as stinkweed).

In a contained and controlled atmosphere (chamber), volatile chemicals from the plants were collected and analyzed. Because the stinkweed near the school was plowed under and managed after the incidents, we looked for another location infested with the plant. 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 top 29 chemicals emitted by stinkweed. Along with the laboratory chamber and plant tissue studies, this ambient air study correlated the stinkweed plant with the phytochemicals.

Passive air sampling was conducted over a year to identify chemicals in ambient air around the school and at other locations on Kauai for comparison. High volume sampling was conducted at

Table 4
Estimated exposure to the pesticides and MITC in ambient air at Waimea Canyon Middle School (WCS) and Hanalei Elementary School (HES).

	DDTs[a]	HCHs	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})	–	–	850	–	15,000	3000	
No observable adverse effect level	1.5×10^6 (ng kg^{-1} day^{-1})	6×10^5 (ng m^{-3})	3×10^4 (ng kg^{-1} day^{-1})	1.3×10^4 (ng kg^{-1} day^{-1})	9.7×10^6 (ng kg^{-1} day^{-1})	3×10^2 (ng m^{-3})	
Daily exposure at WCS (ng day^{-1})[d]	42.3	34.6	587.5	622	363	162	1811
Daily exposure at HES (ng day^{-1})[d]	32.8	21.6				137	191.4

[a] http://www.inchem.org/documents/ehc/ehc/ehc009.htm#lSubSectionNumber:1.1.6
[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.
[d] Daily Exposure was estimated as follows: A person was present on the school campus for 24 h and was breathing 12 L of air per minute.

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, DDTs and HCHs, were widely used historically for mosquito and other insect control and are no longer in use in Hawaii. They have no odor at low concentrations. Because these pesticides do not break down quickly, they can still be detected throughout the islands, and in fact, throughout the world (Zhang et al., 2011). 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.

Harmful effects are dependent upon both the toxicity of the chemical and the amount of exposure to the chemical (Wofford et al., 2009). The State of California 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, metolachlor, 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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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.chemosphere.2017.09.045.

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