UNIFORMED SERVICES UNIVERSITY, SCHOOL OF MEDICINE GRADUATE PROGRAMS
Graduate Education Office (A 1045), 4301 Jones Bridge Road, Bethesda, MD 20814

DISSERTATION APPROVAL FOR THE MASTER IN SCIENCE IN PUBLIC HEALTH DISSERTATION IN THE PREVENTIVE MEDICINE AND BIOMETRICS GRADUATE PROGRAM

Title of Dissertation: "Use of a Box Model to Estimate the Airborne Concentration of Volatilized DDT in an Experimental Hut in a Tropical Climate"

Name of Candidate: LCDR Carlis Brown
Master of Science in Public Health Degree
June 11, 2012

DISSERTATION AND ABSTRACT APPROVED:

DATE: 19 June 2012

LCDR Michael E. Stevens, Jr
DEPARTMENT OF PREVENTIVE MEDICINE AND BIOMETRICS
Committee Chairperson/Advisor

Dr. Philip A. Smith
DEPARTMENT OF PREVENTIVE MEDICINE AND BIOMETRICS
Committee Member

CDR Gerald T. DeLong
DEPARTMENT OF NAVY INSPECTOR GENERAL
Committee Member

UNIFORMED SERVICES UNIVERSITY, SCHOOL OF MEDICINE GRADUATE PROGRAMS
Graduate Education Office (A 1045), 4301 Jones Bridge Road, Bethesda, MD 20814

FINAL EXAMINATION/PRIVATE DEFENSE FOR THE DEGREE OF MASTER OF SCIENCE IN PUBLIC HEALTH
IN THE PREVENTIVE MEDICINE AND BIOMETRICS GRADUATE PROGRAM

Name of Student: LCDR Carlis Brown

Date of Examination: June 11, 2012

Time: 1500

Place: 3176-I

DECISION OF EXAMINATION COMMITTEE MEMBERS:

	PASS	FAIL
LCDR Michael E. Stevens, Jr DEPARTMENT OF PREVENTIVE MEDICINE AND BIOMETRICS Committee Chairperson/Advisor	✓	
Dr. Philip A. Smith DEPARTMENT OF PREVENTIVE MEDICINE AND BIOMETRICS Committee Member	✓	
CDR Gerald T. DeJong DEPARTMENT OF NAVY INSPECTOR GENERAL Committee Member	✓	

The author hereby certifies that the use of any copyrighted material in the thesis manuscript entitled:

A box model can be used to estimate DDT concentrations in an experimental hut.

is appropriately acknowledged and, beyond brief excerpts, is with the permission of the copyright owner.

Carlis Brown
Preventive Medicine & Biometrics
Uniformed Services University
10 Apr 12

ABSTRACT

Title of Thesis: "USE OF A BOX MODEL TO ESTIMATE THE AIRBORNE CONCENTRATION OF VOLATILIZED DDT IN AN EXPERIMENTAL HUT IN A TROPICAL CLIMATE"

Author: LCDR Carlis W. Brown
Masters of Science in Public Health, 2012
Uniformed Services University of the Health Sciences

Thesis Advisor: LCDR Michael Stevens
Assistant Professor
Department of Preventive Medicine and Biometrics

Airborne emission rates for DDT from cloth material generated in a laboratory setting using a thermal micro-chamber over a range of temperatures were integrated into a well mixed box (WMB) model to predict volatilized DDT concentrations emitting from netting material hung inside an experimental hut in Thailand. Field sampling was conducted in order to evaluate agreement between observed samples and model predictions for volatilized DDT inside the hut. Results show the model fit was consistent with empirically derived airborne emission data and theoretical within one order of magnitude. However, field results were not consistent with empirical or theoretical results according to ASTM D5157-97, NMSE= 4.17, and a fractional bias (FS) of 1.45 data when accounting only for volatilized DDT concentration levels. A correlation was observed between data from Weschler *et al*. and the WMB model results when accounting for DDT in both the vapor phase and particulate phase. The WMB model has utility as a tool to estimate occupational exposures with a protective range of one order of magnitude.

TITLE PAGE

USE OF A BOX MODEL TO ESTIMATE THE AIRBORNE CONCENTRATION OF VOLATILIZED DDT IN AN EXPERIMENTAL HUT IN A TROPICAL CLIMATE

by

LCDR Carlis W. Brown

Industrial Hygiene Officer

United States Navy

A thesis submitted to the Faculty of the Department of Preventive Medicine and Biometrics Graduate Program of the Uniformed Services University of the Health Sciences in partial fulfillment of the requirements for the degree

of

MASTERS OF SCIENCE IN PUBLIC HEALTH, 2012

DEDICATION

I dedicate this master's thesis to my wife, Michelle, I could not have completed this work without your support and understanding. Thank you for the sacrifices you have endured throughout my Navy career. To my daughter, Taylor and son, Jackson, for the joy you bring to me each and every day.

-Carlis

ACKNOWLEDGEMENT

I would like to thank Michael Sheely from the Edgewood Chemical Biological Center (ECBC), for the support he provided that was necessary to complete this study.

I would also like to thank the following members of my committee for their patience, faith and confidence in my abilities: Dr. Philip A. Smith, U. S. Department of Labor – OSHA, Health Response Team, CDR Gerald T. Delong, U. S. Naval Inspector General, LCDR Michael E. Stevens, (Chairperson) Assistant Professor, Department of Preventive Medicine and Biometrics.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF EQUATIONS

1. Introduction

1.1 Background

The use of indoor residual spraying (IRS) of pesticides such as dichlorodiphenyltrichloroethane (DDT) in regions of the world with high endemicity for malaria and other vector-borne diseases has proven to be effective in combating morbidity and mortality.[1] During a 40 year span from 1930 to 1970, worldwide malaria deaths dropped from 3,573,000 to 578,800, resultant largely from IRS application of DDT.[2] While proven as an effective repellent, the airborne concentrations produced from IRS have not been well characterized to date, leaving open the question of potential human health concerns for those living within the treated dwellings. While ingestion is the primary exposure pathway for DDT,[2] a secondary exposure pathway for DDT is inhalation.

Exposure to DDT found indoors can occur through skin contact, ingestion or inhalation. Investigations of potential inhalational exposure to IRS-applied spatial repellents have included research by Singh *et al.* In their research, they reported airborne DDT concentrations of 1.0 to 14.6 μg m^{-3} over an eight month period in residential and rural settings which had been treated.[3] Van Dyk *et al*. also studied residual DDT concentrations, with their focus on dwellings located in two villages in South Africa in which IRS had been conducted. The results of the study indicated that the mean indoor air concentration for the exposed group was 3900 ng m^{-3}, while 10 ng m^{-3} for the unexposed group.[4,5] Although no published literature specifically comparing

indoor air concentrations of DDT with serum levels is available, a correlation between elevated serum levels of DDT and residents who use DDT for IRS has been reported.[4,6]

In order to effectively answer the question "is the control measure effective at repelling mosquitoes and will its prescribed use be harmful to humans?", ideally the concentration of the spatial repellent in the indoor air would first be adequately characterized over a range of temperatures while also observing vector behavior. Previous research by Greico *et al*. used treated netting with 0.2 mg cm^{-2} of DDT to observe the repellency effects of DDT. The study showed DDT to be an effective mosquito repellent based on the behavior of the mosquitoes but did not characterize the volatilized concentrations of DDT in the indoor air when repellency was observed.[7] However, no exposure assessment has been conducted to date which characterizes indoor concentrations resulting from the use of DDT treated fabric.

1.2 Public Health Problem

Given its usefulness in combating vector-borne diseases, the use of repellents like DDT continues to play an important public health role in countries with elevated malarial or Dengue Fever risk. Due to the environmental burden and potential toxicity world leaders have restricted the use of DDT. Thus, the ability to determine an effective application amount would have a positive impact on the environment and human health. Judicious application of DDT, in which just enough is applied to repel mosquitoes while also avoiding unnecessarily high airborne concentrations which could be considered harmful to human health, is important. In austere conditions, where

sampling and subsequent analysis may not always be feasible, the use of a simple but effective model could provide a significant benefit in approximating the airborne concentrations of various dwellings and thus could provide a capability for determining the proper application amount needed for spatial repellency and protection of human health.

1.3 Research Objective

To better understand the exposure profile of volatilized DDT in air, measurements or estimates of air concentrations are necessary. However, sampling for DDT in air can be challenging and time consuming. Currently, the standard method used to sample for DDT in ambient air requires 4- to 24-hour sampling periods.[8] As an alternative to this considerable resource-consuming approach, the use of a simple model to characterize DDT concentrations in indoor air could provide valuable information in areas and dwellings in which DDT is applied and air sampling is neither feasible nor acceptable. In these cases, modeling data could be used to approximate indoor DDT concentrations, thus allowing public health officials to proceed with exposure assessments in a timelier manner and in a much more cost effective way. My research attempts to answer the following question: Can a simple box model predict volatilized DDT concentrations in indoor environments in tropical regions where DDT is used? This research will evaluate the Well Mixed Box (WMB) model's ability to predict volatilized DDT concentrations in indoor environments in tropical regions where DDT, or any other spatial repellent, is used.

To accomplish this objective, the four aims of this study were to 1) determine the air change rate (ACR) and environmental conditions inside of an experimental hut located in a tropical region, 2) determine the volatilization rate of DDT from cloth at different temperatures in a laboratory setting, 3) predict the concentration of volatilized DDT in an experimental hut using the WMB model, and 4) statistically evaluate the model's predictions based upon the level of agreement between predicted and observed concentrations of volatilized DDT in air.

2. Literature Review

2.1 DDT repellency, irritancy and mortality

Previous research efforts have indicated that a majority of exposures to DDT occur from ingestion or skin contact. [9,10] However, the widespread incorporation of indoor residual spraying (IRS) for many communities in third world countries has led to concern regarding potential human health risk from inhalational exposure to airborne DDT concentrations over relatively long periods of time. Given the physical and chemical characteristics of DDT, months of potential exposure to unknown airborne concentrations of residual DDT is likely within small dwellings typical of third world countries. Few data sets exist regarding airborne residual concentrations of DDT,[3,4,11] and thus little is known about the residual airborne concentrations of volatilized DDT over time within the hut dwellings or other residences which have been treated.

Empirical and mosquito behavioral data indicate that IRS and long-lasting insecticidal netting (LLIN) have been an effective tandem in vector control.[12,13] Many malaria endemic countries prefer DDT to control the vector-borne disease,[14] largely due to its long residual life (half live ≥ 700 days in soil).[15] Research focused on the efficacy of DDT coated netting has been previously conducted.[16,17] Grieco *et al*. investigated the response of mosquitoes exposed to DDT- treated netting after applying a range of different mass amounts of DDT. The objective of this study was to investigate the spatial repellency (SR) of DDT inside an experimental hut in Thailand, aimed at reducing indoor densities of vectors and reducing the transmission of vector-borne diseases.

Netting treated with DDT was placed/hung near the four walls of an experimental hut. Human volunteers then sat inside the experimental huts for one hour per observation period to attract the mosquitoes. Next, tagged mosquitoes were introduced into the hut via screen accesses at hut windows. The human volunteers documented their observations of mosquito behavior, specifically, the repellency effectiveness of the DDT on the mosquitoes. Mosquito release experiments occurred every three hours from dawn until dusk. There were a couple important findings from this study. First, as DDT mass loading per unit volume of netting increased (0.75 μg cm^{-2} to 750 μg cm^{-2}), the repellency, irritancy and mortality among mosquito populations in the hut also increased. Repelled mosquitoes did not directly come into contact with DDT treated cloth, suggesting volatilized concentrations of DDT exhibit strong repellency effects. However, DDT concentrations in air were not measured. Therefore, an exposure-response relationship for the repellency effects of DDT could not be correlated to known applied amounts of DDT on netting or volatilized airborne concentrations of DDT.

2.2 Evaluation of DDT Indoors

Singh *et al*. investigated indoor air concentrations inside a room following IRS using DDT over an 8-month period.[3] The room used in this particular study was prefabricated to represent accommodations similar to those found at a local village in India. To investigate DDT inside the experimental room, sampling and analysis of DDT in the particulate and gas phases using glass micro fiber filters and impingers. Air samples were collected inside the room for 240 days following initial IRS application with DDT at

2.0 g m^{-3}. During the sampling period the total DDT concentration range was 1.0-14.6 µg m^{-3} , with an average temperature, 27.6 °C, SD=6.03; and average relative humidity 57.09%, SD=19.3. Singh observed similar air concentrations for DDT in the vapor phase and particulate phase up to day 64. After day 64, however, airborne concentrations of DDT were only detected in the vapor phase. Additionally after day 64, vapor phase concentrations increased to levels observed during the initial sampling days. No explanation was posited regarding the increase of DDT concentrations observed in the vapor phase after 64 days. The number of samples collected at each time point, as well as over the course of the study, was not reported, preventing independent analysis.

Van Dyk *et al*. also investigated DDT residual airborne DDT concentrations two months after IRS at villages in South Africa to examine all potential exposure pathways, to include inhalation.[4] This study measured indoor air for DDT immediately following IRS to 84 days post-IRS application. The collection technique employed a high volume air sampling procedure which used high density polyurethane foam discs (PUF). The PUF collection media consist of a filter to collect particulate matter and an adsorption media to collect vapors. Samples were collected for 30 minutes at a flow rate of 350-400 liters per minute. Indoor air sample results (n=12, mean 2.2 µg m^{-3}) taken two months after IRS corresponded to levels reported by Singh *et al*. (1.8 ug m^{-3}). However, there was no time course data available to investigate the residual airborne concentration variability of DDT, if any, over time. The collection of air samples using the PUF method is non-specific; therefore, no information can be ascertained regarding the distribution of samples in the particulate and vapor phases.

The collection and analysis techniques described by Singh and Van Dyk were comparable to EPA Method TO-10A.

2.3 Current Analytical Methods for DDT

Traditionally, characterization of volatilized chemical contaminants indoors is accomplished by collecting and analyzing a sample of air from the area of interest. Standard analytical methods such as EPA Method TO-10A are typically used because they provide reliable methods that have been researched and tested. The determination of an analyte in air begins with sample collection. Sampling for DDT using EPA Method TO-10A requires a sample pump with polyurethane foam (PUF) sampling media; other collection media and materials such as particle filters, Tenax®TA sample tubes and impactors may also be used in conjunction with PUF.[8] The sample pump and collection media make up the 'sample train' and must be calibrated within acceptable tolerances prior to and following each use to correctly calculate air concentrations and to ensure collection efficiency and accuracy. The sample process can take from 4-24 hours. Following collection, samples are prepared for analysis via solvent extraction. This requires the addition of chemical reagents to extract the analyte from the media. Once the sample is prepared for analysis it is introduced into a gas chromatography (GC) unit for separation and subsequent analysis by a detector. This analysis process requires robust laboratory capabilities in order to analyze samples and can add hours or even days to the total time needed to determine the amount of DDT in air. The details of the method have been simplified but reveal the complexity, solvent requirements, time

consumption, financial cost and logistics of analyzing tens to hundreds of air samples over a study time course.

Additionally, TO-10A is a general sampling method used for 57 different pesticides, including DDT and Poly Chlorinated Biphenyls (PCBs). Due to the lack of specificity with this method and the fact that no analytical methods have been developed for short-term interval sampling (less than 1 hr) of DDT at the time of the present study, alternative methods such as the use of simple models should be considered in order to characterize exposures.

2.4 Mathematical Models to Evaluate Indoor Air

Mathematical models can be utilized when sample data is unavailable or when field sampling is not practical or prohibitive. Models commonly used to estimate airborne contaminants can be related to a mass transport system. [18] These types of models follow the law of conservation of mass, which states that mass is neither created nor destroyed.[19] This implies that for any chemical process in a closed system, the mass of the reactants must equal the mass of the products. A mass balance equation can be used to explain the concentration of a chemical contaminant in a space (equation 1).

Equation 1. Mass balance equation.

$$Mass_{gen} + Mass_{in} = Mass_{accum} + Mass_{out}$$

This system can be expressed mathematically: Mass $_{gen}$ refers to mass generated by the source; Mass $_{in}$ refers to the mass of the contaminant brought in by airflow; Mass $_{accum}$ refers to the mass of contaminant generated by the source and brought in from the

outside air; Mass $_{out}$ refers to the mass of contaminant being transferred out of room from airflow (figure 1).

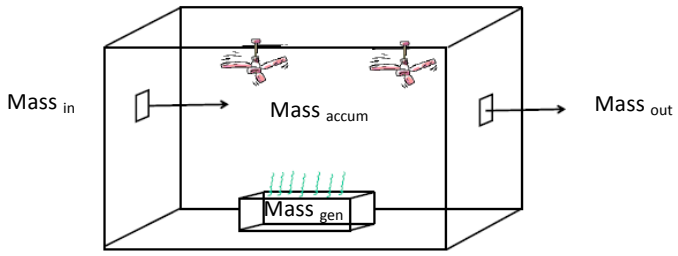

Figure 1. A simple mass balance system for a contaminant emitting from a source to the surrounding air.[20]

These simple mass balance systems are commonly referred to as Well Mixed Box (WMB) models.[20] The WMB model has been utilized to estimate and/or predict airborne chemical concentrations in enclosed spaces in various scenarios, to include estimating personal exposure to chemicals for indoor environments, as well as predicting airborne chemical concentrations resulting from indoor releases of specific hazardous materials of varying spill volumes.[21-23] The simplicity of the typical WMB model is an appealing aspect, as there are few input parameters and an advanced skill level is not necessarily needed to run and interpret the model. There are elevated levels of complexities when using these models, if so desired; such models may be needed to provide added information when attempting to solve a specific problem. However, while the more complex models are more sensitive, they also require greater skill to use and more parameters to input. Experts recommend starting with a simple model before proceeding to a more sophisticated model to answer questions. [24-26]

A common mass balance model used to evaluate material emission indoors is an emission model. Emission models are a type of WMB model that relies on chemical emission data to estimate contaminant concentrations in indoor air. Data on contaminant emissions may be available in literature, estimated, or may be provided in searchable databases.[27] When using models that rely on emission data, emission testing systems are also used if theoretical data is unavailable for direct use or estimation. The emission testing systems can generate chemical emission data in a laboratory setting, which in turn can be applied to various scenario-based emission models for predictions of airborne contaminant concentrations indoors. Typical systems range in size from large scale (50 m^3), down to micro-scale (45 ml) and constructed of stainless steel or silanized glass to minimize the impact on contaminant emission results.[28]

Tichenor *et al*. investigated contaminant emissions of paradichlorobenzene (moth repellent crystal cakes) using two small emission chambers (0.166 m^3), constructed of stainless steel in a laboratory setting.[29] Environmental parameters such as temperature, humidity and air exchange rate (the number of times inside air was replaced with outside air) were monitored inside a test house in order to establish testing conditions for the emission chambers. An emission factor was estimated by observing the moth crystal cake weight loss over time, and then compared to the measured emission factor. There was only a three percent difference between the estimated and observed emission factors. These results suggested that a small chamber could effectively estimate contaminant emission rates.

The second phase of the study involved the use of a mass transfer model in order to estimate paradichlorobenzene concentrations inside the test house. The four rooms that were tested were individually classified as single zones in order to compare observed versus predicted concentrations. The simplified calculations were synonymous with the simple WMB model, which only requires two input variables in order to estimate chemical concentrations: the emission rate, G (also referred to as generation rate), and the flow rate, Q (the rate at which air flows into a space). [20] The agreement between the observed and predicted results was determined in the third and last phase. The last phase reported by Tichenor *et al*. was the validation phase. During this phase, predicted concentrations of paradichlorobenzene were compared to observed concentrations of paradichlorobenzene measured inside the test house. The results for the four rooms indicated no significant difference between the predicted and observed concentrations, with the greatest difference being 0.6 μg m^{-3}. This dynamic process suggested that data generated in the laboratory could be inputted into a simple box model and effectively used to estimate/predict within acceptable tolerances the contaminant concentrations measured in the field.

2.5 Emission Testing Systems

Emission testing has evolved into smaller operating systems for practical reasons.[30] Material emission testing using small chambers can reduce testing time but can still last weeks or even months for low volatilizing materials.[31,32] The demand for faster indoor material emission testing led to the development of micro-scale emission testing

systems. [28,33] Micro-scale emission testing systems can be more than three orders of magnitude smaller than those emission systems classified as small chambers.[30]

- Large Scale - (10 – 100 m^3)
- Small Scale - (0.01 – 1 m^3)
- Micro-Scale - (10^{-5} – 10^{-3} m^3)

Schripp *et al*. conducted a qualitative and quantitative comparative analysis of a small glass chamber (1 m^3) and micro sized stainless steel chamber (4.5 x 10^{-5} m^3) using plastic granules containing both volatile organic chemicals (VOCs) and semi-volatile organic chemicals (SVOCs).[34] Additional variables studied in the comparative analysis included the use of different experimental conditions, such as temperature, air exchange rate and the conditioning period (interval between putting the sample in the micro-chamber and start of vapor sampling). Results of the Schripp study indicated that the micro-chamber approach captured higher amounts of low volatilizing compounds and subsequently better sensitivity, relative to results from small chamber use.

Furthermore, this same study found that micro-chamber equilibration times were less than 8 hours for semi-volatiles, while nearly 24 hours for the small chamber. The results suggested that a key factor in the much shorter equilibration times was the difference in the volume of the two test chambers. The micro-chamber's volume allowed for a much reduced headspace comparatively with the small chamber volume, thus reducing the time required to reach equilibrium.

Schripp *et al*. also had issues comparing the air change rate (ACR) between the two different chambers due to the smaller size of the micro-chamber. When utilizing the

micro-chamber method, the loading factor (the total area of contaminant divided by the volume of the chamber) and ACR used by the small chamber could not be duplicated in the micro-chamber. Therefore, data from the micro-chamber had to be normalized in order to compare with the small chamber. Normalization was performed by using the specific emission rate (SER). The SER was calculated by multiplying the equilibrium concentration measured inside the chamber by the ratio of air change rate and loading factor. To limit deviations in quantitative results, emission rates had to be calculated during equilibrium conditions. The temperature, air exchange rate and the conditioning period were noted as key parameters that affect the SER.

2.6 Physical Chemical Properties for DDT

Pure DDT is a white, crystalline powder consisting of a chemical formula of $C_{14}H_9Cl_5$ and a molecular weight of 354.09 grams per mole (figure 2).[35]

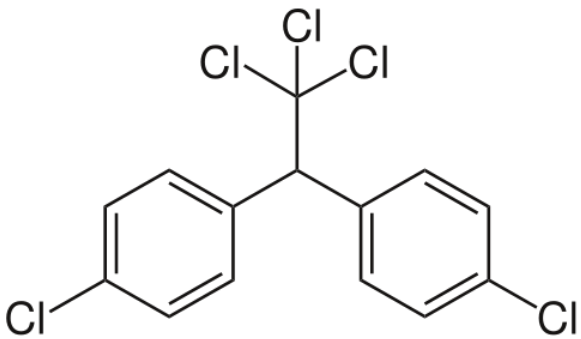

Figure 2. p,p´-DDT

Vapor pressures for DDT range from 5.003 x 10^{-7} Pa at 0° C to 3.846 x 10^{-4} Pa at 40° C (table 1).[36] Vapor pressure is an important parameter for predicting the

propensity to partition into air.[15] Furthermore, vapor pressure has been reported as a driving force for the evaporation rate of pesticides.[37] Based on calculations using the equilibrium concentration, DDT emission is expected to rise exponentially as temperature increases (table 1).

Table 1. Vapor pressure measurements of p,p´ DDT with estimated saturation concentration for temperatures shown using the ideal gas law, Wania *et al*.[36]

Temperature (C˚)	Pressure (Pa)	Estimated Concentration (μg/m^3)
0	5.00×10^{-7}	0.102
10	2.53×10^{-6}	0.501
20	1.71×10^{-5}	3.27
30	8.18×10^{-5}	15.1
40	3.84×10^{-4}	68.79

In order to evaluate the application of DDT indoors, an understanding of the emitting source and the relationship between that source and its surrounding environment must be understood. The literature presented here has shown how other researchers have investigated DDT and other chemicals found in indoor environments. This research attempts to characterize the emission of volatilized DDT inside an experimental hut by investigating the emission of DDT in a laboratory chamber, measuring the air turnover inside the hut, then applying a simple box model to approximate the volatilized concentration of DDT in the air of an experimental hut.

3. Materials and Experimental Methods

3.1 Material Preparation

Material preparation described in this subsection pertains to laboratory work. Material preparation in the field was also performed in a similar manner, but by a different research team. Both methods were consistent with previous studies of Greico *et al*.[7] The only differences between the material preparations in the field versus the laboratory were the type of solvent used to create the stock solution of DDT and the loading factor (*L*) (ratio of the area of treated netting per volume of space).

The stock solution prepared in the field was DDT (98% pure; Sigma Aldrich, St. Louis, MO) dissolved in acetone (100% pure; Burdick and Jackson, Muskegon, MI). In the laboratory 18 mg mL^{-1} concentration stock solution was prepared by dissolving 90 mg of DDT (98% pure; Sigma Aldrich, St. Louis, MO) into 5 ml amount of iso-octane (100% pure; Burdick and Jackson, Muskegon, MI) in a 40 ml amber vial. Both solvents are recognized by EPA method 8000 series as appropriate to dissolve DDT.

In the field, the area of treated netting totaled 19.77 m^2 and was hung inside an experimental hut of 50 m^3 total volume. Using equation 5, the loading factor (*L*) was 0.3954 $m^2 m^{-3}$. In the laboratory, a Markes M-CTE /Thermal Extractor system (µ-CTE TM; Markes International Limited, Llantrisant, UK) was used as a stand-alone unit comprised of six small cylindrical chambers (stainless steel cups), with each cup consisting of an internal volume of approximately 45 ml capable of heating from ambient to 250 °C (figure 4). The size of each individual chamber in the µ-CTE TM

limited the surface area of the polyester netting placed inside each chamber. In order to match loading factor (*L*) in the laboratory to the loading factor (*L*) in the field the area of the netting would have been reduced to 0.0000178 m^2. This would be a size too small to ensure the correct mass of DDT (0.2 mg cm^{-2}) would be loaded onto the polyester netting. An area that maximized the volume of space available inside the chamber was selected, which resulted in a loading factor (*L*) of 100 m^2 m^{-3}. Thus, the laboratory loading factor (*L*) was roughly two and one-half orders of magnitude greater than the loading factor (*L*) in the field. Model results were normalized by using the field loading factor (*L*) in place of the laboratory loading factor (*L*) to determine the generation rate.

A 45 cm^2 piece of white polyester netting (3 cm x 15 cm), 0.023 cm thickness, mesh size approximately 24 x 20/inch (100% pure; BioQuip Products, Inc., Rancho Dominguez, CA) was placed inside a (4 cm x 16 cm x 2 cm) aluminum foil boat (Reynolds Wrap®; Reynolds; Richmond, VA) where 500 µl of stock solution was applied using a manual pipette (200–1000 µl, Pipetman; Gilson Inc., Middleton, WI). Pipette accuracy was verified by pipetting 500 µl (9 mg of DDT) into a 1 ml volumetric flask then weighing on a gram scale (Sartorius, BP61S; Data Weighing Systems, Elk Grove, IL 6007). The mean weight was 507.67 µl with a standard deviation of 3.21 µl (n=3). The loading ratio of DDT to cloth netting was 0.2 mg cm^{-2}. After the stock solution was loaded, the iso-octane was allowed to volatilize off the cloth. Cloth drying took approximately five minutes and was determined dry through observation. Once the cloth appeared dry and white crystalline powder (DDT) had adhered to the entire surface area of the

polyester netting, it was assumed to be dry. Treated material was then placed inside each chamber within ten minutes of preparation. The loading and drying was performed in a chemical fume hood.

3.2 Experimental Methods

3.2.1 Air Change Rate

Calculation of the experimental hut's ACR was performed to establish a set point for a μ-CTE experiment and for the calculation of the predicted concentration of volatilized DDT in ambient air inside the experimental hut. A tracer gas technique using carbon dioxide (CO_2) was used in the field in order to determine the ACR inside the experimental hut. This technique was consistent with an internationally recognized laboratory method ASTM E741-00R06. The concentration of CO_2 in ambient air was measured using a portable gas detector equipped with a Nondispersive Infrared (NDIR) CO_2 sensor (MultiRae IR; Rae Systems San Jose, CA) (figure 3). Carbon dioxide levels inside the hut were artificially elevated then allowed to decrease to background CO_2 levels. Background CO_2 levels were measured prior to starting the tracer gas experiment.

Figure 3. MultiRae IR portable gas detector.

A four point lab calibration was performed with the MultiRae IR detector at 500 ppm, 1000 ppm, 2500 ppm, 5000 ppm to evaluate equipment accuracy using sample bags filled with nitrogen (Zero grade; Air Gas, Bethesda, MD) and CO_2 (99.5% pure; Air Gas, Bethesda, MD). Mean values for the trials (n=3) were within 10% of the known concentration and were consistent with acceptable parameters established by RaeSystems (table 2).[38]

Table 2. Four point laboratory standard curve results. Mean values for trials (n=3) were within acceptable error limits per manufacturer specifications.[38]

	Concentration (ppm)			
	5000	**2500**	**1000**	**500**
Trial 1	4800	2910	1280	530
Trial 2	4670	2470	980	530
Trial 3	4730	2520	970	540
Mean	4733	2633	1076	533
(%) difference from Mean	6	5	7	6

Per manufacturer's specification, a two-point field calibration was performed at 0 ppm and 5000 ppm using sample bags with ultra high purity nitrogen (99.995% pure; Lab Solution and Engineering Co, Ltd., Bangkok, Thailand) and CO_2 (99.8% pure; Lab

Solution and Engineering Co, Ltd., Bangkok, Thailand). The MultiRae IR was programmed to sample air and log data at 10-second intervals.

The single zone used for the decay trials was the 50 m^3 (interior volume) experimental hut with three windows and one door that opened directly to the outside. The windows and doors are equipped with louvers that remained open during the field trials. The detection instrument was located in the center of the hut. Background levels of CO_2 were collected prior to field trials, then a tracer gas consisting of 99.5% pure CO_2 was released from a compressed gas bottle. Mixing of the tracer gas (CO_2) with indoor air was facilitated with a mechanical fan. Equal mixing was assumed.

Upon initial tracer gas release and mixing, the CO_2 levels were allowed to decay from about 4000 ppm to 900 ppm while the detection instrument read and logged the resulting concentrations. The equation used to calculate the ACR is provided as equation 2.[39] Calculated ACRs were compared using a Z-test.

Equation 2. Air change rate equation.

$$f = y_0 + N * t$$

N = air change rate (hr^{-1})
y_o = initial concentration (ppm)
f = final concentration (ppm)
t = time (hr)

3.2.2 Determination of a Generation Rate

Another input variable needed to run a WMB is the generation rate. A dynamic chamber was used to determine the steady-state concentration of volatilized DDT in ambient air over a range of temperatures. The steady-state concentration was then

used to calculate the generation of DDT in micrograms from polyester netting into ambient air. The aforementioned Markes µ-CTE TM system was used to determine the steady-state concentration of DDT volatilizing off of polyester netting (figure 4). The stainless steel cups are inert to minimize chemical reactivity with analytes placed in each cup.

Figure 4. As shown, a Markes µ-CTE with (n=6) 45 ml stainless steel cups. DDT treated polyester netting (3cm x 15cm) placed inside each stainless steel cup.

3.2.3 Preliminary Data Collection to Establish Laboratory Experimental Conditions

The temperature range during field data collection was 22.0 - 33.5 °C with a mean temperature of 25.7 °C and a median temperature of 28.5 °C (figure 5). To cover an evenly distributed range, the field median temperature was selected as the median temperature for the chamber experiments. The temperature setting on the µ-CTE was limited to whole number increments; therefore, the median value was rounded down to 28 °C. Also, due to laboratory and equipment limitations, the lowest temperature achieved in the chamber was the ambient temperature in the laboratory (24°C ±1 °C).

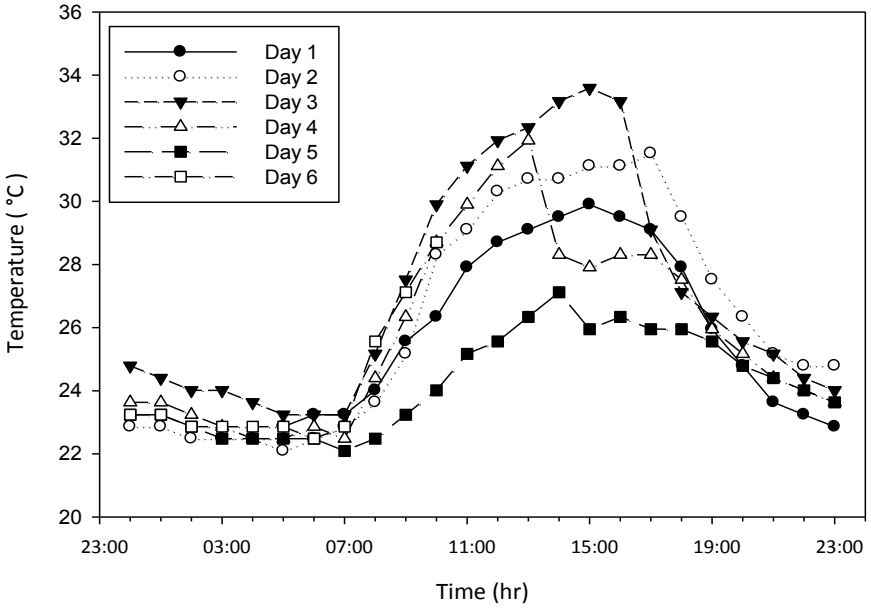

Figure 5. An illustration of the temperature range inside the experimental hut over a six day period. Temperature measurements (n=1) were taken every 20 minutes. The morning air temperature at 0700 held steady between 22°C and 24°C, gradually climbing to a maximum of 33 °C at 1500 and dropping to approximately 26 °C by 1900.

The average RH inside the experimental hut over the six day sampling period was 86%, SD=13.1. RH could not be regulated in the laboratory so humidity was removed from the chamber air intake using compressed air (Zero grade; Air Gas, Bethesda, MD). The RH level was verified at zero RH with a thermo anemometer (VelociCalc 9555, Thermo Scientific Inc.; Shoreview, MN). The average ACR in the field was measured at 7.21 ACH $^{-1}$. In order to match the same ACR inside the chambers, the flowrate inside the μ-CTE would need to be set at 5 ml min^{-1}. However, the flowrate lower limit of the μ-CTE was 10 ml min^{-1}. In addition, to allow for fluctuation in flowrate, a 20% margin above the flowrate lower limit for the μ-CTE was established (12 ml min^{-1} (± 1 ml min^{-1}). Thus, the laboratory ACR was 17 ACH (hr^{-1}), approximately one order of magnitude greater than the ACR measured in the field. The WMB model results were normalized by using the field results in place of the laboratory ACR to determine the generation

rate. The flowrate was verified using a primary flow meter (Defender, model 510; BIOS International Corp., Butler, NJ). The carrier gas pressure to the µ-CTE was regulated between 10 and 60 psi and frit filters ensured a constant gas flow through each chamber. The flow rate was determined by measuring the gas flow from the exhaust side of the metal sampling tubes (89 mm X 4 mm i.d. X 6.4 mm o.d.) packed with 200 mg Tenax® TA adsorbent (Markes International Limited, Llantrisant, UK) when the tube was inserted into the lid of the µ-CTE with the lid closed (figure 6). The gas flow was verified at the beginning of the test and at the conclusion of the test at each time point using a primary flow meter. Samples were collected from chamber exhaust with metal sampling tubes (89 mm X 4 mm i.d. X 6.4 mm o.d.) packed with 200 mg Tenax® TA adsorbent (Markes International Limited, Llantrisant, UK). After each experiment, the interior surface of each chamber was cleaned with detergent (Alconox; Alconox Inc., White Plains, NY), then rinsed with tap water, followed by a rinse with deionized water and a final rinse with acetone (100% pure; Burdick and Jackson, Muskegon, MI).

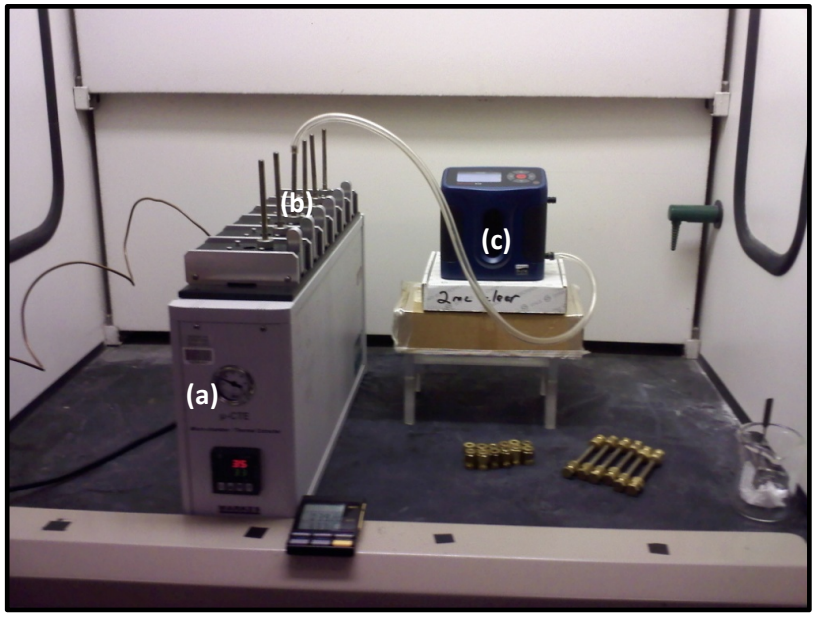

Figure 6. Laboratory set up to measure the flowrate (Q) in each chamber. (a) µ-CTE, treated material inside each chamber with temperature and Q set; (b) sampling tubes inserted into each chamber exhaust port; (c) primary flow meter measuring the Q. Flowrate was maintained at 12 ml min^{-1} (±1 ml min^{-1}).

3.2.4 Preliminary Testing

To develop a baseline for sample collection, the µ-CTE was set at 33°C and samples were initially collected at intervals of 10 minutes, 20 minutes, 30 minutes, 1 hour and 2 hour. Using the initial time intervals, all samples were below detectable or quantifiable limits of the standard curve. To improve the likelihood of detection, the sample collection time was increased to three hours, thus increasing the amount of analyte mass collected. Following a three hour sampling period, replicate sample (n=3) results yielded a mean concentration of 18.4 µg m^{-3} and a standard deviation of 0.036.

A preliminary experiment was conducted at 33 °C to show stability of experimental design parameters. A standard method (ASTM D5116-10) was used to determine the

steady-state concentration and follow-on generation rate of DDT from polyester netting. The ASTM method recommends a minimum of three samples taken after equilibrium is achieved.[33] Samples were collected every three hours for the first 27 hours, then every 12 hours thereafter. According to the ASTM method, a minimum of three consecutive samples were collected after the chamber reached equilibrium and steady-state was achieved.[33] Steady-state concentration was considered achieved at the 39 hour time point (figure 7).

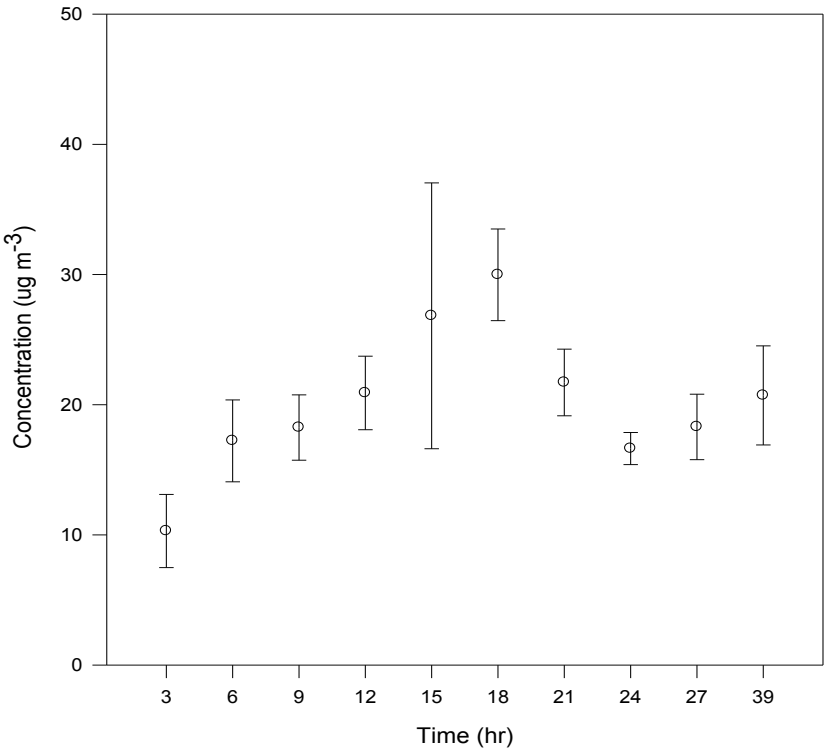

Figure 7. Volatilization of DDT from polyester netting at 33 °C. Steady-state concentration achieved at 39 hr time point after no significant difference was found between time points 24-39 hours (p = 0.138; SD=9.48).

3.2.5 Determination of Steady-State Concentration and Generation Rate

Following equilibrium and observation of steady-state concentration, an ANOVA was performed. If the results showed no significant difference (p=0.05), the experiment was concluded and the mean concentration was assumed to be the steady-state concentration at the tested temperature. The steady-state chamber concentration (C_s) was determined using the equation provided as equation 3.

Equation 3. Steady-state concentration equation.

$$C_s = \frac{total\ mass\ of\ DDT\ collected}{total\ sample\ volume}$$

The contaminant source area *A*, was 4.5 x 10^{-3} m^3 inside the chamber and 50 m^3 inside the experimental hut. From the ACR, the flowrate can be calculated,

Equation 4. Flowrate equation.

$$Q = N\ x\ V$$

The loading factor (*L*), was determined using the following equation,

Equation 5. Loading factor equation.

$$L = \frac{area\ of\ contaminant\ source}{volume\ of\ chamber}$$

The equation used to calculate a generation rate once steady-state was achieved was,

Equation 6. Generation rate equation.

$$G = A\ [C_s * {}^{N}/_{L}]$$

G = Generation Rate (mg m^{-3} hr^{-1})
A = Area of contaminant source (m^2)
C_s = Steady-state concentration (mg m^{-3})
N = air change rate (hr^{-1})
L = Loading factor (m^2 m^{-3})

3.2.6 Test Conditions

Laboratory testing conditions were matched as closely as possible to environmental conditions measured in the field (table 3). Temperature and time were the only variables evaluated for the experiment. Relative humidity (RH%), flowrate, fabric type and fabric loading were controlled and/or normalized. Temperature was varied during replicate (n=6) testing to represent the range of field experimental hut temperatures: 24°C, 28°C, 33°C. Experimental design was set to reflect the temperature range observed in the field (figure 5).

Table 3. Micro-chamber test matrix to determine the generation rate of DDT from polyester netting.

Temperature (°C)	Time Point (hr)	Samples per trial	RH (%)	Flowrate (ml min^{-1})	Mass Loading (mg cm^{-1})
24	3	6	0	12.0	0.2
	15	6			
	27	6			
	39	6			
	51	6			
	63	6			
	75	6			
28	3	6	0	12.0	0.2
	15	6			
	27	6			
	39	6			
	51	6			
	63	6			
	75	6			
33	3	6	0	12.0	0.2
	15	6			
	27	6			
	39	6			
	51	6			
	63	6			
	75	6			

3.3 Sample Analysis

The following method description developed by Martin *et al*. pertains to both laboratory and field analysis.[40] Samples were introduced into a gas chromatograph (GC)-mass spectrometer (MS) instrument (5975T, Agilent Technologies Inc., Santa Clara, CA) through a thermal desorption (TD) unit (Unity 2; Markes International Limited, Llantrisant, UK) (figure 8). Samples were thermally desorbed into the GC/MS using a two-stage method. Analytes were initially desorbed from the sampling tube onto a trap at 280°C for five minutes with a 5:1 split (80% of the sample was vented, 20% was desorbed to the GC column) before introduction onto the GC column. The trap was maintained at 20°C during desorption and rapidly heated to 300°C then held for 10 min during splitless desorption of trapped sample onto the GC column. A DB-5 (5% Phenyl-methylpolysiloxane) 30 m length × 0.25 mm i.d. × 0.25 μm film thickness (d_f) fused silica open tubular column was used for GC separation. The heating conditions were 200°C for the thermal desorber transfer line, 250°C for the GC transfer line, 230°C for the GC/MS interface, and 150°C and 250°C, respectively, for the MS ion source and quadrupole regions. The GC/MS was operated under the following conditions: initial temp of 50°C (hold for 30 sec), followed by linear ramp of 50°C/min to 200°C (no hold time), 10°C/min to 270°C (no hold time), and 30°C/min to 300°C (hold for 30 sec), for a total run time of 12 min. Mass range was scanned from m/z 75 to 360 at 3.75 scans/sec, with selected ion monitoring (SIM) mode utilized for m/z 165 and 235. Peaks were identified using both retention index and mass spectra data from the National Institute

of Standards and Technology (NIST) GC/MS mass spectra library (version 2.0, Gaithersburg, MD).

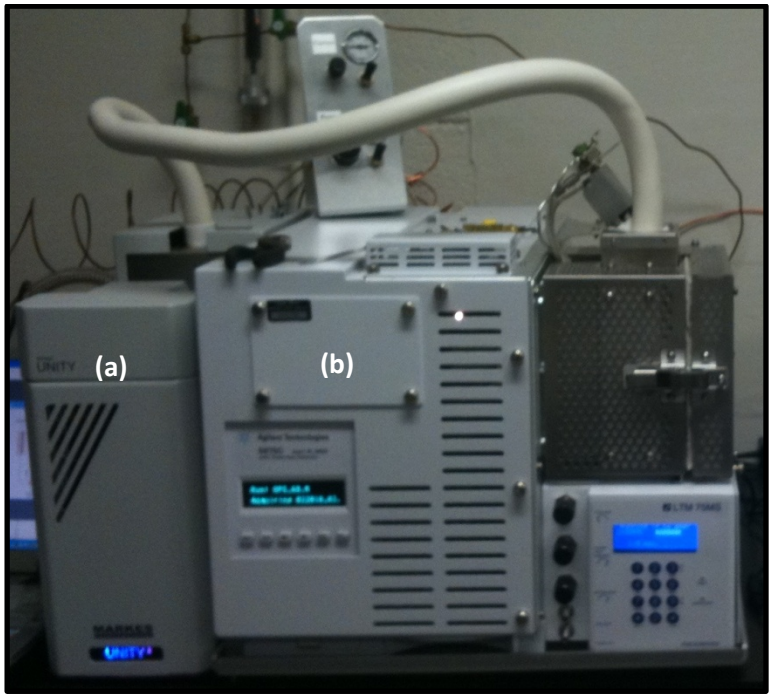

Figure 8. As shown, (a) Markes Unity 2 thermal desorber (b) Agilent 5975T GC/MS.

Calibration curves were prepared by serially diluting stock solutions in iso-octane to a final concentration between 1.0 ng μl^{-1} to 250 ng μl^{-1} for standard solutions. Calibration standards were drawn into a microsyringe (Hamilton, Reno, NV) in the following manner: a 0.5 µl of iso-octane, followed by 0.5 µl of air and subsequently by a 1.0 µl of standard solution. Next, the microsyringe contents were injected into a Tenax® tube. The sample tube was then loaded into a Markes tube loader with 100 ml/min of He flow through the sample tube. Sample quantification was accomplished by integrating the area under the curve from SIM analysis (m/z 165 and m/z 235). As established in EPA method 8000, the following quality control criteria were adhered to in this study: an analytical sequence with a blank and two standard samples were

analyzed every 10-15 samples; within group RSD ≤ 20%; calibration of the response curve ≤ 15% of the initial calibration curve.

3.4 Model Simulation

A WMB model was used to estimate DDT concentrations inside the experimental hut. DDT concentrations were estimated using the equation 7. The model's input parameters were derived from field and laboratory data. Manipulation of outcome data was limited to the generation rates empirically determined from the chamber experiments and as observed from the ACR in the hut as aforementioned. Predictive WMB results were compared to actual sample results from the experimental hut.

Equation 7. Well Mixed Box (WMB) equation.

$$C = \frac{G}{Q}$$

C = Contaminant concentration (μg m^{-3})
G = Generation rate of the contaminant (μg hr^{-1})
Q = Flowrate of air entering and leaving the experimental hut (m^3 hr^{-1})

3.5 Field Testing (Environmental Sampling)

Analysis of field samples collected inside the experimental hut were compared to the predicted results derived from using the WMB model. The dimensions for the experimental hut were 4m wide x 5m deep x 2.5m high resulting in an internal volume of 50 m^3. The overhead space was sealed off. The dimensions for the windows and door are as follows: window 1: 85.7 cm x 53.8cm; window 2: 86.2 cm x 53.7 cm; window 3: 86.0 cm x 55.7 cm; door: 77.9 cm x 208.9 cm (figure 8).

Figure 9. Experimental hut with 50 m^3 room volume. The interior hut dimension resembles a rectangle (4 m wide x 5 m deep x 2.5 m high). During sample collection doors and windows remained closed but all door and window louvers were fully opened.

Low flow pumps (model 222; SKC Inc., Eighty Four, PA) were calibrated at 0.2 lpm with inline sampling train consisting of steel tubes packed with 200 mg Tenax®TA adsorbent material. Sample collection proceeded for 60 min to collect the required 12 l sample. Tubes samples were collected every three hours beginning at 0600 through 1900 over a six day period. Pumps were pre- and post-calibrated with a sample tube inline prior to placement inside the hut using a primary flow meter. Pre-and post-calibration fell within the 5% error range considered acceptable by the American Industrial Hygiene Association. Samples were collected from the center and each of the four corners of the experimental hut to test for homogeneity of DDT concentrations in air (figure 9). Sample collection was located at the vertical midline, 1.52 m from the

floor. After sampling, the packed tubes were capped and placed in a refrigerator awaiting analysis. All samples were analyzed within 24 hours based on the aforementioned TD-GC/MS method.

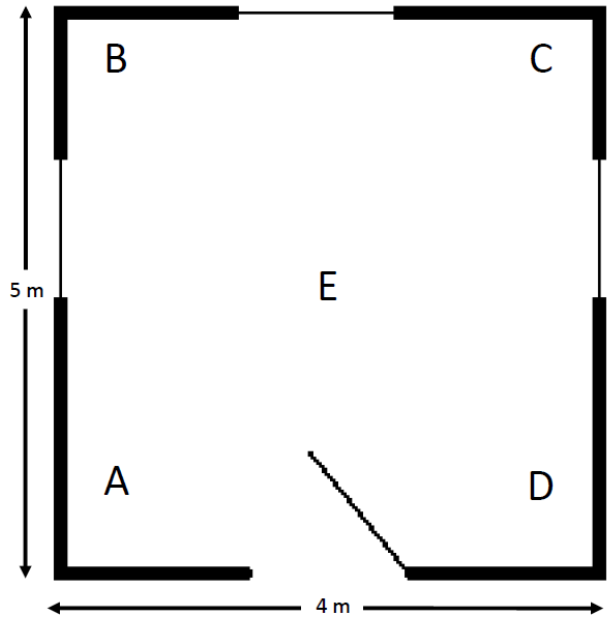

Figure 10. Experimental hut (top view) with sample locations (A through E). Corner samples (A, B, C, D) were placed approximately 30 cm away from wall that a corner is formed. The center sample (E) was centrally located within the hut (equidistant from the length and width of the hut).

3.6 Statistical Analysis

Statistical analysis was carried out using Sigmaplot (Version 11.0, Systat Software, Inc., Chicago, IL). Data was managed using an Excel® spreadsheet. The ASTM D5157-98 (2008) method criteria was applied for the comparison of the WMB model predictions to the experimental hut measurements.[41] This method provides guidance to evaluate model performance for agreement, error and bias. Statistical analyses are provided in table 4.

Table 4. Research AIMS with associated statistical tests.

AIMS	*Dependent Variable*	*Independent Variable*	*Description of Analyses*
AIM 1	*Concentration*	*Temp*	• *Homogeneity and Normality* • *Appropriate test for Variance (parametric or nonparametric)* • *Appropriate Post Hoc (if necessary)*
AIM 2	*ACR*	*Trial*	• *Descriptive statistics (mean, range and standard error)* • *Z-Score*
AIM 3			*No statistical analysis*
AIM 4	*Concentration*	*Location*	• *Homogeneity and Normality* • *Appropriate t-test (parametric or nonparametric)* • *Appropriate test for Variance (parametric or nonparametric)* • *Appropriate Post Hoc (if necessary)*
AIM 5[a]	*Observed*	*Expected*	• *Correlation coefficient is 0.9 or greater,* • *The regression slope is between 0.75 and 1.25,* • *The regression intercept is not greater than 25% of the measured concentration,* • *Normalized mean square error (NMSE) is less than or equal to 0.25,* • *Fractional bias (FB) is less than or equal to 0.25 and* • *Variance bias (FS) is less than or equal to 0.25,*

[a] Analysis in accordance with standard method ASTM D5157-97

4. Results

4.1 Determination of Air Change Rate in the Field

Field trials (n=4) for the decrease of CO_2 concentrations from approximately 4000 parts per million (ppm) to approximately 900 ppm for a naturally ventilated hut were completed in 10.67-16.17 minutes (figure 11). The measured decline in CO_2 concentration correlated with an exponential decay (R^2=0.94-0.98). The air change rate (ACR) range was 6.27-9.07 air changes per hour (ACH) (hr^{-1}) with a mean ACR of 7.21 hr^{-1} and a standard deviation (SD) of 1.26. A Z-test comparing ACR estimates revealed a significant difference between trials 1 vs 2, 2 vs 3 and 2 vs 4. There was no significant difference between trials 1 vs 3, 1 vs 4, 3 vs 4.

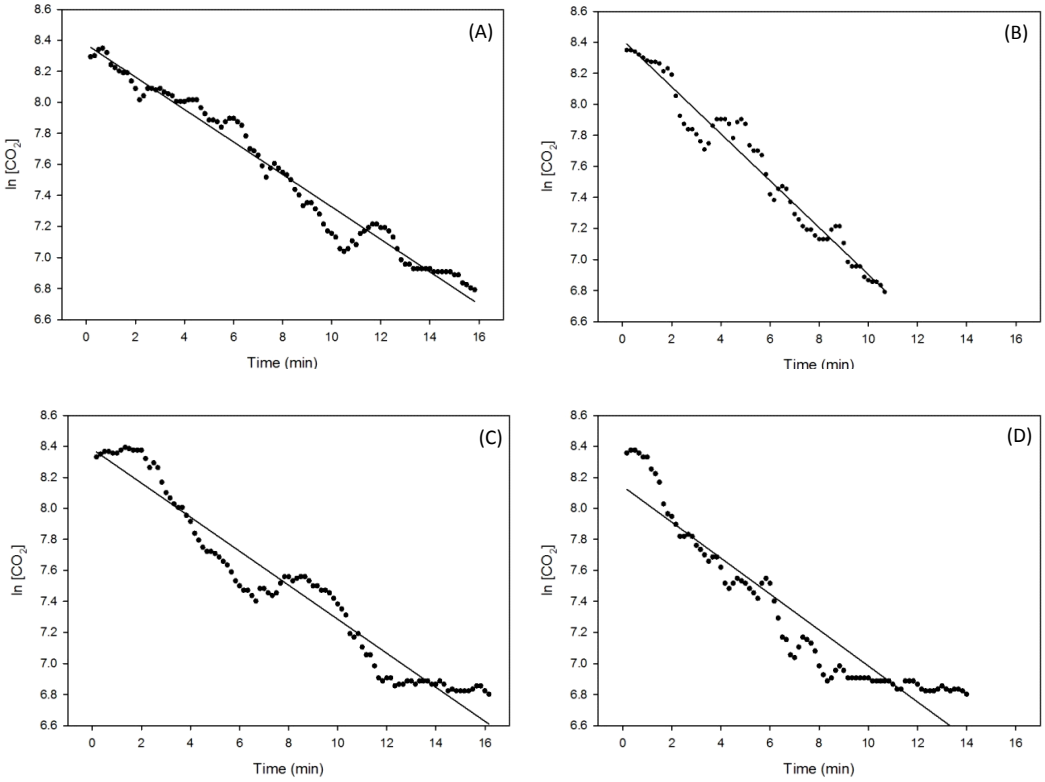

Figure 11. Successive testing (n=4) for the regression of CO_2 concentrations inside an experimental hut in order to determine ACR. (A) Trial 1, 6.27 ACH, R^2=0.98, SE= 0. 114; (B). Trial 2, 9.07 ACH, R^2=0.98, SE= 0. 2331; (C) Trial 3, 6.57 ACH, R^2=0.97, SE= 0.1669; (D) Trial 4, 6.95 ACH, R^2=0.94, SE= 0.2641.

4.2 Sample Analysis

(D)

The analytical curves for laboratory and field analysis were determined by integrating the area under the curve from SIM analysis (m/z 165 and m/z 235). The RSD and R^2 for the field results were outside acceptable limits as set by EPA Method 8000 guidance (table 5).

Table 5. Calibration data for the analysis of DDT in the field and laboratory.

Location	Range (ng)	R^2 ($R^2 \geq 0.99$)[a]	RSD (RSD≤ 20%)[a]
Field	5-100	0.933	15.1-49.0 (26.8)[b]
Laboratory	1-250	0.991	0.8-9.0 (5.1)[b]

[a] guidance from EPA Method 8000
[b] mean RSD

4.3 Micro-Chamber Experiment

A total of 118 samples were collected from the micro-chamber experiments. Data was segregated into three groups based on temperature setting: group 1, 24° C (n=36), group 2, 28° C (n=42), group 3, 33° C (n=40). The average ACH^{-1} was 17.0. The loading factor L was 100 m^2 m^{-3}. Summary statistics and data set points are provided in table 6.

Table 6. µ-CTE experiment data summary.

Parameter	Set point	Average	Standard Deviation	Maximum/ Minimum
Temp (°C)	24	24.7	0.44	25/24
	28	28	0	28
	33	33	0	33
RH (%)	0	0	0	0
Flow (m^3 hr^{-1})	7.2×10^{-4}	7.6×10^{-4}	1.2×10^{-5}	8.0×10^{-4}/ 7.3×10^{-4}

In group 1, six samples were considered invalid at time point 39 hours due to different collection times as compared to the rest of the samples. At time point 39 hours, the collection duration was 12 hours versus the intended 3 hours. In group 3, two samples were lost due to equipment malfunction. At time point 15 hours, the GC did not run the first sample in that series. As a result, DDT was left on the trap and was

analyzed with the next sample, increasing its peak abundance value by two-fold. The samples were identified as outliers using Tukey's criteria.

Flowrates did not vary significantly among the micro-chamber sample cups. An ANOVA showed no significant difference for the flowrates among the cups for each temperature group (Group 1, Mean = 12.9, p = 0.103, SD = 0.23; Group 2, Mean = 12.7, p = 0.334, SD = 0.199; Group 3, Mean = 12.7, p = 0.223, SD =0.168).

The steady-state concentration for Group 1 was established using chamber results at time points 27, 51 and 63 hours. There was no significant difference between the time points (p = 0.437; SD = 0.34). Group 2 was established using chamber results at time points 27, 39, 51 hours (p = 0.278; SD = 0.22). Group 3 was established using chamber results at time points 27, 39, 51 hours (p = 0.606; SD = 0.47).

A test for normality of steady-state concentration measurements using Shapiro-Wilk passed (p=0.078), but failed for equal variance (p= < 0.050). Analysis using Kruskal-Wallis One Way Analysis of Variance Ranks test indicated a statistically significant difference between median values among the groups (H = 68.77; d_f=2; p = <0.001). A Dunn's Post Hoc determined no significant difference between groups 1 and 2 but group 3 was significantly different from groups 1 and 2. (figure 12).

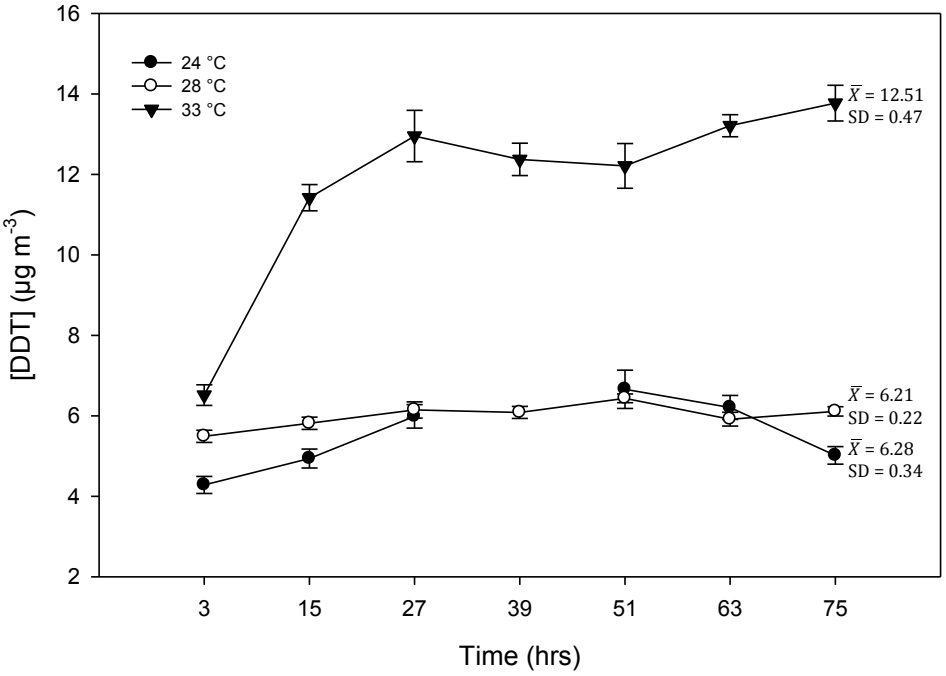

Figure 12. Laboratory µ-CTE results for the volatilization of DDT from polyester netting at three different temperatures (24°C, 28°C, and 33°C). There was no significant difference between 24°C and 28°C (p=>0.05). The concentration at 33°C was significantly different than the concentration at 24°C and 28°C (p=<0.05).

4.4 Field Testing (Environmental Sampling)

During field testing, 98 total air samples were collected for DDT inside an experimental hut; 67 of the 98 samples collected over the initial field days were lost due to a subsequent change in analytical method. Intra-hut comparison accounted for 22 of the remaining 31 samples, with one sample that could not be analyzed, for a total of 21 valid air samples.

An ANOVA revealed no statistically significant difference (p = 0.454) (F=0.970) between the five sample locations inside the experimental hut (table 7). Additionally, samples collected from two different huts at similar locations (center of hut), were not

significantly different. A Mann-Whitney Rank Sum Test revealed no significant difference T=0.149 (hut B, n=13) (hut C, n=14) (p = 0.115) between the two huts.

Table 7. Summary of results for ANOVA on multiple locations inside an experimental hut.

Location	Sample Size	Mean ($\mu g\ m^{-3}$)	SD
A	4	1.416	1.561
B	2	1.242	0.130
C	3	1.207	0.458
D	4	2.142	0.979
E	8	1.109	0.273

4.5 WMB Model Validation

Model estimates for volatilized DDT concentrations were compared to measured DDT concentrations taken inside an experimental hut using criteria established by ASTM 5157-97. In order to use the standard method to compare the average concentration observed to the average concentration predicted at all three temperatures, the following criteria were established:

- The mean values (n=3) used to determine the chamber steady-state concentration at each temperature were used to create the average predicted values for each temperature.
- The number of field samples collected at the temperatures of interest varied (24 °C (n=4), 28 °C (n=11), 33 °C (n=6)). The observed sample group means were matched to the mean predicted samples at (24 °C, 28 °C, 33 °C).

Table 8 shows the comparison between observed and predicted concentrations. The difference between the observed and predicted concentration at 24 °C, 28 °C, 33 °C were within one order of magnitude. The correlation coefficient (R) 0.91 was above the threshold of 0.90. The slope (*m*) and variance bias (FS) were outside the acceptable range as determined by ASTM 5157-97. The Normalized Mean Square Error (NMSE) was outside the acceptable range. The Normalized Mean Square Error (NMSE) and Fractional Bias (FB) were also outside the acceptable range.

Table 8. Model predictions and validation using ASTM 5157-97 criteria at three different temperatures (24 °C, 28 °C, 33 °C) for [DDT] inside an experimental hut. Predicted concentrations were normalized to observed concentrations by using the field loading factor (*L*=0.3954) and ACR (*N*=7.21).

Temp (°C)	$\overline{C}$ observed (μg m^{-3})	$\overline{C}$ predicted (μg m^{-3})	NMSE (≤ 0.25)[a]	FB (≤ 0.25)[a]
24	1.01	6.28		
28	1.48	6.22	4.17	1.45
33	1.96	12.5		

[a] ASTM recommended values

5. Discussion

The intent of this research was to show the Well Mixed Box (WMB) model could predict volatilized DDT concentrations inside a DDT-treated experimental hut located in a tropical region where DDT was used. In order to properly evaluate the model, practical methods were investigated to determine input parameters for a WMB model. There were two key objectives: the determination of a generation rate (G) for volatilized DDT concentrations from polyester netting and the evaluation of variables that affect *G,* specifically, temperature and the replacement of air inside the experimental hut with outside air.

5.1 Determination of Air Change Rate in the Field

As stated previously, the evaluation of the ACR served two purposes: the determination of a flowrate set point for the micro-chamber DDT volatilization experiments and the determination of a WMB model variable, flowrate (Q), inside the experimental hut. The concentration decay method using a tracer gas provided a good estimate for the replacement of inside air with outside air (R^2= 0.94-0.98). Results from the four trials varied significantly. Potential reasons for these differences have been addressed by Yugou and Delesante, who discussed thermal buoyancy and wind as the two key natural forces that affect natural ventilation in buildings.[42] Thermal buoyancy is the result of air movement caused by temperature differences between the indoor air and outdoor air.[43] Yugou and Delesante explained that thermal buoyancy was not a

significant contributing factor for the significant differences observed from their ACR measurements, given that the recorded temperature before, during and after the ACR measurement period varied by less than 1 °C (0.39 °C). In this current research effort, a one degree difference in temperature (26-27°C), was observed. The difference in temperature was assumed to be negligible. A 4-fold difference in the wind speed was recorded (0.43-1.66 mph) during the four trials which may explain the trial variability. The measured ACR for this naturally ventilated building represents a point in time. Due to the unpredictability of meteorological conditions, an ACR is limited to the observed period of wind and temperature measurements.

5.2 Sample Analysis

Laboratory and field analysis was performed using the TD-GC/MS method previously discussed.[40] Linearity and precision during field analysis were outside EPA Method 8000 guidance. The uncertainty for the field analysis may have affected quantification for air samples of volatilized DDT concentrations inside the hut by as much as ± 0.41 μg m^{-3} of DDT in the air. A EUROCHEM method was used to account for error that may have been introduced due to the high RSD of calibration points (> 15) and low R^2 (<0.99).[44] The ± value from the EUROCHEM method accounts for the effect of the less than desirable calibration performed in the field. Given that the sampling approach in this research utilized a new method developed to reduce the sampling and analysis time for volatilized DDT in air, the use of the EUROCHEM accounting for error seemed reasonable. This is the first report, to the author's knowledge, of a method

developed to quantify DDT in small volume (<12L) samples of air collected during short intervals (≤1 hr). Thus, there may be other limitations to the method that have not been considered that may affect results.

5.3 Micro-chamber Experiment

Results from the statistical analysis for temperature and flowrates within all six of the μ-CTE cup volumes demonstrated that chemical emission rates among groups could be compared with confidence, as no significant difference was found between the 6 separate cup volumes. After making these observations, the primary laboratory objective of determining the equilibrium and subsequent steady-state concentration was the focal point. According to ASTM D5116, the steady-state concentration is determined when there is no significant difference between three consecutive measurements after the airborne concentration appears to achieve equilibrium. For constant emission sources, ASTM D5116 discusses using a calculation to estimate 99.9% equilibrium. An equation based on the ACR (N) and the amount of time in hours (t) needed to achieve 99.9% was presented as equation 8,

Equation 8. Calculate the estimated time to reach 99% equilibrium for a constant emission source inside a chamber.

$$0.999 = 1 - e^{-Nt},$$

This equation can be rearranged to take the following form,

$$e^{-Nt} = 1\text{-}0.999,$$

$$Nt = \ln (0.001),$$

$$t = 6.9/N$$

The ACR for the μ-CTE was determined to be 17 ACH^{-1}, therefore the time estimated to achieve equilibrium according to ASTM D5116 would be about 24 minutes. However, an issue with the ASTM standard is that the word "equilibrium" is too ambiguous. There is no established and standard definition for the term equilibrium as it pertains to chamber testing, leaving it to the interpretation of the reader. This ambiguity can lead to a premature selection of data points for comparison and use when attempting to determine the steady-state concentration.

A practical approach using limited data sets has been attempted in previous research that compared the initial data point to a data point collected four days later.[45] If the calculation yielded a difference of less than 10% from the initial data point collected, the emission testing was ended and a "quasi" steady-state was assumed. The initial data point was shifted to the next successive data point and additional data points were collected if the aforementioned difference of less than 10% was not achieved. For the present study, this approach by Colombo *et al*. was adopted to determine equilibrium. Based on this approach, "equilibrium" was determined at the 27 hour time point in this study, given that a minimum of three subsequent time points did not significantly vary (figure 12, Results section).

In addition, a correlation coefficient of less than 0.50 was also used to determine equilibrium. Colombo *et al*. used a large emission chamber (12-52 m^3) that needed long run times to reach equilibrium. The emission chambers used for the current study were much smaller (0.000045 m^3) and presumed to take much less time to equilibrate. This

rationale was used to determine a total run time for emission testing in order to achieve steady-state and could be accomplished in three days.

The results of the μ-CTE experiments suggest that DDT concentrations volatilize in air at an exponentially higher rate as temperature increases above 28 °C (figure 12, Results section). The experimental results validated the assumption that the volatilization of DDT in air would be significantly different at the higher temperature (33 °C) versus lower temperatures (24 °C and 28 °C).

Both the theoretical and experimental approaches demonstrated an order of magnitude difference in DDT airborne concentrations between the lower temperatures (24 °C and 28 °C) and the highest temperature used in this study (33 °C) (table 9). There was no significant difference between groups 1 (24 °C) and 2 (28 °C), but group three (33 °C) was significantly different from groups 1 and 2. The mean concentration at 24 °C was 6.21 μg m^{-3}, which was half the measured concentration at 33 °C.

Table 9. A comparison of [DDT] derived from theoretical and experimental values at temperature range shown. (a) Estimated saturation concentration for DDT using the ideal gas law and vapor pressures for DDT at the listed temperatures, Wania *et al*.[36] (b) Measured [DDT] from μ-CTE.

Temperature (°C)	[a][DDT] Wania *et al* (μg m^{-3})	[b][DDT] μ-CTE (μg m^{-3})
0	0.08	—
10	0.38	—
20	2.49	—
24	4.61	6.28
28	8.57	6.21
30	11.50	—
33	18.60	12.51
40	52.27	—

Due to equipment limitations, there were three key variables measured or associated with field conditions that could not be duplicated in the laboratory: the air change rate (ACR), the loading factor and the relative humidity. The ACR in the field averaged 7.21 air changes per hour (ACH), whereas the micro-chamber ACR in the laboratory averaged 17 ACH. Thus, the flowrate applied in the laboratory was more than double what was measured in the field. Despite these necessary differences, a comparison between the theoretical estimation of volatilized DDT and measured chamber concentration values for volatilized DDT were significantly different. (table 9).

The inability to match field and laboratory conditions, specifically, the loading factor and ACR required additional work in order to properly interpret the data collected. The determination of a generation rate is significantly influenced by the ACR and loading factor. The generation rate equation provided as equation 6 (Methods section) shows the ACR and loading factor as variables used in its calculation. The ACR is located in the numerator and the loading factor is located in the denominator of the equation. As a result, a value greater than one order of magnitude in the numerator or denominator would greatly influence the generation rate. In order to provide meaningful comparisons between the predicted and observed data, the predicted results were normalized by applying the same loading factor and ACR values from the field to the laboratory. Using this approach, the value for the ACR changed from 17 ACH to 7.21 ACH. The generation rate changed from 0.0048 to 1.21 µg per hr at 24 °C, 0.0047 to 1.20 µg per hr at 28 °C, and 0.00957 to 2.42 µg per hr at 33 °C. In doing so, predicted results were reduced from two and one half orders of magnitude difference from

observed results to less than one order of magnitude difference, a margin often expected when using a WMB model for estimation.[46]

The mean RH measured in the field was 85.5 % with a range of 51.4-100 % RH. However, the μ-CTE was operated at 0 % humidity, given that humidity could not be regulated in the μ-CTE. Given that published studies have reported statistically significant RH influence on the emission of pesticides, future studies should investigate the effects of humidity on DDT emissions from polyester netting.[47,48]

5.4 Field Testing (Environmental Sampling)

Sample results collected from the experimental hut of focus in this study were not statistically different from sample results from a similar hut nearby. These results suggest that the airborne concentrations of DDT within the experimental hut in this study are representative of similar dwellings that have been treated with DDT. Thus, an approach that would call for sampling only one hut in order to characterize airborne DDT concentration values may likely be representative of the concentration levels of DDT within multiple huts in the same general area, thus potentially requiring far less resources to provide a good approximation of DDT residual concentrations.

The median DDT air concentrations measured at the center of the hut in treatment Huts B and C were 0.98 μg m^{-3} (n = 13) and 1.02 μg m^{-3} (n = 14), respectively. A Mann-Whitney Rank Sum Test revealed no significant difference T=.149 (p = 0.115) between the two groups. The work in the field was not as well controlled due to variation in ambient conditions (temperature and humidity). Thus, a high T-value was not

surprising. Sample results represent samples collected over a wide temperature range (24 °C – 33 °C). As demonstrated in figure 12 (Results section), mass was significantly different between the low and high temperature range. The temperature range for the two highest distributions (Location A, mean, 1.41 μg m^{-3}, SD 1.56; location D, mean 2.14 μg m^{-3}, SD 0.979) was 27 – 33 °C. Another potential contributing factor was the low sample population at each location due to logistical constraints. Increasing the sample size will likely lower the SD.

This study did not attempt to discriminate between vapor and particulate forms of DDT. Other studies have investigated the partitioning of SVOCs between vapor and particulate organic matter phases, then reported DDT in both gas vapor and particulate form as total semi-volatile organic chemicals (TSVOCs).[3,11,49] Previous research by Weschler *et al*. focused on the impact of sorptive uptake of pesticide molecules onto and into room surfaces, as well as onto airborne particulate matter in the indoor air.[11] Given the potentially significant impact that this phase partitioning can have on the airborne gaseous concentration of the SVOC within a hut dwelling, Weschler developed an estimate for the gas-phase concentration of the pesticide to account for the loss to 'sinks', such as room surfaces and particulates. Equation 9 displays this equation. When applying this equation in the analysis of the observed data from this current research, the predicted vs. observed values within the hut were found to be well correlated. Values at 24 ^{o}C and 28 ^{o}C were found to be within 93% and 71% agreement, while only a two-fold difference was found at the highest temperature used in the study. These values represent significant improvements in correlation between observed and

predicted relative to using the Wania *et al*. method, which is based solely on ideal gas law and vapor pressure characteristics. Additionally, the predictive WMB method based on these two factors while ignoring the impact of sorptive sinks has much less predictive strength compared to the same WMB method which accounts for sorptive uptake of airborne chemical, as displayed in table 9. Both Singh *et al.* and Weschler *et al.* reported that SVOCs in the particulate phase were more prevalent at the introduction (days to weeks) of the emission source to the environment. The chamber experiment and field experiment for this study ran in less than a week. If volatilized DDT initially sorbed to indoor surfaces and airborne particulate, airborne sample results provided in this study would understandably be measured at a lower total airborne concentration for DDT inside the experimental hut. This may account for some of the disparity between the observed and predicted values of volatilized DDT concentrations reported in this study. As air to solid phase interactions would be considered to occur far less frequently due to the inert nature of the micro-chamber's stainless steel cups, differences from predictive and actual values were found to be much more comparable in the laboratory setting. Modifying a field sampling plan that would account for DDT in the gas phase and particulate phase should be investigated in future work.

Equation 9. Estimate equation for pesticides shortly after introduction to the indoor air.

$$C_o \sim \frac{A_m}{A} * C_{sat}$$

C_o = Initial Vapor Phase Concentration ($\mu g\ m^{-3}$)

C_{sat} = Saturation Concentration ($\mu g\ m^{-3}$)

A_m = Total area of emitting material (m^2)

A = Total area of indoor surfaces (m^2)

Table 10. A comparison of [DDT] derived from theoretical, observed, and predicted values at temperature range shown. (a) Estimated saturation concentration for DDT using the ideal gas law and vapor pressures for DDT at listed temperatures, Wania *et al*.[36] (b) Estimated vapor phase [DDT] shortly after introduction to experimental hut indoor air using Weschler *et al* equation.[11] (c) Observed [DDT] inside experimental hut (d) Predicted [DDT] for experimental hut using the WMB model.

Temperature (°C)	[a][DDT] Wania *et al.* (μg m^{-3})	[b][DDT] Weschler *et al.* (μg m^{-3})	[c][DDT] Observed (μg m^{-3})	[d][DDT] Predicted (μg m^{-3})
0	0.08	0.02	—	—
10	0.38	0.12	—	—
20	2.49	0.76	—	—
24	4.61	1.07	1.01	6.28
28	8.57	1.99	1.48	6.21
30	11.50	3.53	—	—
33	18.60	4.32	1.96	12.51
40	52.27	16.0	—	—

[d] Results normalized using the loading factor (0.3954) and ACR (7.21) from the field

5.5 WMB Model Validation

Statistical analysis presented in table 8 (Results section) show agreement to guidelines established in ASTM D5157. Results show the model fit is consistent with empirically derived laboratory airborne emission data and theoretical data. As expected the high correlation coefficient reflects a positive correlation between DDT emissions and temperature. However, field results were not consistent with empirical results or theoretical results derived from Wania *et al*. The NMSE indicates the differences between observed and predicted results were less than one order of magnitude. The fractional bias (FB) for the three temperatures was near the upper range of what should be expected for indoor air quality models, with a range of -2 to 2. The model performance would be considered conservative but acceptable for a simple box model. The emissions process for analytes from indoor materials can be generalized into three phases,[30]

- phase 1- the movement of the analyte within the material to the surface of the material,
- phase 2- the transfer of the analyte from the surface of the material to the boundary layer,
- phase 3- then the transfer of the analyte from the boundary layer to the ambient air.

The model used in this study was a simple mass transfer model that only investigated the transfer of the analyte from the boundary layer to the ambient air in vapor form. In its current form, the WMB model has utility as a tool to estimate occupational exposures even with a protective range of one order of magnitude. Thus, allowing for an exposure evaluation for DDT below established exposure limit values by the Occupational Safety and Health Administration (OSHA), 1.0 mg m^{-3}, National Institute of Occupational Safety and Health (NIOSH), 0.5 mg m^{-3}, or the American Industrial Hygiene Association (AIHA), 1.0 mg m^{-3}. A more sophisticated approach that investigates all three phases of the mass transfer from indoor materials, as well as accounts for the potential for significant sorption to room surfaces and airborne particulates, may be necessary to enhance the predictive ability of the WMB model. However, given that WMB models have been successfully used for decades for estimating airborne chemical concentrations at points in time, a more robust sampling plan and data set relative to the small sets in this study may likely provide a reasonably good estimation result.

6. Conclusion

The overall objective of this study was to determine the predictive ability of a simple box model when applied to volatilized concentrations of DDT within experimental hut dwellings post-DDT application. The WMB model was selected as an initial approach to estimate volatilized DDT concentrations because of its simplicity and likely ease of application to the experimental hut's box construct. Results from this study suggest that use of this model has utility as a screening and estimation model especially compared to US based occupational exposure limits. In this study, the WMB model approach provided a reasonably good approximation and characterization of volatilized concentrations of DDT inside the airspace of an experimental hut at modest temperatures.

The diminishing correlation between the WMB model and the experimental hut's observed DDT airborne concentration values at higher temperatures may be explained by accounting for factors that govern the fate and transport of DDT into the experimental hut's airspace. These factors may include the impact of mass transfer coefficient from within the material to the surface of the material, the partition coefficient between the material and the air and sorption onto indoor surfaces and particles in the air.[49-53] The estimation capability of the WMB model was significantly improved by accounting for potential sorptive phenomena within a pesticide-treated dwelling, suggesting such interactions between air and solid phases exist to a considerable degree. Humidity ranges were also not considered in this study, and may

be another potential factor when explaining the less than expected airborne concentration levels of DDT observed at the highest temperature within the experimental hut relative to laboratory micro-chamber observations.

In this study, the estimation of volatilized DDT was found to be mostly dependent on the emission rate of DDT, as it was affected by temperature and the air change rate inside the hut. Future studies should focus on additional mechanisms that drive the volatilization of DDT into indoor air as well as further study their sorption to indoor surfaces and particles in the air. While representing an approximate method of determining airborne concentrations (within a two-fold difference relative to observed values when accounting for sorptive phenomena), results of this study suggest that the simple WMB model approach may have utility in such efforts, especially in third world environs where comprehensive sampling and analysis approaches are not always feasible or cost prohibitive.

Bibliography

1. World Health Organization. *Scaling Up The Responses To Infectious Diseases.* Geneva: WHO;2002.

2. Agency for Toxic Substances and Disease Registry. Toxicological Profile for DDT, DDE, and DDD,. 2002. Accessed October 21, 2010, 2010.

3. Singh PP, Udeaan AS, Battu S. DDT and HCH residues in indoor air arising from their use in malaria control programmes. *Sci Total Environ.* 1992;116(1-2):83-92.

4. Van Dyk JC, Bouwman H, Barnhoorn IE, Bornman MS. DDT contamination from indoor residual spraying for malaria control. *Sci Total Environ.* Jun 1 2010;408(13):2745-2752.

5. USEPA. p,p'-Dichlorodiphenyltrichloroethane (DDT): USEPA; 2011.

6. Eskenazi B, Chevrier J, Rosas LG, *et al.* The Pine River statement: human health consequences of DDT use. *Environ Health Perspect.* Sep 2009;117(9):1359-1367.

7. Grieco JP, Achee NL, Chareonviriyaphap T, *et al.* A New Classification System for the Actions of IRS Chemicals Traditionally Used For Malaria Control. *PLoS ONE.* 2007;2(8):e716.

8. Lewis RG. Determination Of Pesticides And Polychlorinated Biphenyls In Ambient Air Using Low Volume Polyurethane Foam (PUF) Sampling Followed By Gas Chromatographic/Multi-Detector Detection (GC/MD). In: USEPA, ed. 2ND ed. Cincinnati: USEPA; 1999:37.

9. Kannan K, Tanabe S, Giesy JP, Tatsukawa R. Organochlorine pesticides and polychlorinated biphenyls in foodstuffs from Asian and oceanic countries. *Rev Environ Contam Toxicol.* 1997;152:1-55.

10. Darnerud PO, Atuma S, Aune M, *et al.* Dietary intake estimations of organohalogen contaminants (dioxins, PCB, PBDE and chlorinated pesticides, e.g. DDT) based on Swedish market basket data. *Food Chem. Toxicol.* 2006;44(9):1597-1606.

11. Weschler CJ, Nazaroff WW. Semivolatile organic compounds in indoor environments. *Atmos. Environ.* 2008;42(40):9018-9040.

12. Organization WH. *2010 Malaria Report.* Geneva2010.

13. World Health Organization. *2010 Malaria Report.* Geneva2010.

14. Donald R Roberts. International advocacy against DDT and other public health insecticides for malaria control. *Dove Press,.* January 19, 2011 2011.

15. Mackay D. *Multimedia Environmental Models*. 2nd, ed: Lewis Publishers,; 2001.

16. Chareonviriyaphap T. The use of an experimental hut for evaluating the entering and exiting behavior of Aedes aegypti (diptera: Culicidae), a primary vector of dengue in Thailand. *J Vector Ecol,.* 2005;30(2).

17. Polsomboon S, Poolprasert P, Suwonkerd W, *et al.* Biting patterns of Anopheles minimus complex (Diptera: Culicidae) in experimental huts treated with DDT and deltamethrin. *J Vector Ecol.* Dec 2008;33(2):285-292.

18. Jayjock MA, Hawkins NC. A PROPOSAL FOR IMPROVING THE ROLE OF EXPOSURE MODELING IN RISK ASSESSMENT. *Am. Ind. Hyg. Assoc. J.* 1993;54(12):733 - 741.

19. Neufeldt V, Guralnik DB. *Webster's new world college dictionary*. 3rd ed., [1997 update] ed. New York: Macmillan; 1997.

20. AIHA Exposure Assessment Strategies Committee MS. *Mathematical Models for Estimating Occupational Exposure to Chemicals*. 2nd ed. Fairfax: AIHA Press; 2009.

21. Taylor JR, O'Shaughnessy PT, Reynolds SJ. Estimating Personal Exposures Based on Mass Balance Material Usage Rates: Validation of a Ventilation Model in a Spray Paint Booth. *J. Occup. Env. Hyg.* 2004;1(4):213 - 221.

22. Keil CB, Nicas M. Predicting Room Vapor Concentrations Due to Spills of Organic Solvents. *AIHA Journal.* 2003;64(4):445 - 454.

23. Nicas M. Using mathematical models to estimate exposure to workplace air contaminants. *Chemical Health and Safety.* 2003/2//;10(1):14-21.

24. Committee A, Keil C. *Mathematical Models for Estimating Occupational Exposure to Chemicals*: AIHA Press; 2000.

25. AIHA Exposure Assessment Strategies Committee MS. *AIHA Exposure Assessment Strategies Committee, Modeling Subcommittee*. 2nd ed. Fairfax: AIHA Press; 2009.

26. Jayjock MA, Chaisson CF, Arnold S, Dederick EJ. Modeling framework for human exposure assessment. *J Expos Sci Environ Epidemiol.* 2007;17(S1):S81-S89.

27. Howard-Reed C. Development of IAQ Model Input Databases: Volatile Organic Compound Source Emission Rates. In: Brian P, Dols WS, eds. Gaithersburg, MD: National Institute of Standards and Technology, Indoor Air Quality and Ventilation Group; 2006.

28. Schripp T, Nachtwey B, Toelke J, *et al.* A microscale device for measuring emissions from materials for indoor use. *Anal Bioanal Chem.* Mar 2007;387(5):1907-1919.

29. Tichenor BA. Evaluating Sources of Indoor Air Pollution. *J. of Air & Waste Mgmt Asso.* 1990;40(4):6.

30. Salthammer T, Uhde E. *Organic indoor air pollutants : occurrence, measurement, evaluation*. 2nd, completely rev. ed. Weinheim: Wiley-VCH; 2009.

31. Horn W. Suitability of small environmental chambers to test the emission of biocides from treated materials into the air. *Atmos. Environ.* 2003;37:5477-5483.

32. Afshari A, Gunnarsen L, Clausen PA, Hansen V. Emission of phthalates from PVC and other materials. *Indoor Air.* Apr 2004;14(2):120-128.

33. ASTM. Standard Guide for Small-Scale Environmental Chamber Determinations of Organic Emissins from Indoor Materials/Products. *D5116-10*. Philadelphia, PA: American Society for Testing and Materials; 2010:25.

34. T. Schripp U, M. Wensing, Salthammer T. *Comparison of a Quick Analytical Method to test chamber measurements: Emission of plastic samples.* Braunschweig, Germany: Fraunhofer Wilhelm-Klauditz-Institute, Material Analysis and Indoor Chemistry;2006.

35. CDC, Control CfD, Prevention. DDT Chemical and Physical Information. In: Astdr, ed: CDC; 2002:497.

36. Wania F, Shiu W-Y, Mackay D. Measurement of the Vapor Pressure of Several Low-Volatility Organochlorine Chemicals at Low Temperatures with a Gas Saturation Method. *J. of Chem. & Eng. Data.* 1994;39(3):572-577.

37. Yoshihide M, Van Veen M. Predictive Residential Models. In: Franklin C, Worgan J, eds. *Occupational and residential exposure assessment for pesticides*: Wiley; 2005:209-239.

38. Kelley W. Rae Systems Technical Support. In: Carlis Brown, ed. Interview with Rae Systems technical support. Inquiry on the accuracy of the MultiRae IR. ed2011.

39. ASTM. Standard Test Method for determining Air Change in a Single Zone by Means of a Tracer Gas Dilution. *E741-00*. Philadelphia, PA: American Standards for Testing and Materials; 2000:17.

40. Martin NJ, Smith PA, Brown CW, Achee NL, DeLong GT. Dichlorodiphenyltrichloroethane (DDT) Determination in Air by Thermal Desorption Gas Chromatography-Mass Spectrometry. *Pest Manage. Sci.* 2012:n/a-n/a.

41. ASTM. Standard Guide for Statistical Evaluation of Indoor Air Quality Models. Vol D5157-97. Philadelphia, PA: American Society for Testing and Materials; 2008:4.

42. Li Y, Delsante A. Natural ventilation induced by combined wind and thermal forces. *Build. Environ.* 2001;36(1):59-71.

43. Liddament MW. *A guide to energy efficient ventilation*: Air Infiltration and Ventilation Centre; 1996.

44. Nicholas J. Martin PAS, Nicole L. Achee, Gerald T. DeLong. Determination of Airborne Semi-volatile Spatial Repellent Concentrations in Laboratory and Field Mosquito Behavior Assay Systems: Uniformed Services University of the Health Sciences, Bethesda, MD 20814; 2012.

45. Colombo A, Jann O, Marutzky R. The estimate of the steady state formaldehyde concentration in large chamber tests. 1994.

46. Riley DM, Newby CA, Leal-Almeraz TO, Thomas VM. Assessing elemental mercury vapor exposure from cultural and religious practices. *Environ Health Perspect.* Aug 2001;109(8):779-784.

47. Jansma J, Linders, JBHJ. *Volatilization of Pesticides from Soil and Plants After Spraying.* Bilthoven, Netherlands: National Institute of Public Health and Environmental Protection;1995. 679102030.

48. Schummer C, Mothiron E, Appenzeller B, Wennig R, Millet M. Gas/particle partitioning of currently used pesticides in the atmosphere of Strasbourg (France). *Air Quality, Atmosphere & Health.* 2010;3(3):171-181.

49. Xu Y, Little JC. Predicting emissions of SVOCs from polymeric materials and their interaction with airborne particles. *Environ Sci Technol.* Jan 2006;40(2):456-461.

50. Tichenor BA, Guo Z, Sparks LE. Fundamental Mass Transfer Model for Indoor Air Emissions from Surface Coatings. *Indoor Air.* 1993;3(4):263-268.

51. Sparks LE, Guo Z, Chang JC, Tichenor BA. Volatile Organic Compound Emissions from Latex Paint--Part 2. Test House Studies and Indoor Air Quality (IAQ) Modeling. *Indoor Air.* 1999;9:18.

52. Sparks LE, Guo Z, Chang JC, Tichenor BAT. Volatile Organic Compounds Emissions from Latex Paint-- Part 1. Chamber Experiments and Source Model Development. *Indoor Air.* 1999;9:10.

53. Van Loy MD, Riley WJ, Daisey JM, Nazaroff WW. Dynamic behavior of semivolatile organic compounds in indoor air. 2. Nicotine and phenanthrene with carpet and wallboard. *Environ Sci Technol.* Feb 2001;35(3):560-567.