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Volatile Organic Compounds (VOCs) in Indoor Air: Emission from Consumer Products and the Use of Plants for Air Sampling

Todd A. Wetzel
Utah State University

VOLATILE ORGANIC COMPOUNDS (VOCs) IN INDOOR AIR: EMISSION FROM CONSUMER PRODUCTS AND THE USE OF PLANTS FOR AIR SAMPLING

by

Todd A. Wetzel

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Approved:

Dr. William J. Doucette Environmental Chemistry Major Professor	Dr. R. Ryan Dupont Environmental Engineer Committee Member
Dr. Erik Dettenmaier Environmental Engineer Committee Member	Mark R. McLellan Vice President for Research and Dean of Graduate Studies

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Logan, Utah

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ABSTRACT

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by

Todd A. Wetzel, Master of Science

Utah State University, 2014

Major Professor: Dr. William J. Doucette
Department: Civil & Environmental Engineering

Indoor air concentrations of volatile organic compounds (VOCs), including many with documented adverse health effects, vary widely but are generally higher than found outdoors. Volatile organic compounds can enter indoor environments via internal (e.g. paints, paint strippers, fuels, cleaning supplies, pesticides, building materials, adhesives) and external sources (e.g. vapor intrusion (VI) from contaminated soil and/or groundwater and ambient air from automobiles and industrial facilities). Since many consumer products contain volatile organic compounds (VOCs) that are also the focus of soil and groundwater cleanup projects, emissions of these VOCs can lead to false source identifications during VI investigations. Laboratory-measured emissions of VOCs from several consumer products were used with a standard box model to predict indoor air concentrations. The predicted concentrations were compared to measured values generated by introducing the same consumer products into an actual residence. The screening level agreement between measured and estimated air concentrations suggests

that a standard box model can be used with laboratory measured emission rates to show if an emission source can cause a potential health risk or lead to false assumption during VI investigations. The use of plant leaves as a simple, cost-effective and sustainable approach to sampling indoor air concentrations of VOCs was also investigated in three studies: 1) a headspace approach; 2) a flow-through glass and stainless steel plant growth chamber, and 3) a house-scale study where plant leaf and air concentrations of VOC were simultaneously measured. Similar relationships between the leaf and air concentrations observed in the three studies suggest that plant leaf concentrations can be used as a surrogate for indoor air concentrations of VOCs.

(90 pages)

PUBLIC ABSTRACT

Volatile Organic Compounds (VOCs) in Indoor Air: Emissions from Consumer Products and the Use of Plants for Air Sampling

Adults living in North America spend an estimated 80-90% of their time indoors where they can be exposed to a wide range of volatile organic chemicals (VOCs) found in home construction materials and consumer products (e.g. molded plastics, adhesives, cleaning products, paints, etc.). Some of these VOCs are known to be harmful if exposure concentrations are high or occur over a long period of time. Vapor intrusion (VI), the process by which VOCs in the soil or groundwater migrate to indoor air from a contaminated site, can also contaminate indoor air. Since remediation activities to prevent or stop VI are often very expensive, it is important to determine if the source of indoor air VOCs is internal or external.

The focus of this study was twofold. First to show that consumer products can have a significant effect on VOC concentration within indoor air and that screening level calculations can be made using a products emission rate to estimate the potential effects of a product on indoor air quality. Second to suggest a simple, cost-effective and sustainable approach to sampling indoor air VOC concentrations using plant leaves as samplers.

A full-scale house level study, monitoring air concentrations over time with consumer products acting as a source of VOCs in indoor air, was performed to determine if VOC concentrations could reach levels that can confound VI studies or pose a health risk. The full-scale house level study was used along with two other studies, a small-

scale headspace study and a bench top scale flow-through glass and stainless steel chamber study to evaluate the relationship between measured leaf-air distribution coefficients, as well as leaf kinetics in an attempt to establish a relationship that could be used to calculate indoor air concentrations.

The comparison of estimated indoor air VOC concentrations to measured concentrations suggests that a standard box model can be used to evaluate the risk level of a certain product to contaminate indoor air, given its emission rate. Measured VOC concentrations from a craft glue (E-6000), gun cleaner and a molded plastic lamp base showed that objects can cause indoor air concentrations above the United States Environmental Protection Agencies (USEPA) screening levels for carcinogenic risk-based compounds. These concentrations are thus capable of providing false positives in VI investigations. Correlations between leaf and air concentrations in the different scales of plant studies suggest that leaves can be used to monitor indoor air concentrations for VOCs. Plant species appears to play a role in the plants effectiveness as a sampler. This difference appears to result from physical/chemical differences between species most notably lipid content and density.

Todd A. Wetzel

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Todd A. Wetzel

CONTENTS

LIST OF TABLES

LIST OF FIGURES

Figure Page

CHAPTER 1

INTRODUCTION

Adults living in North America spend an estimated 80-90% of their time indoors (Orwell et al., 2004; Dales et al., 2008). Concerns about the potential exposure to volatile organic compounds (VOCs) in indoor air have increased as new home construction techniques and improvements in heating, ventilation, and air conditioning (HVAC) efficiency have significantly reduced indoor air exchange rates (Yang et al., 2009), potentially increasing indoor air VOC contamination due to the lack of fresh air being introduced. Concentrations of VOCs in indoor air are generally 5 to 10 times higher than outdoors, with even higher indoor air concentrations where extreme cold weather conditions exist (Dales et al., 2008). Some of the VOCs identified in indoor air are considered suspected or confirmed carcinogens by the U.S. Environmental Protection Agency.

During the past decade, there has been increased concern about the potential for VOC contaminants present in soil and groundwater to migrate into indoor air and pose unacceptable health risks to residents. This process is referred to as vapor intrusion (VI). In addition, some of the same VOCs found as soil and groundwater contaminants are also found in consumer products and building materials (e.g. paints, paint strippers, fuels, cleaning supplies, pesticides, adhesives, molded plastics). The presence of these VOCs from internal sources can confound VI investigations (Gorder, 2008). For example, a long term VI study performed at two known contamination sites near Denver, Colorado conducted from 1998 to 2009, found large increases of 1,2-DCA in indoor air from 2004

to 2009 despite the presence of only trace amounts of 1,2-DCA in one of the two sites, pointing towards indoor sources (Krutz et al., 2010).

Many consumer products such as adhesives and cleaning solvents contain volatile organic compounds (VOCs) such as trichloroethene (TCE) and tetrachloroethene (PCE) that are also the focus of CERCLA (Superfund) soil and groundwater cleanups in the USA (Dawson and McAlary, 2009). In addition, reactions of sodium hypochlorite (bleach) with surfactants within consumer products (e.g. toilet bowl cleaners and surface sprays) can result in the unintended formation of carbon tetrachloride (CCl_4) and other VOCs (Odabasi, 2008). The formation of chloroform ($CHCl_3$) has also been reported from the reaction of free chlorine with triclosan containing products (Fiss et al., 2007) and plastic holiday ornaments that emit 1,2-dichloroethane (1,2-DCA) (Doucette et al., 2010) have been identified.

Sack et al. (1992) conducted a survey of 31 VOCs, including nine chlorinated compounds and 15 aromatic hydrocarbons, in 1159 household products. They found that 81% of the products contained one or more of the VOCs of interest above 0.1% by weight; a threshold limit that suggested the product would be a likely source of VOCs in indoor air. While VOCs from indoor sources and consumer products have been well documented, emission rates from these sources are not widely available.

Studies have also been performed on homes with attached garages and they were found to have increased gasoline vapor concentrations (aromatic hydrocarbons) found throughout the home (Dales et al., 2008). Additional studies have shown that cigarette smokers exhale 10 times more benzene than nonsmokers, adding to indoor VOC concentrations (Dales et al., 2008). When indoor sources are identified as emission

sources during vapor intrusion investigations, it is important to determine if they are the primary source of the VOCs detected in the home before implementing any VI mitigation strategies.

Determining VOC concentrations in indoor air is typically accomplished by one of two methods; using active or passive sorbent sampling techniques, or direct air sampling using Tedlar® bags or Summa canisters.

Active sampling with sorbents uses a pump to draw air through a specific collection media where the VOCs are concentrated. After sampling the VOCs are desorbed from the collection media using solvents or heat, and then analyzed, typically by gas chromatography. Sorbent passive sampling, also called diffusive sampling, does not require a pump as it relies on the diffusion of the contaminants from the air to the adsorptive media. Sorbent sampling techniques have holding times around 30 days, but can vary based on sorbent media, and require chilling for sample preservation.

Direct air sampling techniques use collection devices such as Tedlar bags, a bag designed to hold a "grab sample" for 24-72 h. Summa canisters are canisters under a vacuum that require no additional equipment for sampling. They are commonly used for 24-h. integrated samples, and have a holding time up to 30 days.

These sampling techniques can be obtrusive, expensive and difficult to implement due to the lack of cooperation from the homeowner, making identification of indoor sources complicated.

The use of ornamental plants to reduce indoor air concentrations of VOCs has been studied for decades (NASA, 1989; Cornejo et al., 1999; Liu et al., 2007; Yang et al., 2009). However, stated removals differ widely and the variety of experimental

approaches used to determine removals complicate comparisons among studies. Depending on the plant and chemical of interest, VOC removal mechanisms that have been reported include stomatal uptake and metabolism (Baur et al., 1997), microbial transformation within plant growth media (Orwell et al., 2004), and sorption to leaves (Bacci et al., 1990; Keymeulen et al., 1997; Orwell et al., 2004). Modeling results suggest that the high plant biomass to air ratio necessary to make meaningful reductions in indoor air VOC concentrations make the use of houseplants as air cleaners impractical in most cases (Girman et al., 2009). However, even if plants are unable to significantly impact indoor air concentrations, the waxy cuticle of leaves may allow common houseplants to be used as simple, cost-effective and sustainable passive indoor air samplers for VOCs. Successful implementation of this approach would potentially reduce costs associated with conventional passive sorbent samplers or active canisters, minimize sampler intrusions into the home, and potentially allow residents to directly participate in the sample collection activities.

Plants have been widely used as passive samplers for SVOCs in outdoor environments for compounds like PAHs (Lin et al., 2006; Li and Chen, 2009), PCBs (Nizzetto et al., 2006), dioxins (Nizzetto et al., 2006), herbicides and pesticides (Bacci et al., 1990) and predictive models relating leaf-air concentration ratios (bioconcentration factors) to octanol-air partition coefficients (Koa) have been developed (Bacci et al., 1990; Cornejo et al., 1999). Far fewer studies have examined the effectiveness of plants as samplers for more volatile compounds.

Hiatt (1998) investigated the use of plant leaves to sample outdoor air for VOCs such as benzene, toluene, TCE and PCE and found that leaf-air concentration ratios could

generally be predicted using existing Koa based models, but leaf concentrations in species containing higher amounts of monoterpenes were greatly under predicted. It was also reported that VOC uptake by leaves was rapid and higher vapor pressure compounds reached equilibrium concentrations faster than for those concentrations with lower vapor pressure values. In a subsequent publication, Hiatt (1999) reported that leaves provided a good indication of early morning exposures but the windy conditions quickly removed their VOC content with the introduction of clean air. The relatively fast uptake and release of VOCs from plant leaves may limit outdoor sampling applications where concentrations can rapidly change as a function of wind speed and direction but this is likely less important in indoor environments.

Objectives

The overall objectives of this study were twofold. First, show that consumer products have a significant effect on VOC concentration within indoor air. Second, understand the mechanisms governing the distribution of VOCs between air and leaves in order to evaluate the ability of using leaves as indoor air samplers. These objectives were met by conducting several specific experiments, including:

1) Emission rates of several commonly identified indoor air VOCs including: benzene, toluene, m-xylene, trichloroethene (TCE), tetrachloroethene (PCE), and 1,2-dichloroethane (1,2-DCA), were measured from opened and unopened consumer products using a flow through emission chamber

2) A standard box model approach was used to estimate indoor air concentrations of these VOCs from the measured emission rates and the interior dimensions of a specific residence

3) The estimated indoor air concentrations were compared to measured concentrations obtained after consumer products with known VOC emission rates were introduced into the residence

4) Leaf-air distribution coefficients for four species of common ornamental house plants, measured using three approaches, were used to evaluate the potential of using leaves to sample indoor air VOCs

The compounds used in this study were chosen based on relative abundance in the indoor environment, recent studies in the literature, VI concerns, as well as environmental concern associated with these compounds. Benzene, toluene, and m-xylene are aromatic hydrocarbons and common components in gasoline. Sources of contamination to indoor air are attached garages, newsprint ink, lubricants and degreasers. TCE, PCE, and 1,2-DCA are chlorinated volatile organic compounds (CVOCs) and are used as solvents or degreasers. These compounds enter the home through vapor intrusion or household products. For detailed properties of the compounds used in this study see Appendix A.

Four different species of houseplants were used in this study, each of a different type: a woody plant, ficus (*Ficus benjamina)*; a vine, golden pothos (*Epipremnum aureum)*; a flowering plant, spider fern (*Chlorophytus comsosum* 'vittatum'); and a succulent, Christmas cactus (*Schlumbergera truncate* 'harmony'). The plants were selected for their commonality and accessibility as well as their low light requirements.

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CHAPTER 2

EMISSIONS OF CHLORINATED SOLVENTS FROM CONSUMER PRODUCTS AS A SOURCE OF INDOOR AIR CONTAMINATION[1]

Abstract

Many consumer products contain volatile organic compounds (VOCs) that are also the focus of soil and groundwater cleanups in the USA. The emissions of these VOCs from consumer products into indoor environments can lead to false assumptions during vapor intrusion (VI) investigations. In this study, the emissions rates of several VOCs (1,2-dichloroethane, trichloroethene, tetrachloroethene and carbon tetrachloride) found in consumer adhesives, cleaning products, and molded plastic objects were measured under laboratory conditions using a flow through chamber system. The laboratory determined emission rates were used along with a standard box model to estimate the indoor air concentrations that would be found in a residence containing these products. The estimated concentrations compared favorably to measured concentrations obtained during several controlled experiments conducted in an actual residence. This suggests that laboratory determined emission rates, combined with a standard model can predict indoor air concentrations that are suitable for screening level risk evaluations and for determining the relative impact of internal versus external VOC sources.

[1]Coauthored by W.J.Doucette

1. Introduction

Volatile organic compounds (VOCs), including some with short and long-term adverse health effects, can enter indoor environments through internal (e.g. consumer products, building materials) and external sources (e.g. vapor intrusion (VI) from contaminated soil and/or groundwater and ambient air from automobiles and industrial facilities). Indoor air concentrations of VOCs vary widely, but concentrations of most VOCs are consistently higher indoors than outdoors (Dales et al., 2008).

Over the past decade, there has been increased concern about the potential for VOC contaminants present in the subsurface of buildings to migrate into indoor air (vapor intrusion) and pose unacceptable health risks to residents. However, in some cases, the presence of consumer products emitting VOCs in a home has and can lead to false conclusions during vapor intrusion (VI) investigations (Gorder, 2008).

Many consumer products such as adhesives and cleaning solvents contain VOCs such as trichloroethene (TCE) and tetrachloroethene (PCE) that are also the focus of soil and groundwater cleanups in the USA (Dawson and McAlary, 2009). In addition, reactions of sodium hypochlorite (bleach) with surfactants within consumer products (e.g. toilet bowl cleaners and surface sprays) can result in the unintended formation of carbon tetrachloride (CCl_4) and other VOCs (Odabasi, 2008). The formation of chloroform ($CHCl_3$) has also been reported from the reaction of free chlorine with triclosan containing products (Fiss et al., 2007) and plastic holiday ornaments that emit 1,2-dichloroethane (1,2-DCA) (Doucette et al., 2010) have been identified. When consumer products are identified as emission sources during vapor intrusion investigations, it is

important to determine if they are the primary source of the VOCs detected in the home before implementing any VI mitigation strategies.

In this study, we measured the emissions rates of VOCs from several opened and unopened consumer products including adhesives (PCE), cleaning solvents (TCE), household cleaning products (CCl_4) and molded plastic objects (1,2-DCA & PCE) using a flow through system. The consumer products used in this study were identified as VOC sources during VI investigations using a room-by-room indoor air monitoring approach (Doucette et al., 2010; Gorder and Dettenmaier, 2011). The measured emissions were used to estimate indoor air concentrations that were compared to measured concentrations obtained during several experiments conducted in an actual residence.

2. Methods and Materials

2.1. Chemicals

Calibration standards for the GC/MS analysis of 1,2-DCA, TCE and PCE were made from methanol dilutions of a Haloethanes Mixture (DWM-520) purchased from Ultra Scientifc (N. Kingstown, RI). The standard mixture contained 200 µg/ml of the compounds of interest and several other CVOCs dissolved in methanol. Dynacal® permeation tubes containing 1,2-DCA, TCE and PCE were purchased from VICI Metronics (Poulsbo, WA) at emission rates of 100 ng/min at 30˚C.

2.2. Consumer Products

The consumer products used in this study included a gun cleaner (Gun Scrubber; Birchwood Casey, Eden Prairie, MN), a toilet bowl cleaner (Lysol with bleach), a craft

glue (E-6000), an injection molded plastic gingerbread man ornament (obtained from Hobby Lobby), and an injection molded plastic lamp base (obtained from Lowes Home Improvement Center) (Appendix B). Products were stored in plastic containers placed with in a vented metal solvent storage cabinet when not in use.

2.3. Emission Chamber Measurements

Volatile chlorinated solvent emissions from individual objects were quantified using a flow through emission chamber system (Fig. 2-1) previously described by Doucette et al. (2010).

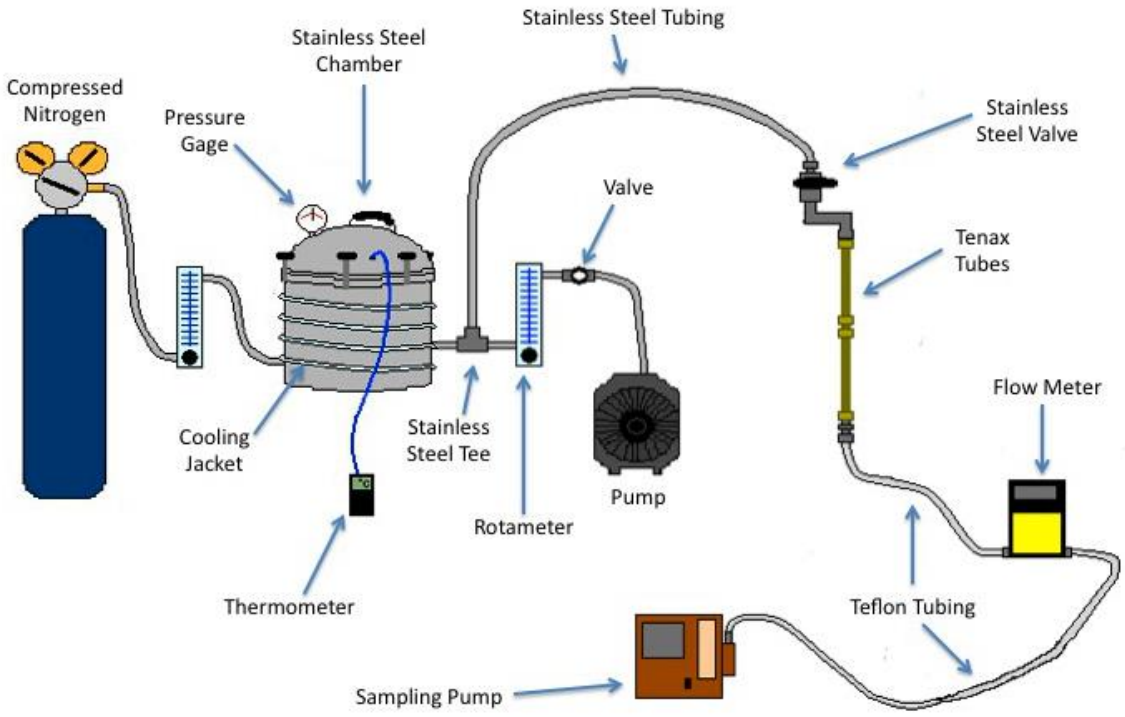

Fig. 2-1. Schematic of the flow through emission chamber system

The chamber consists of a modified aluminum pressure cooker containing mixing fans and gas inlet and exit ports. A stainless steel manifold uniformly distributes nitrogen

or high-purity compressed air depending on lab availability into the chamber while the exit gas is simultaneously withdrawn from the center of the chamber using a high volume air pump set to match the inlet flow rate. Tygon tubing connected to a circulating water bath was wrapped around the outside of the chamber to maintain the desired temperature. Chamber air temperature was continuously monitored using a Thermo Fisher Scientific Type K thermocouple with the probe inserted into the chamber. Samples of the exit gas were collected using two Tenax© tubes connected in series. Mass flow meters (Aalborg, Orangeburg, NY) were used to determine the volume of gas passing through the sampling tubes.

Objects were placed in the chamber and sealed. The fans were turned on and supply air was introduced into the chamber. After the exit air concentrations reached a constant level (approximately 120 min, determined from preliminary studies), three additional exit samples were consecutively collected and used to determine the final steady state concentration. After objects were removed, the chamber was purged to remove any residual compound for about 90 min or until blank samples no longer showed detectable compounds.

2.4. Evaluation of Emission Chamber Measurements

Constant rate emitters purchased from VICI Metronics were used to assess the reproducibility and accuracy of the emission rates generated from the chamber. The emitters are factory calibrated to yield a specific emission rate for the chemical of interest under specific temperature and pressure conditions. The reported accuracy of these emitters ranges from 15-25% depending on the chemical.

2.5. Controlled House Product Emission Studies

A 20-year-old, two-story residence with a basement was used for the consumer products emissions experiments. The house was equipped with a forced air heating, ventilation and cooling (HVAC) system and had a total air volume of approximately 600 m^3 (estimated from measured room dimensions) including the basement. Hobo® thermocouple dataloggers (Onset Computer Corporation, Bourne, MA) were placed in HVAC vents to determine the frequency and duration of the HVAC system operation with the house thermostat set at 78 °F during the summer months. The basement was equipped with a separate forced air heating system.

Four separate house studies were conducted. In each case, emission sources (consumer products) were placed in an upstairs bedroom (source room) with a fan blowing across them to simulate the mixing conditions used in the flow through chamber and reduce the time required to reach a steady state concentration in the source room. Air samples were collected from different locations over time throughout the residence under several HVAC operating scenarios (always off, always on, thermostat control). Background air samples were collected prior to introducing the emission sources into the house and outdoor air samples were collected throughout the study. Recording thermometers, placed in the air ducts, were used to monitor the frequency of HAVC operation by changes in temperature. The basement was equipped with a separate HVAC system that was run continuously during the first study and was turned off during the last three studies. Objects were also removed during the last half of the study to monitor the decline of VOC air concentrations and determine air exchange rates.

2.6. Air sampling

Air samples were collected using two Tenax© sorbent tubes attached in series to a constant flow rate pump following the general approach outlined in EPA Method TO-17. Samples were collected for approximately 10-30 min at known flow rates (100 to 150 ml/min) depending on the expected concentrations. Additional air sampling and analysis was conducted during the first house study using a HAPSITE® field portable GC/MS customized analytical method that was developed to enable both a rapid sample turnaround time and low detection limits for the target VOCs (Gorder and Dettenmaier, 2011). The HAPSITE® was used to monitor room concentrations more frequently than the sorbent tube approach. The data from the HAPSITE® was used to calculate air exchange rates within the residence.

2.7. Sample Analysis

Tenax© sorbent tube samples were analyzed using a thermal desorption GC/MS procedure. Sorbent tube samples were introduced into a Agilent® 6890/5793 GC/MS equipped with a J&W Scientific (Folsom, California) DB-624 capillary column (30 m x 0.25 mm ID x 1.4 µm film thickness) using a Perkin Elmer TurboMatrix ATD Automated Thermal Desorber operating under the following conditions: 5 min trap purge; cryo-trap temperature = –30 °C; Tenax© tube desorb = 300 °C for 10 min; cryo-trap temperature program –30 °C initial temperature to 320 °C at 40 °C/s, transfer line to GC/MS at 225 °C. The moisture control system, traps, and tubes were thermally cleaned between each sample. Chromatographic conditions were as follows: temperature program oven start at 35 °C hold for 2 min, followed by a ramp of 30 °C/min to 170 °C,

then 170 to 230 °C at 70 °C/min followed by a 1 min hold once the final temperature was reached. The MS was operated in selected ion monitoring (SIM) mode (TCE: 60, 95, and 130 m/z; 1,2-DCA: 49, 62, 64 m/z; PCE: 94, 131, 166 m/z). An external standard approach was used to quantify the mass of compounds collected in each trap. Standards were prepared by injecting 1 µL of standards dissolved in methanol onto clean Tenax© traps with a micro-syringe. Masses of compound injected on the tubes ranged from 100 to 100,000 pg. New standard curves were prepared every 2 weeks or when concentrations of the continuous calibration verification (CCV) standards deviated more than 10% from the expected value.

3. Results and Discussion

3.1. Emission Chamber Verification

The Dynacal® permeation tubes are designed to be inserted into a constant carrier gas flow to generate a steady test atmosphere at stable temperatures for testing and calibrating equipment. These tubes were used to evaluate the precision and accuracy of emissions obtained from the flow through chamber system by placing a permeation tube (5.9 cm length and 0.64 cm diameter) emitting TCE at 100 ng/min +/-15% at 30^{o}C into the chamber and comparing the measured emissions to those calculated using the VICI Metronics provided calibration equations to compensate for differences in environmental conditions (Appendix C), (Fig. 2-2).

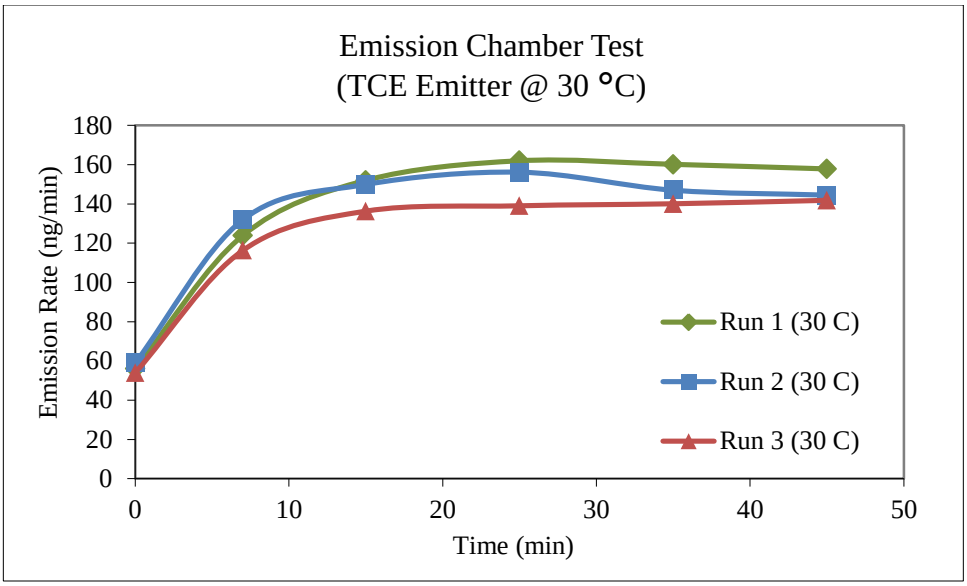

Fig. 2-2. Emission chamber, TCE emitter results at 30 °C

The average emission rate for triplicate experiments was 150 ng/min with a standard deviation of 9.9 ng/min and a 95% confidence interval of 11.2 ng/min. This compares favorably to the factory calibrated and adjusted emission rate of 150 ng/min.

3.2. Consumer Product Emission Rates

Average measured emission rates and standard deviations for a minimum of triplicate experiments for opened and unopened products are listed in Table 2-1. The molded plastic objects were not enclosed in any packaging when purchased and an unopened emission rate could not be determined.

The lamp base, provided by Hill Air Force Base, and was identified as a source of 1,2-DCA emissions during VI investigations but PCE emissions were not observed. This suggests that PCE emissions from the lamp base observed in the laboratory studies are associated with surface contamination due to sorption possibly acquired during storage (personal communication with Dr. Erik Dettenmaier).

Table 2-1
Measured VOC emission rates (± one standard deviation) for opened and unopened consumer products

Object	VOC Emitted	Emission Rate (µg/min) Unopened	Emission Rate (µg/min) Opened
E6000 Glue	PCE	1.33 ± 1.13	23.9 ± 2.93
Gun Cleaner	TCE	1.35 ± 0.14	2.38 ± .053
Lysol Toilet Cleaner	CCl_4	0.015 ± 0.005	0.019 ± 0.001
Lamp Base	1,2-DCA	NA	4.06 ± 0.15
Lamp Base	PCE	NA	6.08 ± 0.61

NA= not applicable

3.3. House Product Emission Studies

The consumer products used as emission sources varied slightly between the four studies based on the results from previous studies. For example, carbon tetrachloride was not detected during the first house study, thus the toilet bowl cleaner (Lysol with bleach) was not used in the subsequent house studies. Table 2-2 shows which products were used during each study.

Table 2-2
Consumer products (compound associated) used during each house product emission study

House Study	Objects used
1	Gun Cleaner (TCE), E-6000 Glue (PCE), Toilet Bowl Cleaner (CCl_4), Gingerbread Man (1,2-DCA)
2	Gun Cleaner (TCE), E-6000 Glue (PCE), Lamp base (1,2-DCA & PCE)
3	Gun Cleaner (TCE), Lamp Base (1,2-DCA & PCE)
4	Gun Cleaner (TCE), Lamp Base (1,2-DCA & PCE)

Also, to investigate the potential impact of product use patterns on the indoor air concentrations, the aerosol can gun cleaner containing TCE was introduced into the residence at various times after its last use, 2 days, 2 h, the night before use, and 10 min. Indoor air concentrations of 1,2-DCA, TCE and PCE measured in the four house studies are summarized in Tables 2-3, 2-4 and 2-5, respectively.

Concentrations were measured with the HVAC system off (unmixed) and on (mixed). The HVAC off columns refer to measurements taken 24-38 h after the objects were introduced into the residence. The HVAC on columns show the first measured air concentrations; 2-24 h after the HVAC system was turned on, with the objects still in the residence.

Table 2-3
1,2-Dichloroethane house product emission study results

1,2 - Dichloroethane (sources: gingerbread man, lamp base)								
	House Study 1		House Study 2		House Study 3		House Study 4	
Location	HVAC Off ($\mu g/m^3$)	HVAC On ($\mu g/m^3$)	HVAC Off ($\mu g/m^3$)	HVAC On ($\mu g/m^3$)	HVAC Off ($\mu g/m^3$)	HVAC On ($\mu g/m^3$)	HVAC Off ($\mu g/m^3$)	HVAC On ($\mu g/m^3$)
Source Room	0.20	0.13	3.15	1.15	2.13	NS	17.54	6.66
Upstairs Bedroom	0.12	0.13	2.24	1.42	0.85	NS	NS	NS
Living Room	0.11	0.11	1.72	1.33	0.62	NS	0.97	2.84
Basement	0.09	0.15	0.76	1.29	0.19	NS	0.55	1.14
Average		0.13		1.30				3.55
Outside	NS	NS	0.12	0.18	0.12	NS	0.19	0.20

NS = Not sampled

Table 2-4
Trichloroethene house product emission study results

Trichloroethene (source: gun cleaner)								
	House Study 1		House Study 2		House Study 3		House Study 4	
Location	HVAC Off ($\mu g/m^3$)	HVAC On ($\mu g/m^3$)	HVAC Off ($\mu g/m^3$)	HVAC On ($\mu g/m^3$)	HVAC Off ($\mu g/m^3$)	HVAC On ($\mu g/m^3$)	HVAC Off ($\mu g/m^3$)	HVAC On ($\mu g/m^3$)
Source Room	0.95	0.39	1.39	0.52	15.70	NS	170.12	36.76
Upstairs Bedroom	0.37	0.29	1.18	0.66	6.78	NS	NS	NS
Living Room	0.28	0.25	0.92	0.60	5.48	NS	48.29	24.44
Basement	0.11	0.25	0.53	0.59	1.15	NS	54.62	23.50
Average		0.30		0.59				28.23
Outside	NS	NS	0.06	0.13	≥ 0.05	NS	1.89	1.56

NS = Not sampled

Table 2-5
Tetrachloroethene house product emission study results

Tetrachloroethene (sources: E-6000 glue and lamp base)								
	House Study 1		House Study 2		House Study 3		House Study 4	
Location	HVAC Off ($\mu g/m^3$)	HVAC On ($\mu g/m^3$)	HVAC Off ($\mu g/m^3$)	HVAC On ($\mu g/m^3$)	HVAC Off ($\mu g/m^3$)	HVAC On ($\mu g/m^3$)	HVAC Off ($\mu g/m^3$)	HVAC On ($\mu g/m^3$)
Source Room	28.62	11.62	19.48	8.73	1.20	NS	6.18	2.22
Upstairs Bedroom	11.04	7.88	23.17	12.31	0.47	NS	NS	NS
Living Room	8.69	7.66	19.18	11.20	0.42	NS	0.40	1.00
Basement	2.81	7.68	14.38	11.02	0.18	NS	0.30	0.49
Average		8.71		10.82				1.24
Outside	NS	NS	0.91	1.11	0.26	NS	0.28	0.33

NS = Not sampled

3.4. House Air Exchange Rate (AER) Determination

HAPSITE® measured TCE concentrations for the source room during house study one were used to determine overall house air exchange rate. The AER was calculated using the concentration decay method:

$$N = {}^{1}/_{T} \times \ln({}^{C_O}/_{C_T}) \qquad (2.1)$$

where N = number of exchanges per day; T = time (days); C_O = concentration (µg/m^3) at T=0; C_T = concentration (µg/m^3) at T. Table 2-6 shows calculated air exchange rates with the HVAC system on using the HAPSITE® data as well as Tenax air samples collected 2 years later during house study four. An average air exchange rate from the 3-h decay in the source room using the HAPSITE® data of 4.5 volumes/day was used for the box model.

Table 2-6
Calculated air exchange rates using the concentration decay method and two sampling methods (portable GC/MS (HAPSITE®) and Tenax© sorbent tubes)

Sampling Method		TCE (3 hr decay)	PCE (3 hr decay)
HAPSITE®	Source Room	4.45	4.58
	Main Floor	2.58	2.99
Tenax©	Source Room	4.92	3.72
	Main Floor	4.82	4.82

3.5. Estimated and Measured Air Concentrations

The laboratory measured product emission rates were used to estimate indoor air concentrations in the test residence using a standard box model. The estimated concentrations were then compared to measured indoor air concentrations in order to

determine the ability of this approach to accurately predict potential air concentrations and assess the potential risk associated with the use of the products.

The following equation for a standard box model was used:

$$C_{air} = {}^{E}/_{IV} \qquad (2.2)$$

where C_{air} = indoor air concentration (µg/m^3); *E* = product emission rate (µg/d) measured; *I* = air exchange rate (volumes/day); *V* = indoor air volume (m^3). The test residence has a total air volume, estimated from measured room dimensions, including the basement of 600 m^3. Air exchange rates were measured as stated above and the average air exchange rate of 4.5 volumes/day was used.

Using the emission rates measured in the laboratory, estimates of potential indoor air concentrations were made using a standard box model assuming the air in the residence was well mixed (Table 2-7). Emissions from the 1,2-DCA containing lamp base, the E-6000 craft glue containing PCE, and the gun cleaner containing TCE resulted in estimated concentrations that were above the EPAs carcinogenic screening level risk concentrations. Table 2-7 also shows the average measured indoor air concentration using Tenax© tubes if that object was used in the house product emission study.

As both modeled concentrations and measured values from the whole house study indicate, objects are capable of causing indoor air concentrations approaching or exceeding the USEPA's risk assessment values. Brenner (2010) measured maximum indoor air concentrations using SUMMA canisters for TCE and PCE caused by vapor intrusion to be 1.69 and 0.51 µg/m^3, respectively, a factor of 3 to 16 lower than average concentrations measured in this study. These results demonstrate the potential for vapor

intrusion investigations to be confounded by consumer products, which may result in higher indoor air concentrations than those in some VI exposure scenarios.

Table 2-7
Estimated vs. Measured vs. Risk based indoor air concentrations resulting from VOC emitting products.

Product	VOC Emitted	Emission rate (µg/min)	Estimated indoor air concentration (µg /m^3)	Average measured mixed indoor air concentration (µg /m^3)	EPA Screening Level Carcinogenic Risk based concentration* (µg /m^3)
E-6000 Glue Unopened	PCE	1.3±1.1	0.69	NS	9.4
E-6000 Glue Opened	PCE	24±2.9	12.74	10.82	9.4
Gun Scrubber Unopened	TCE	1.3±0.11	0.69	0.30	0.43
Gun Scrubber Opened	TCE	2.4±0.5	1.27	28.23	0.43
Toilet Cleaner Unopened	CCl_4	0.015±0.005	0.008	NS	0.41
Toilet Cleaner Opened	CCl_4	0.019±0.001	0.01	ND	0.41
Lamp Base	1,2-DCA	4.06 ± 0.15	2.16	3.55	0.094
Lamp Base	PCE	6.08 ± 0.61	3.23	1.24	9.4

* http://www.epa.gov/reg3hscd/risk/human/rb-concentration_table/Generic_Tables/docs/resair_sl_table_run_MAY2013.pdf
*Indoor residential air concentrations, risk factor ($1X10^{-6}$)
NS = Not sampled; ND = Non detect

3.6. Conclusion

Both opened and unopened consumer products emit signifiant amounts of chlorinated volitile organic compounds (VOCs) that have the potential to confound VI investigations, as well as pose substancial health risks to home occupants. Initial indoor air concentrations of chlorinated solvents were highest in the room where the consumer products were introduced but were quickly and uniformly distributed throughout the three levels of the house when circulated with the HVAC system. The approach of using laboratory determined emission rates from consumer products combined with a standard box model can be used to predict indoor air concentrations suitable to screening level risk evaluations for determining the relative impact of indoor objects on VOC concentrations.

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CHAPTER 3

USE OF PLANTS AS PASSIVE SAMPLERS FOR VOLATILE ORGANIC COMPOUNDS (VOCS) IN INDOOR ENVIRONMENTS[1]

Abstract

Volatile organic compounds (VOCs), including many with documented adverse health effects, can enter indoor environments through internal (e.g. paints, paint strippers, fuels, cleaning supplies, pesticides, building materials, adhesives) and external sources (e.g. vapor intrusion (VI) from contaminated soil and/or groundwater and ambient air from automobiles and industrial facilities). Indoor air concentrations of VOCs vary widely, but concentrations of most VOCs are higher indoors than outdoors. Plants have been promoted as indoor air purifiers for decades but reports of their actual effectiveness for removing VOCs have varied widely. However, while remediation applications may be limited, the waxy cuticle coating on leaves may provide a simple, cost-effective and sustainable approach to sampling indoor air concentrations of VOCs. To investigate the potential use of plants as indoor air VOC samplers, three types of studies were performed. The first used a headspace approach to measure equilibrium leaf-air partition coefficients. The second study used a flow-through glass and stainless steel plant growth chamber to evaluate the relationship between air and plant leaf VOC concentrations in a flow through environment. The third study placed several VOC emission sources into a residential building and collected corresponding air and plant leaf samples over time. Good correlations between the leaf and air distribution coefficients in the three different

[1]Coauthored by W.J.Doucette

studies suggest that plant leaves can be used to monitor indoor air concentrations of VOCs.

1. Introduction

Adults living in North America spend an estimated 80-90% of their time indoors (Orwell et al., 2004; Dales et al., 2008) and concerns about the potential exposure to volatile organic compounds (VOCs) in indoor air have increased as new home construction techniques and improvements in heating, ventilation, and air conditioning (HVAC) efficiency have significantly reduced the introduction of outdoor air (Cohen, 1996).

Concentrations of VOCs in indoor air are generally 5 to 10 times higher than outdoors, with even higher indoor air concentrations where extreme cold weather conditions exist (Dales et al., 2008). Some of the VOCs identified in indoor air are considered suspected or confirmed carcinogens by the World Health Organizations (WHO) International Agency for Research on Cancer (IARC) and enter indoor environments through internal (e.g. paints, paint strippers, fuels, cleaning supplies, pesticides, building materials, adhesives) and external sources (e.g. vapor intrusion (VI) from contaminated soil and/or groundwater and ambient air from automobiles and industrial facilities).

The use of ornamental plants to reduce indoor air concentrations of VOCs has been studied for decades (NASA, 1989; Cornejo et al., 1999; Liu et al., 2007; Yang et al., 2009). However, stated removals differ widely and the variety of experimental approaches used to determine removals complicate comparisons among studies.

Depending on the plant and chemical of interest, VOC removal mechanisms that have been reported include stomatal uptake and metabolism (Baur et al., 1997), microbial transformation within plant growth media (Orwell et al., 2004), and sorption to leaves (Bacci et al., 1990; Keymeulen et al., 1997; Orwell et al., 2004). Modeling results suggest that the high plant biomass to air ratio necessary to make meaningful reductions in indoor air VOC concentrations make the use of houseplants as air cleaners impractical in most cases (Girman et al., 2009).

However, even if plants are unable to significantly impact indoor air concentrations, the waxy cuticle of leaves may allow common houseplants to be used as simple, cost-effective and sustainable passive indoor air samplers for VOCs. Successful implementation of this approach would potentially reduce costs associated with conventional passive sorbent samplers or active canisters, minimize sampler intrusions into the home, and potentially allow residents to directly participate in the sample collection activities.

Plants have been widely used as passive samplers for semi volatile organic compounds (SVOCs) in outdoor environments for compounds like PAHs (Lin et al., 2006; Li and Chen, 2009), PCBs (Nizzetto et al., 2006), dioxins (Nizzetto et al., 2006), herbicides and pesticides (Bacci et al., 1990) and predictive models relating leaf-air concentration ratios (bioconcentration factors) to octanol-air partition coefficients (Koa) have been developed (Bacci et al., 1990; Cornejo et al., 1999). Far fewer studies have examined the effectiveness of plants as samplers for more volatile compounds, especially in indoor environments.

Hiatt (1998) investigated the use of plant leaves to sample outdoor air for VOCs such as benzene, toluene, TCE and PCE and found that leaf-air concentration ratios could generally be predicted using existing Koa-based models, but plant species containing higher amounts of monoterpenes were greatly under predicted using the Koa-based models, suggesting the importance of lipid character. It was also reported that VOC uptake by leaves was rapid and higher vapor pressure compounds reached equilibrium concentrations faster. In a subsequent publication, Hiatt (1999) reported that leaves provided a good indication of early morning exposures when air concentrations were relatively constant but in the afternoon pulses of clean air during windy conditions quickly desorbed the VOCs from the leaves. The relatively fast uptake and release of VOCs from plant leaves observed by Hiatt (1999) may limit outdoor sampling applications where air concentrations can rapidly change due to changes in wind speed and direction but this is likely less important in indoor environments.

To investigate the potential of using plant leaves as passive samplers for indoor air VOC concentrations; three types of studies were performed. The first study used a headspace approach to measure equilibrium leaf-air partition coefficients as a function of VOC concentration and plant type. The second study used a glass and stainless steel plant growth chamber to more evaluate the distribution between VOCs in air and leaves in a more realistic flow-through system. The third study consisted of monitoring VOC concentrations in corresponding air and plant leaf samples over time after introducing several VOC sources into a residential building.

2. Materials and Methods

2.1. Plants

Four common houseplants were selected for study: a woody plant, ficus (*Ficus benjamina)*; a vine, golden pothos (*Epipremnum aureum)*; a flowering plant, spider fern (*Chlorophytus comsosum* 'vittatum'); and a succulent, Christmas cactus (*Schlumbergera truncate* 'harmony'). The plants were selected because they are commonly available hardy and have relatively low light requirements. Plants were purchased locally from several different vendors and re-potted in stainless steel planters from Stainless Lux (Livermore, CA) using a 50% peat moss and 50% vermiculate mix. Prior to their use, plants were kept under a 400-watt metal halide grow lamp with a 10-h photoperiod and were watered as needed to maintain health.

2.2. Chemicals

Glass ampules of custom mixed standards were purchased from Ultra Scientific (Haloethanes Mixture, DWM-520 mixed with BTEX) as 200 µg/ml solutions dissolved in methanol. Analytical standards were made from dilutions of these solutions. Dynacal® permeation tubes containing the compounds of interest (benzene, toluene, xylene, 1,2-dichloroethane, trichloroethene, tetrachloroethene) and calibrated to provide known emission rates (100 ng/min) at specific temperatures were purchased from VICI Metronics (Poulsbo, WA).

2.3. Solvent Extractable Lipid Content, Surface Area, and Water Fraction of Leaves

Leaves were collected from multiple plants of the same species using gloved hands and ethanol wiped scissors. Fresh tissue weights were recorded using a Mettler AJ100 analytical balance and the plant tissue was air-dried by placing on aluminum foil for 7 to 21 days with a lightly fitting aluminum foil covering. The tissue was then placed in a desiccator until a constant mass was obtained, usually 24-36 h. The water content was determined from the difference of the fresh and dry weights. After drying, the tissue was finely ground in a coffee grinder and approximately 1 grams dry weight was placed in 25/80 mm cellulose thimbles. Thimbles were then placed in desiccators until a constant mass was obtained, again typically 24 h. After noting the dry weight, thimbles were placed in a Soxhlet Extractor and extracted for 24 h with ethyl ether. At the end of the extraction, the remaining ethyl ether was evaporated and the flasks containing the extracted lipids were placed in desiccators until a constant mass was obtained. Differences in post-experiment and pre-experiment flask weights were used to determine the mass of lipid extracted. Spike recovery experiments were performed by adding known quantities of olive and vegetable oil to selected thimbles. Lipid content was calculated by dividing the extracted lipid weight by the dry tissue weight added to the thimble.

Surface areas, determined using a leaf area meter (LICOR Instruments, Model 6000) were plotted against fresh weights for approximately 30 leaf samples to generate correlations to predict surface area from fresh weight for each of the four plant species.

2.4. Static Headspace Determination of Leaf Air Distribution Coefficients

Leaf cuttings (whole ficus leaf, one segment of cactus, 4 to 6 inch lengths of spider fern, and half a pothos leaf cut along the midrib) were placed in pre-weighed 20 ml headspace vials and then re-weighed to determine plant sample mass. Mixtures of the six VOCs were then spiked into the vials containing the leaf samples and blank vials containing glass slides to yield six headspace concentrations: 0.25 mg/m^3, 0.5 mg/m^3, 1.25 mg/m^3, 2.5 mg/m^3, 3.75 mg/m^3, and 5 mg/m^3. The vials equilibrated for approximately 24 h at room temperature after spiking. Triplicate samples were run at each concentration for each of the four plant species.

A Hewlett-Packard® 7890A gas chromatograph (GC)/5973C mass spectrometer (MS) operated in Selected Ion Monitoring (SIM) mode and equipped with a CTC PAL autosampler configured for headspace sampling was used to measure headspace VOC concentrations. After a 30-min equilibration at 30°C, headspace samples were introduced into the GC/MS equipped with a J&W Scientific (Folsom, CA) 122-1334 capillary column (30 m x 0.25 mm ID x 1.4 μm film thickness), with an automated oven temperature program as follows: 35 °C initial temperature to 105 °C at 10 °C/min, followed by 50 °C/min to a final temperature of 180 °C. The concentrations of VOCs in the leaf samples were determined indirectly from the concentrations within the headspace.

The concentration of leaf-sorbed (pg VOC/kg fresh leaf weight) compound was calculated by subtracting the leaf-spiked headspace concentration value from the blank-spiked headspace concentration and then dividing by leaf weight. Leaf concentration factors (LCFs) in units of L/kg, were generated from the slope of the regression line

obtained by plotting the concentrations of VOC sorbed to the leaves by the vial headspace VOC concentration.

2.5. Flow Through Chamber

The flow through chamber used for the plant uptake studies consisted of a rectangular stainless steel tank (608 x 380 x 457mm (2 x 1.25 x 1.5 ft), 100 L) equipped with a mixing fan and gas inlet (bottom) and exit (top opposite side of inlet) ports. During experiments, the top was covered with a sheet of heavy tempered glass (650 x 430 x 6 mm) that rested against foam weather stripping that had been applied to the top rim of the tank (Fig. 3-1).

A pump (927CA18, Thomas) provided outside air to the chamber through a rotometer (FL. 2040, Omega Engineering, Inc., Stamford, CT) at a flow rate of 2 L/min. Another pump connected the exit side pulled the exhaust air at the same flow rate to prevent chamber pressure buildups. A hollow stainless steel cylinder (I.D. 10 mm x 450 mm long) was placed in the inlet flow path to hold the Dynacal® permeation tubes (VICI Metronics, Poulsbo, WA) containing the compounds of interest (1,2-dichloroethane, trichloroethene, tetrachloroethene, benzene, toluene, m-xylene). The permeation tubes were factory calibrated to provide known emission rates at specific flows and temperatures. Ports located just outside the chamber inlet and outlet enabled the collection of influent and effluent samples. Samples were drawn from the ports though two Tenax© sorbent tubes, a mass flow meter (Aalborg Model GFS-010343, Orangeburg, NY) and a constant flow rate pump (SKC Inc.) connected in series.

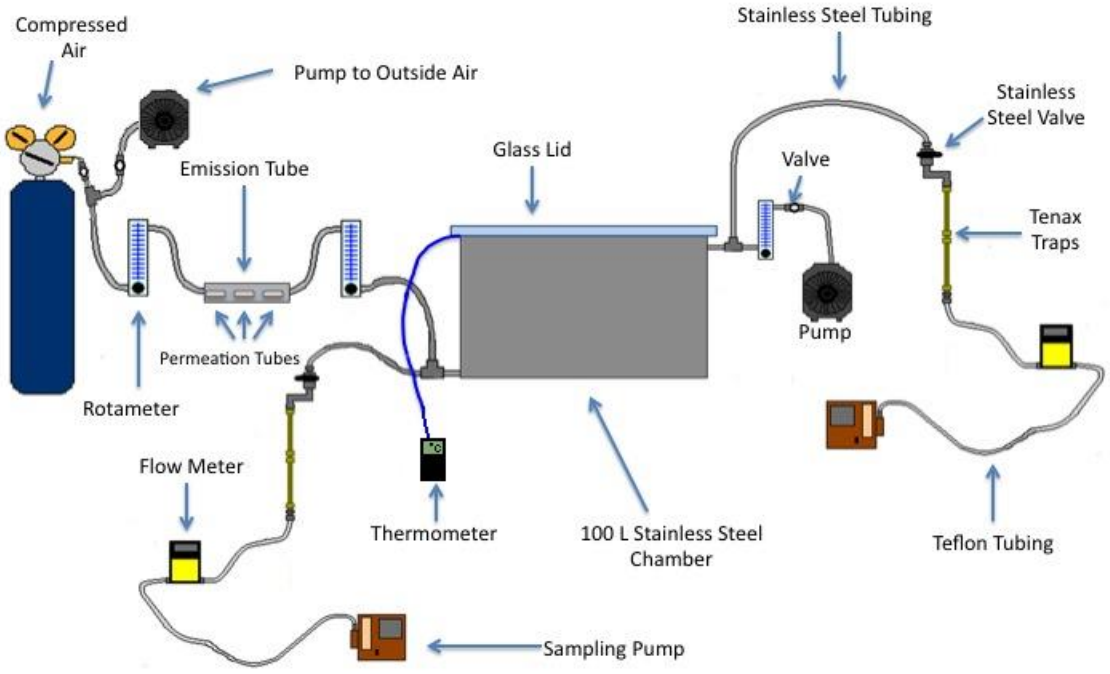

Fig. 3-1. Plant flow through chamber

To evaluate the uptake within the flow through system, two plants of the same species were placed into the chamber and the top was sealed with the glass sheet. Two plants were used to increase the plant to air ratio and increase the difference in effluent concentrations between chambers with and without plants. Permeation tubes were added to the inline cylinder, and the pump supplying outdoor air was turned on. Chamber influent and effluent samples were simultaneous collected on the Tenax traps for approximately 5 min at 100 ml/min at intervals of 15, 35, 55, 90, 120, 150 and 180 min. During desorption, supply air was diverted to bypass the permeation tubes and samples were taken at the following intervals: 195, 215, 235, 270, 300, 330, and 360 min.

To determine leaf air partition coefficients for comparison to the static headspace method, specimens of all four plant species were placed in the chamber with the permeation tubes releasing VOCs into the supply air. After a steady state effluent concentration was reached (~3 h, determined from preliminary studies), an air sample was taken, immediately following the air sample the glass cover was removed and triplicate leaf samples were collected and quickly placed into 20 ml headspace vials using a gloved hand and ethanol wiped scissors. The concentrations of VOCs in the leaves were determined using the same GC/MS protocol as previously described. However, in this case the headspace vials were equilibrated at 100 °C for 10 min prior to injection to increase desorption of the leaf bound VOCs.

2.6. House Studies

The object emission tests took place in a 20-year old, two-story residence with a basement. The house was equipped with a forced air heating, ventilation and cooling (HVAC) system and had a total air volume, including the basement, of 600 m^3 (estimated from measured room dimensions). Recording thermocouples were placed in HVAC vents to determine the frequency and duration of the HAVC operation with the house thermostat set at 78 °F. The basement had a separate forced air heating system.

Background air samples were collected just before the emitting objects were added to the house. Emitting objects were then quickly transported to a room on the second story of the residence (subsequently referred to as the source room) inside an airtight container. To minimize concentration increases within the container, objects were introduced just prior to transport and removed immediately removed upon arrival into the residence. After the objects were placed in the source room, the door was closed

and sealed (using a towel under the door) and the HAVC system turned off to prevent mixing and allow the concentrations in the source room to increase mimicking the approach used in the room to room sample scheme that originally identified the objects during VI investigations (Doucette et al., 2010). Twenty-four h after the objects were placed in the source room the door to the room was opened, and the HVAC system was turned on, mixing the house air. Twenty-four h after the objects were released throughout the home the objects were removed. Sampling occurred 4 to 6 times a day beginning with the background samples previously mentioned and continuing for 24 h after the objects were removed. During each air sampling event leaf samples from each of the four plant species were collected at the same time and placed in a headspace vial analysis as previously described.

Air samples were collected using two Tenax© sorbent tubes (Alltech Associates, Deerfield, Illinois) attached in series to a SKC Air Chek Sampler Model 224-43XR (Eighty Four, Pennsylvania) following the general approach outlined in EPA Method TO-17. Samples were collected for approximately 10 to 30 min at known flow rates from 100 to 150 ml/min depending on the expected concentrations. An Alltech Digital Flow Check™ model DFC™ Flowmeter (Nicholasville, Kentucky) was used to confirm flow measurements at the beginning and end of each sampling event.

Tenax sorbent tube samples were analyzed using a thermal desorption GC/MS procedure. Sorbent tube samples were introduced into a Agilent® 6890/5793GC/MS equipped with a J&W Scientific (Folsom, California) DB-624 capillary column (30 m x 0.25 mm ID x 1.4 μm film thickness) using a Perkin Elmer TurboMatrix ATD Automated Thermal Desorber operating under the following conditions: 5 min trap purge; cryo-trap

temperature = –30 °C; Tenax© tube desorb = 300 °C for 10 min; cryo-trap temperature program –30 °C initial temperature to 320 °C at 40 °C/s, transfer line to GC/MS at 225 °C.

The moisture control system, traps, and tubes were thermally cleaned between each sample. Chromatographic conditions were as follows: oven temperature program start at 35 °C hold for 2 min then ramp at 30 °C/min to 170 °C, followed by 70 °C/min from 170 to 230 °C with a 1 min hold at the final temperature. The MS was operated in selected ion monitoring (SIM) mode. An external standard approach, was used to quantify the mass of compounds collected in each trap. Standards were prepared by injecting 1 μL of standards dissolved in methanol onto clean Tenax© traps with a micro-syringe. Masses of compound injected on the tubes ranged from 100 to 100,000 pg. New standard curves were prepared every 2 weeks or when concentrations of the continuous calibration verification (CCV) standards deviated more than 10% from the expected value.

3. Results and discussion

3.1. Static Headspace Determination of Leaf Concentrations Factors (LCFs)

Leaf concentration factors (LCF), defined as the mass of compound per kilogram of leaf, C_L, divided by the mass of compound per liter of air, C_A,

$$\mathrm{LCF} = \frac{C_L\,(\mathrm{g/kg})}{C_A\,(\mathrm{g/L})} \tag{3.1}$$

were used to express the relationship between leaf and air concentrations of VOCs. The LCFs from the static headspace experiment are shown in Table 3-1. They were generated from the slope of the linear regression line obtained by plotting leaf to air concentrations.

The LCF is listed in Table 3-1 along with the 95% confidence interval determined from the regression line. As shown in Table 3-1, the LCFs generally increase as the Koa of the VOC increases and as the lipid content of the leaf increases, detailed leaf properties can be seen in Appendix D. This general trend is most evident for ficus, the plant species with the highest leaf lipid content.

Table 3-1
Leaf concentration factor (LCF ± 95% C.I.) results of static headspace

Compound	Log Koa	Ficus [12.4%] Log LCF (L/Kg)	Spider [9.30%] Log LCF (L/Kg)	Pothos [6.67%] Log LCF (L/Kg)	Cactus [3.82%] Log LCF (L/Kg)
Benzene	2.78[a]	1.48E0 ± 2.28E-1	1.07E0 ± -3.62E-2	9.57E-1 ± 1.64E-1	8.43E-1 ± -6.02E-1
1,2-DCA	2.78[a]	1.65E0 ± 8.60E-3	1.43E0 ± 1.37E-1	1.37E0 ± 5.31E-2	1.28E0 ± -3.28E-1
TCE	2.99[a]	1.62E0 ± 2.62E-1	1.22E0 ± -9.69E-2	9.63E-1 ± 1.24E-1	8.65E-1 ± -5.09E-1
Toluene	3.31[b]	1.87E0 ± 3.96E-1	1.46E0 ± 8.24E-1	1.53E0 ± 4.32E-3	1.24E0 ± -1.25E-1
PCE	3.48[b]	1.98E0 ± 7.53E-1	1.24E0 ± -2.68E-1	1.17E0 ± 1.46E-1	1.16E0 ± -2.08E-1
Xylene	3.78[b]	2.28E0 ± 9.57E-1	1.86E0 ± 1.47E0	BDL	1.69E0 ± 5.69E-1

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[%] – Lipid % by dry weight; BDL = Below detection limit; Error shows 95% C.I.

3.2. Flow Through Chamber Studies: Uptake and Release Studies, LCF Determinations

The bench top flow through chamber was designed to determine LCFs under more realistic flow through conditions and evaluate the potential for mass removal of the VOCs by the planted pots. Figure 3-2 shows the effluent concentration over time with

one or two plants in the chamber. See Appendix E for all compounds. As expected an increase in plant mass shows a larger decrease in the effluent concentration during the time that VOCs are being introduced into the chamber. Based on these results, two plants were used in each run to increase the difference in effluent concentrations when compared to blank chamber runs.

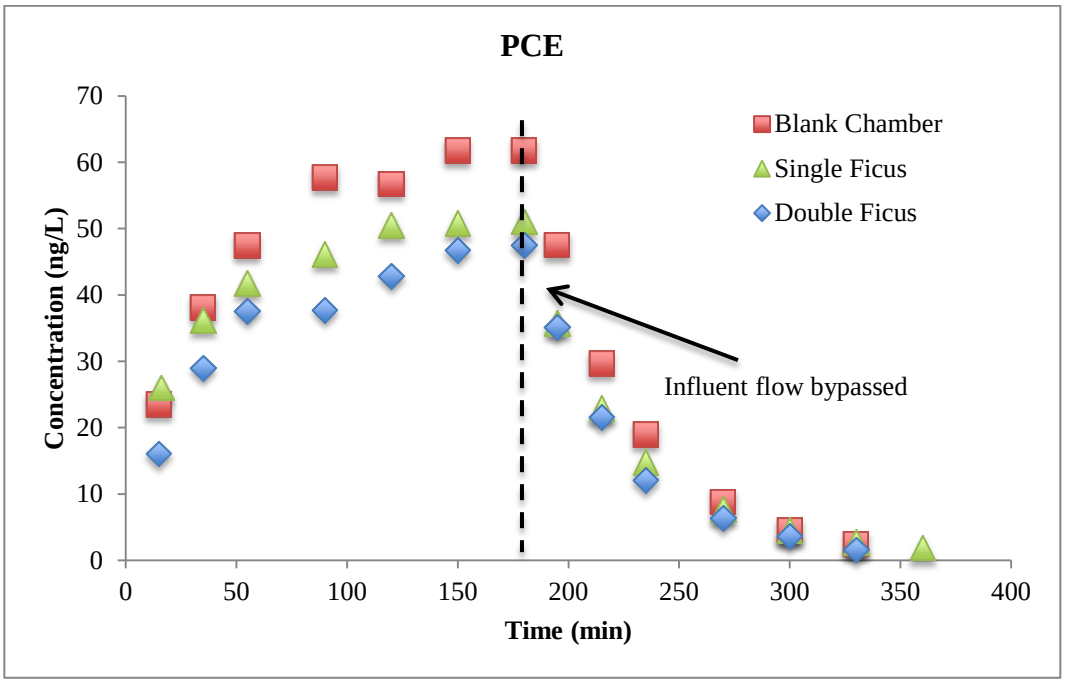

Fig. 3-2. Effluent concentration time series plot determination of PCE with single and double ficus mass compared to a blank chamber

The lack of an observable lag phase during either the uptake or release phase of the effluent concentration time series plots (Figure 3-2), suggests that foliar sorption of VOCs is occurring rapidly relative to the 30-min sampling interval.

Unfortunately, the determination of LCF values using the flow through chamber approach was not successful because of the sampling approach used. After collecting an effluent sample to determine the VOC concentration in the chamber, the chamber was opened and triplicate leaf samples were collected as quickly as possible. However, once

the chamber was opened for sample collection, VOC concentrations in the air surrounding the leaves rapidly decreased. With the rapid decrease in air concentrations, the leaves quickly released the sorbed VOC. This is illustrated in Figure 3-3 showing that declining ficus leaf concentrations during a triplicate leaf-sampling event where sample collection time was approximately one minute per sample. The rapid change in concentration suggested that plant samples used to sample indoor air would provide a time specific air concentration rather than an integrated air concentration.

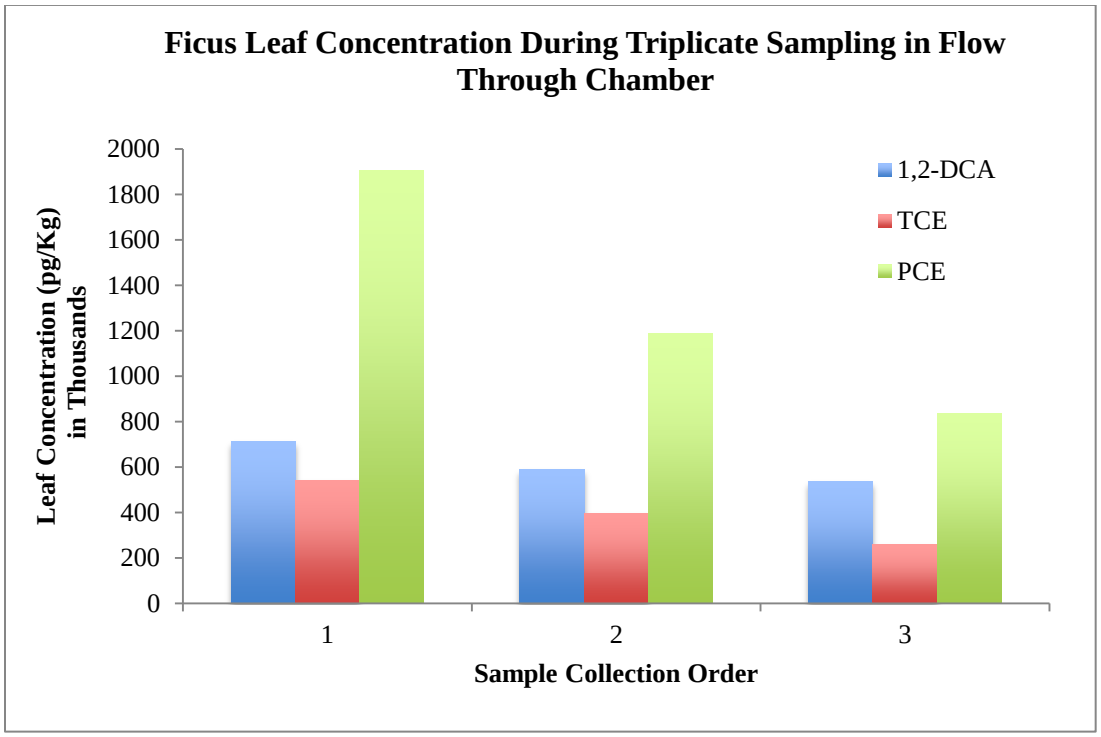

Fig. 3-3. Ficus leaf concentrations during a triplicate leaf-sampling event for the flow through chamber.

3.3. Mass Recovery

Mass balance was performed on the flow through chamber effluent concentration time series plots to determine the mass not recovered during the experiments, and can be seen in Table 3-2.

Table 3-2
Mass unrecovered (percent ± standard deviation) during flow through chamber experiment

Run Type	Benzene	1,2-DCA	TCE	Toluene	PCE	Xylene
Blank	-3.26 ± 6.18	-4.02 ± 1.51	-7.24 ± 5.23	-1.42 ± 9.20	-2.24 ± 1.02	-2.57 ± 1.82
Ficus	35.1 ± 13.5	16.5 ± 6.39	13.8 ± 7.61	46.0 ± 11.1	18.7 ± 6.51	48.4 ± 12.5
Spider	48.3 ± 6.22	11.2 ± 6.80	4.42 ± 6.94	62.7 ± 10.0	8.81 ± 7.30	62.3 ± 9.79
Pothos	34.5 ± 20.9	13.2 ± 3.38	8.88 ± 5.16	55.4 ± 21.7	11.8 ± 3.39	58.2 ± 19.3
Cactus	15.2 ± 9.21	13.1 ± 1.40	9.26 ± 2.33	53.6 ± 6.47	11.8 ± 2.25	56.9 ± 4.69

Table 3-2 shows the mass not recovered from the flow through chamber runs with and without plants present. The negative mass values reported for the blank runs indicate that contamination within the chamber or tubing could be occurring but is occurring so mildly that it is not a concern. Hydrocarbons are being removed at larger concentrations than that of the chlorinated compounds most likely due to the rapid degradation in the soil. With the occurrence of foliar sorption and desorption the unrecovered mass for chlorinated compounds, given that degradation in the soil is unlikely, should be near that of the blank runs. This is not observed however, suggesting the plant is either degrading the chlorinated compounds or there is some fraction of the compounds that are not desorbing over the time frame of the study (Table 3-2).

3.4. House Studies: LCFs

LCFs were calculated for the house studies using the same regression approach described previously. A similar trend to that observed in the static headspace studies of increasing LCF with increasing leaf lipid content as well as compound Koa was observed as shown in Table 3-3. Using the VOC sources described earlier, the air concentrations measured during the full-scale house studies were a factor of two to six lower than that of

the flow through chamber and factors of five to a hundred lower from that of the static headspace experiment. Due to the lower air concentrations, leaf concentrations for some compounds were below detectable levels.

Table 3-3
Leaf concentration factor (LCF ± 95% C.I.) results from house study

Compound	Log Koa	Ficus [12.4%] Log LCF (L/Kg)	Spider [9.30%] Log LCF (L/Kg)	Pothos [6.67%] Log LCF (L/Kg)	Cactus [3.82%] Log LCF (L/Kg)
Benzene	2.78[a]	BDL	BDL	5.81E-1 ± 1.70E-2	BDL
1,2-DCA	2.78[a]	1.18E0 ± 8.46E-1	7.44E-1 ± 6.73E-1	9.03E-1 ± 4.39E-1	8.97E-1 ± 3.47E-1
TCE	2.99[a]	1.41E0 ± 3.95E-1	1.04E-1 ± 1.59E-1	7.56E-1 ± - 1.95E-1	9.47E-1 ± - 6.08E-1
Toluene	3.31[b]	BDL	BDL	4.77E-1 ± - 3.02E-1	BDL
PCE	3.48[b]	1.47E0 ± 1.11E0	BDL	5.24E-1 ± 6.37E-1	2.42E-1 ± 5.92E-1
Xylene	3.78[b]	1.85E0 ± 1.12E0	8.89E-1 ± 3.74E-2	6.14E-1 ± - 3.15E-2	BDL

a- Gruber D, Langebheim D, Gmehling J. Measurement of activity coefficients at infinite dilution using gas-liquid chromatography. 6. Results for systems exhibiting gas-liquid interface adsorption with 1-octanol. J. Chem. Eng. Data 1997; 42:882-885.
b- Abraham MH, Le J, Acree Jr WE, Carr PW, Dallas AJ. The solubility of gases and vapors in dry octan-1-ol at 298 K. Chemosphere 2001; 44:855-863.

[%] – Lipid % by dry weight; BDL = Below Detection Limit; Error shows 95% C.I.

3.5. Comparison of LCF between studies

Comparison between the LCFs generated for the static headspace and the house studies techniques for ficus, spider, pothos and cactus can be seen in Tables 3-4, 3-5, 3-6 and 3-7, respectively. The overlap in confidence intervals between the two studies shows that the LCFs generated are not statistically different. The static headspace study

provided more precise data, perhaps due the reduced analytical variability associated with the higher concentrations evaluated.

Table 3-4
Leaf concentration factor (LCF) comparisons for ficus from the static headspace and house study experiments

Ficus [12.4%]						
Experiment	Benzene Log LCF (L/Kg)	1,2-DCA Log LCF (L/Kg)	TCE Log LCF (L/Kg)	Toluene Log LCF (L/Kg)	PCE Log LCF (L/Kg)	Xylene Log LCF (L/Kg)
Static Headspace	1.48E0 ± 2.28E-1	1.65E0 ± 8.60E-3	1.62E0 ± 2.62E-1	1.87E0 ± 3.96E-1	1.98E0 ± 7.53E-1	2.28E0 ± 9.57E-1
House Study	BDL	1.18E0 ± 8.46E-1	1.41E0 ± 3.95E-1	BDL	1.47E0 ± 1.11E0	1.85E0 ± 1.12E0

[%] – Lipid % by dry weight; BDL = Below Detectable Limit; Error shows 95% C.I.

Table 3-5
Leaf concentration factor (LCF) comparisons for spider from the static headspace and house study experiments

Spider [9.30%]						
Experiment	Benzene Log LCF (L/Kg)	1,2-DCA Log LCF (L/Kg)	TCE Log LCF (L/Kg)	Toluene Log LCF (L/Kg)	PCE Log LCF (L/Kg)	Xylene Log LCF (L/Kg)
Static Headspace	1.07E0 ± -3.62E-2	1.43E0 ± 1.37E-1	1.22E0 ± -9.69E-2	1.46E0 ± 8.24E-1	1.24E0 ± -2.68E-1	1.86E0 ± 1.47E0
House Study	BDL	7.44E-1 ± 6.73E-1	1.04E-1 ± 1.59E-1	BDL	BDL	8.89E-1 ± 3.74E-2

[%] – Lipid % by dry weight; BDL = Below Detectable Limit; Error shows 95% C.I.

Table 3-6
Leaf concentration factor (LCF) comparisons for pothos from the static headspace and house study experiments

Pothos [6.67%]						
Experiment	Benzene Log LCF (L/Kg)	1,2-DCA Log LCF (L/Kg)	TCE Log LCF (L/Kg)	Toluene Log LCF (L/Kg)	PCE Log LCF (L/Kg)	Xylene Log LCF (L/Kg)
Static Headspace	9.57E-1 ± 1.64E-1	1.37E0 ± 5.31E-2	9.63E-1 ± 1.24E-1	1.53E0 ± 4.32E-3	1.17E0 ± 1.46E-3	BDL
House Study	5.81E-1 ± 1.70E-2	9.03E-1 ± 4.39E-1	7.56E-1 ± -1.95E-1	4.77E-1 ± -3.02E-1	5.24E-1 ± 6.37E-1	6.14E-1 ± -3.15E-2

[%] – Lipid % by dry weight; BDL = Below Detectable Limit; Error shows 95% C.I.

Table 3-7
Leaf concentration factor (LCF) comparisons for cactus from the static headspace and house study experiments

Cactus [3.82%]						
Experiment	Benzene Log LCF (L/Kg)	1,2-DCA Log LCF (L/Kg)	TCE Log LCF (L/Kg)	Toluene Log LCF (L/Kg)	PCE Log LCF (L/Kg)	Xylene Log LCF (L/Kg)
Static Headspace	8.43E-1 ± -6.02E-1	1.28E0 ± -3.28E-1	8.65E-1 ± -5.09E-1	1.24E0 ± -1.25E-1	1.16E0 ± -2.08E-1	1.69E0 ± 5.69E-1
House Study	BDL	8.97E-1 ± 3.47E-1	9.47E-1 ± -6.08E-1	BDL	2.42E-1 ± 5.92E-1	BDL

[%] – Lipid % by dry weight; BDL = Below Detectable Limit; Error shows 95% C.I.

3.6. Comparison of LCF to Koa

Figure 3-4 shows the relationship between ficus LCF generated during the static headspace study and log Koa value for the compounds used in this study, other plant species graphs can be seen in Appendix F (Figures F-1 – F-4). The trend of increasing LCF for increased chemical Koa value was observed in all three studies.

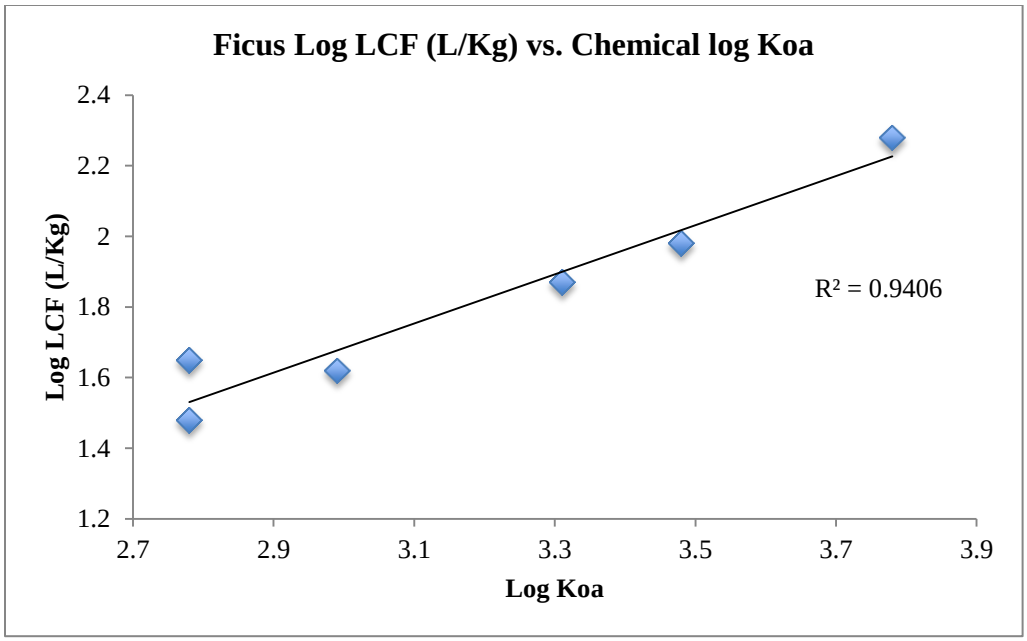

Fig. 3-4. Static headspace ficus LCF vs Chemical Koa value

3.7. Relationship to Other Studies

The LCFs obtained from the static headspace experiments, which yielded the most precise data, were compared to bioconcentration factors by volume (BCF_V) estimated using the relationship developed by Patterson et al. (1991):

$$BCF_V = 0.19 + 0.7K_{WA} + 0.05K_{OA} \quad (3.2)$$

where Kwa is defined as the water to air partition coefficient and Koa is defined as the octanol air partition coefficient. Patterson et al. (1991) calculated BCF_V using wet weights and leaf and air concentrations in g/m^3, resulting in a unitless BCF_V value. In order to compare LCF generated in this study (L/kg) to the estimated BCF_V values, the BCF_V values were converted to L/kg using the leaf density reported by Patterson et al. (1991) of 0.89 g/cm^3. As shown in Table 3-8, the estimated LCF are most similar to the experimental LCFs for ficus, which have the highest lipid content (12.4%) of the four plant species evaluated in this study.

Table 3-8
Static headspace leaf concentration factors (LCFs ± 95% C.I.) compared to chemically derived bioaccumulation factors by volume (BCF_V)

Compound	Log BCF_V (L/Kg)	Ficus [12.4%] Log LCF (L/Kg)	Spider [9.30%] Log LCF (L/Kg)	Pothos [6.67%] Log LCF (L/Kg)	Cactus [3.82%] Log LCF (L/Kg)
Benzene	1.53	1.48E0 ± 2.28E-1	1.07E0 ± -3.62E-2	9.57E-1 ± 1.64E-1	8.43E-1 ± -6.02E-1
1,2-DCA	1.53	1.65E0 ± 8.60E-3	1.43E0 ± 1.37E-1	1.37E0 ± 5.31E-2	1.28E0 ± -3.28E-1
TCE	1.74	1.62E0 ± 2.62E-1	1.22E0 ± -9.69E-2	9.63E-1 ± 1.24E-1	8.65E-1 ± -5.09E-1
Toluene	2.06	1.87E0 ± 3.96E-1	1.46E0 ± 8.24E-1	1.53E0 ± 4.32E-3	1.24E0 ± -1.25E-1
PCE	2.23	1.98E0 ± 7.53E-1	1.24E0 ± -2.68E-1	1.17E0 ± 1.46E-1	1.16E0 ± -2.08E-1
Xylene	2.53	2.28E0 ± 9.57E-1	1.86E0 ± 1.47E0	BDL	1.69E0 ± 5.69E-1

[%] - Lipid % by dry weight; Error shows 95% C.I.

Lipid normalization of the LCFs reduces the variability between species but does not fully explain the difference among them. This suggests that some other factor besides lipid content is driving foliar uptake of these compounds. Normalizing the LCFs to the surface area of the leaves was also evaluated (data not shown) but this did not improve the relationship between LCFs and species. Lipid quality and/or type might play an important role in foliar uptake and may help explain some of the species differences, but measuring these factors was beyond the scope of this study.

Welke et al. (1998) studied the sorption of VOCs to plant surfaces by generating a polymer matrix membrane from digested and extracted cuticles from mature tomato fruits. The study was conducted in a similar fashion to the static headspace experiment,

using the matrix membrane in vials rather than leaf samples. Welke et al. (1998) described a partition coefficient K_{MXa} generated by:

$$K_{MXa} = C_{MX}/C_a \quad (3.3)$$

where C_{MX} was the concentration in the matrix (mol/L) and C_a was the concentration in the air (mol/L). For comparison, the K_{MX} values of Welke were converted to LCF in L/kg using the density of the matrix (1.12 kg/L). The resulting values are listed in Table 3-9.

Table 3-9
Static headspace, lipid normalized leaf concentration factors (LCFs) compared to citicular matrix/air (K_{MXa}) partition coefficients

Compound	Log Corrected K_{MXa}	Ficus Lipid Normalized Log LCF (L/Kg)	Spider Lipid Normalized Log LCF (L/Kg)	Pothos Lipid Normalized Log LCF (L/Kg)	Cactus Lipid Normalized Log LCF (L/Kg)
Benzene	2.58	2.38	2.10	2.13	2.26
1,2-DCA	2.72	2.56	2.46	2.55	2.69
TCE	2.83	2.52	2.25	2.14	2.28
Toluene	3.10	2.78	2.50	2.70	2.66
PCE	2.93	2.89	2.27	2.35	2.58
Xylene	3.51	3.19	2.89	NA	3.10

Although LCF values differ from that of the K_{MXa} values it shows that lipid content is the driving factor for VOC sorption. The difference in values can perhaps be explained by the enzymatically digested fruit tissue used by Welke et al. (1998) rather than the fresh leaves corrected based on extractable lipid content.

3.8. Conclusion

Leaf concentration factor (LCF) increases with increasing chemical Koa value as well as increasing plant lipid content. This relationship held true for the two experiments

that generated LCF values conducted within this study. This suggests that plants can provide a simple and unobtrusive media for sampling indoor air. The rapid change in plant VOC concentrations observed in the flow through chamber experiments during leaf sampling suggests that leaf samples can provide time specific air concentrations rather than intergrated concentrations. Additional investigations need to be completed to further understand the driving factor between sorbed volatiles and LCF, as lipid content and chemical Koa alone does not fully explain the relationship.

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CHAPTER 4

SUMMARY AND CONCLUSIONS

Used and unused consumer products can be the source of measurable concentrations of volatile organic compound (VOC) concentrations in the indoor air of residences. These products have the potential to confound VI investigations as well as pose health risks. In a product emission study conducted within an actual residence, it was found that VOC air concentrations were highest in the room where the consumer products were located. However concentrations were quickly and uniformly distributed throughout the three levels of the house as soon as the HVAC system was turned on and the resulting VOC air concentrations exceeded USEPA carcinogenic risk based concentrations for indoor environments.

Indoor air concentrations predicted using laboratory measured VOC emission rates from consumer products with a standard box model calibrated to the house closely matched the measured air concentrations obtained during several controlled house studies. This suggests that the approach is suitable for screening level risk evaluations and for determining the relative impact of consumer products on VOC concentrations.

The correlation between leaf concentration factor (LCF) and air concentration suggest that plants can be used as passive samplers for VOCs. LCFs increased with increasing chemical octanol air partition coefficients (Koa) as well as increasing plant lipid content. The relationship held true for the two experiments conducted within this study that generated LCFs. This suggests that plants can be used as passive samplers in indoor environments, and plants with a higher leaf lipid content are the more senstive. Additional investigations need to be completed to further understand the controlling

factors between sorbed VOCs and LCFs, as lipid content and chemical Koa alone does not fully explain the relationship.

CHAPTER 5

ENGINEERING SIGNIFICANCE

This study helps to assess the impact of consumer products on indoor air. It was shown that known VOC emission rates from consumer products can be used with a standard box model to generate screening level predictions of indoor air concentrations.

This approach can be used during VI studies to help prevent false positives due to indoor sources, and prevent the costs associated with mitigation systems when they are not needed. It also provides an important tool for the evaluation of consumer products on indoor air quality.

Based on the similarity between leaf concentration factors (LCF) obtained using the different experiments, the results of this work also suggest that plants can be used as passive samplers for determining VOC concentrations in indoor air. A strong relationship between the lipid content of the leaves and the octanol air partition coefficient (Koa) of the compound of interest was also observed but does not fully explain the sorption of VOCs to leaf surfaces. Nevertheless, it suggests that plant species with a higher lipid contents are the best species to use due to increased sorption. Results from the attempted determination of LCFs during the flow through chamber study suggest rapid kinetics, this suggests that leaf samples will provide time specific air concentrations rather than integrated air samples.

APPENDICES

APPENDIX A

CHEMICAL PROPERTIES

Table A-1: Chemical Properties Table

Cas #	Chemical Compound	Molecular Weight	Melting Point (°C)	Boiling Point (°C)	Log Koa	Log Kow	Henrys Law Constant $(\frac{atm \cdot m^3}{mole})$	Vapor Pressure (mm Hg)	Solubility (mg/L)	OSHA 8-hour Exposure Limit (ppm_v)
71-43-2	Benzene	78.11	5.5	80.1	2.78[6]	2.13[7]	5.55E-03[10]	94.8[4]	1790[11]	10[12]
108-88-3	Toluene	92.14	-95	111	3.31[6]	2.73[7]	6.64E-03[10]	28.4[4]	526[14]	200[12]
108-38-3	m-Xylene	106.16	-48	139	3.78[6]	3.20[7]	7.18E-03[14]	8.29[3]	161[14]	100[12]
107-06-2	1,2-Dichloroethane	98.96	-35	84	2.78[1]	1.48[7]	1.18E-03[9]	78.9[4]	8600[8]	50[12]
79-01-6	Trichloroethylene	131.39	-73	87.2	2.99[1]	2.42[7]	1.00E+00[9]	69.0[2]	1280[8]	100[12]
127-18-4	Tetrachloroethylene	165.83	-19	121.1	3.48[1]	3.40[7]	1.77E-02[5]	18.5[13]	206[8]	100[12]

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APPENDIX B

CONSUMER PRODUCTS

Fig. B-1. E-600 Glue (PCE)

Fig. B-2. Lamp base (1,2-DCA & PCE)

Fig. B-3. Toilet bowl cleaner (Lysol with bleach) (CCl_4)

Fig. B-4. Gun scrubber (Birchwood Casey) (TCE)

Fig. B-5. Gingerbread man (1,2-DCA)

APPENDIX C

EMISSION CHAMBER SUPPORTING MATERIAL

VICI Metronics permeation tube calibration equations

VICI Metronics provided calibration equations that allowed emission rates to be calculated at different temperatures and pressures:

$$C = \frac{P \text{ x } (\frac{24.46}{mw})}{F_M}$$

where: C = concentration, P = permeation rate, F_M = Total flow of the calibration mixture at observed conditions found using the equation below, and mw = molecular weight.

A higher flow rate was used (4 L/min) in the emission flow through chamber than VICI Metronics initially calibrated the permeation tubes. The following equation was used along with the equation above to determine the adjusted permeation rate (P) for the emitters in the chamber:

$$F_C = F_M \sqrt{\frac{P}{760} \text{ x } \frac{298}{(t + 273)}}$$

F_c = flow rate at reference conditions (25°C and 760 mm Hg), F_M = indicated flow rate at observed conditions.

APPENDIX D

LEAF DATA AND CHARACTERISTICS

Table D-1: Ficus leaf data

Ficus					
Sample ID	Wet Weight (g)	Surface Area (sq cm)	Surface Area / Weight	Dry Weight (g)	Fractional water content
1	0.3138	15.40	49.08	0.0897	0.7141
2	0.3767	16.73	44.41	0.1073	0.7152
3	0.516	29.13	56.45	0.1547	0.7002
4	0.3626	17.79	49.06	0.1155	0.6815
5	0.376	17.29	45.98	0.1180	0.6862
6	0.4621	22.97	49.71	0.1500	0.6754
7	0.6371	32.04	50.29	0.1856	0.7087
8	0.3571	18.11	50.71	0.1395	0.6094
9	0.4891	24.95	51.01	0.1434	0.7068
10	0.4454	21.79	48.92	0.1234	0.7229
11	0.5266	26.59	50.49	0.1630	0.6905
12	0.4048	21.11	52.15	0.1511	0.6267
13	0.396	20.32	51.31	0.1136	0.7131
14	0.2121	10.94	51.58	0.0678	0.6803
15	0.2055	11.17	54.36	0.0657	0.6803
16	0.3995	27.00	67.58	0.1159	0.7099
17	0.3094	16.81	54.33	0.0763	0.7534
18	0.2715	15.09	55.58	0.0815	0.6998
19	0.6906	32.92	47.67	0.2261	0.6726
20	0.5669	28.45	50.19	0.1741	0.6929
21	0.3274	17.31	52.87	0.0849	0.7407
22	0.2095	10.89	51.98	0.0566	0.7298
23	0.3973	18.94	47.67	0.1202	0.6975
24	0.2987	14.75	49.38	0.0790	0.7355
25	0.3677	17.71	48.16	0.1230	0.6655
26	0.2274	14.17	62.31	0.0672	0.7045
27	0.1845	11.37	61.63	0.0453	0.7545
28	0.2053	10.37	50.51	0.0543	0.7355
29	0.2156	10.51	48.75	0.0708	0.6716
30	0.1336	6.24	46.71	0.0415	0.6894
	0.4588	23.93		NA	NA
	0.638	31.28		NA	NA
	0.3592	21.86		NA	NA
	0.6537	35.91		NA	NA
	0.3705	24.89		NA	NA
Average	0.3629	18.62	51.69	0.1102	0.6988
Standard Dev.	0.1380	6.92	4.99	0.0454	0.0325

Table D-2: Ficus lipid extraction data

Ficus Lipid Extractions						
Sample ID	Sample Type	Sample Weight (g)	Pre Weight (g)	Post Weight (g)	Extraction Weight (g)	Lipid % / % Recovery
1	Ficus A	1.0114	109.8552	109.9714	0.1162	
2	Ficus B	0.9921	109.7791	109.9072	0.1281	0.1291
3	Ficus C	1.0725	124.6491	124.7859	0.1368	0.1276
4	Olive Oil	0.1065	114.2842	114.4026	0.1184	1.1117
5	Veggie Oil	0.1086	109.9325	110.0502	0.1177	1.0838
6	Blank		113.3223	113.3224	0.0001	
					Lipid % by dry weight	
					Average	0.1239
					Std Dev.	0.0078
	Ficus Dry Weight %=			0.3012		
	Ficus Lipid % =			0.1239		
	Surface Area/Wet weight =			51.69		

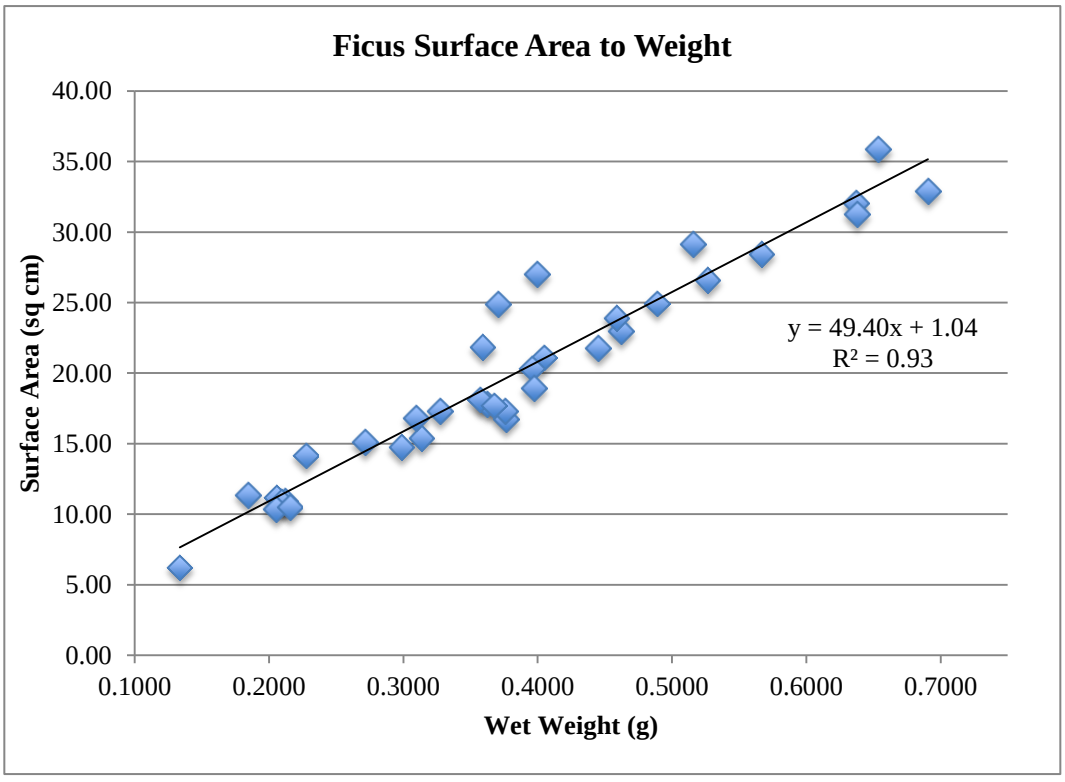

Fig. D-1. Ficus weight to surface area determination

Table D-3: Pothos leaf data

Pothos					
Sample ID	Wet Weight (g)	Surface Area (sq cm)	Surface Area / Weight	Dry Weight (g)	Fractional water content
1	0.9705	30.85	31.79	0.0830	0.9145
3	1.3136	40.55	30.87	0.1173	0.9107
4	1.2584	36.34	28.88	0.1292	0.8973
5	1.0961	37.64	34.34	0.0873	0.9204
6	1.5838	51.09	32.26	0.1443	0.9089
7	1.8208	52.11	28.62	0.1994	0.8905
8	1.2425	40.91	32.93	0.1461	0.8824
9	1.5148	47.09	31.09	0.1718	0.8866
10	0.8121	25.82	31.79	0.1034	0.8727
11	1.1887	35.22	29.63	0.1441	0.8788
12	0.9858	33.85	34.34	0.1134	0.8850
13	0.6578	20.05	30.48	0.0837	0.8728
14	0.7001	24.05	34.35	0.0636	0.9092
15	0.7608	24.34	31.99	0.0561	0.9263
16	0.7637	26.85	35.16	0.0877	0.8852
17	1.0324	36.41	35.27	0.1328	0.8714
18	1.1203	41.25	36.82	0.1467	0.8691
19	0.7099	21.09	29.71	0.0956	0.8653
20	0.8471	29.61	34.95	0.0615	0.9274
21	0.6530	21.33	32.66	0.1009	0.8455
	1.7662	56.65		NA	NA
	1.8353	57.45		NA	NA
	1.4916	50.63		NA	NA
Average	1.1359	36.5733	32.40	0.113395	0.8910
Standard Dev.	0.3844	11.6958	2.34	0.0382	0.0225

Table D-4: Pothos lipid extraction data

Pothos Lipid Extractions						
Sample ID	Sample Type	Sample Weight (g)	Pre Weight (g)	Post Weight (g)	Extraction Weight (g)	Lipid % / % Recovery
1	Pothos A	0.6951	109.8464	109.891	0.0446	0.0642
2	Pothos B	0.7644	109.8105	109.8609	0.0504	0.0659
3	Pothos C	0.9824	124.6471	124.7158	0.0687	0.0699
4	Olive Oil	0.1333	114.2807	114.4151	0.1344	1.0083
5	Veggie Oil	0.1042	109.9309	110.0369	0.106	1.0173
6	Blank		113.3016	113.3103	0.0087	
					Lipid % by dry weight	
					Average	0.0667
					Std Dev.	0.0030
	Pothos Dry Weight =			0.1090		
	Pothos Lipid % =			0.0667		
	Surface Area/Wet weight =			32.4		

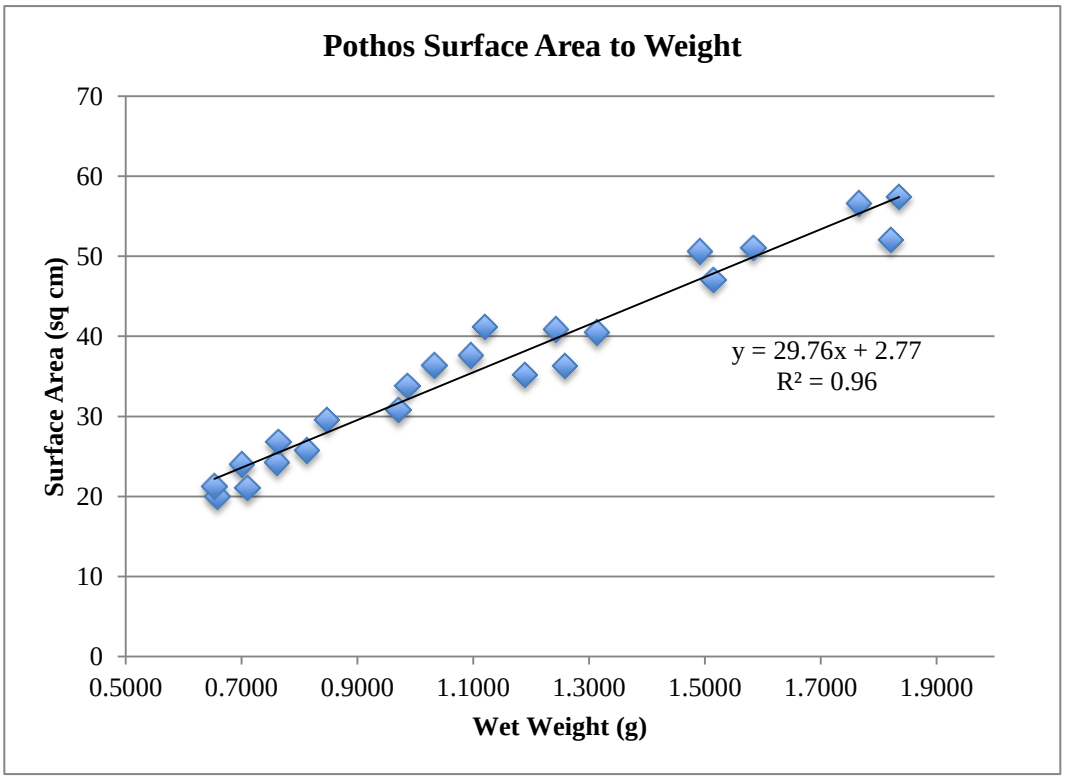

Fig. D-2. Pothos weight to surface area determination

Table D-5: Spider leaf data

Spider					
Sample ID	Wet Weight (g)	Surface Area (sq cm)	Surface Area / Weight	Dry Weight (g)	Fractional water content
1	2.0801	45.39	21.82	0.2272	0.8908
3	1.1095	20.12	18.13	0.3570	0.6782
4	0.9915	26.65	26.88	0.0670	0.9324
5	1.0482	20.24	19.31	0.0682	0.9349
6	0.6211	21.94	35.32	0.0896	0.8557
7	0.6571	21.95	33.40	0.0662	0.8993
8	0.9016	18.95	21.02	0.0591	0.9344
9	0.5481	15.71	28.66	0.0660	0.8796
10	0.6379	16.45	25.79	0.0640	0.8997
12	1.5298	26.93	17.60	0.0731	0.9522
13	0.9888	25.17	25.46	0.0981	0.9008
14	1.8156	41.55	22.88	0.1226	0.9325
15	1.4485	38.12	26.32	0.0841	0.9419
16	1.6716	36.55	21.87	0.1680	0.8995
17	1.4169	41.81	29.51	0.1729	0.8780
18	1.0640	30.42	28.59	0.1609	0.8488
19	1.0706	27.71	25.88	0.1294	0.8791
	1.1847	31.83	26.87	0.1234	NA
	0.7137	27.11	37.99	0.1098	NA
	1.0221	32.11		NA	NA
Average	1.1261	28.34	25.20	0.1220	0.8905
Standard Dev.	0.4210	8.77	5.03	0.0781	0.0626

Table D-6: Spider lipid extraction data

Spider Lipid Extractions						
Sample ID	Sample Type	Sample Weight (g)	Pre Weight (g)	Post Weight (g)	Extraction Weight (g)	Lipid % / % Recovery
1	Spider A	0.6793	109.8375	109.899	0.0615	0.0905
2	Spider B	0.6005	109.8295	109.8876	0.0581	0.0968
3	Spider C	0.7896	124.6421	124.7144	0.0723	0.0916
4	Olive Oil	0.0892	114.3466	114.4362	0.0896	1.0045
5	Veggie Oil	0.0777	109.9699	110.0478	0.0779	1.0026
6	Blank		113.3285	113.3282	-0.0003	
					Lipid % by dry weight	
					Average	0.0930
					Std Dev.	0.0033
	Spider Dry Weight =			0.1095		
	Spider Lipid % =			0.0930		
	Surface Area/Wet weight =			25.2		

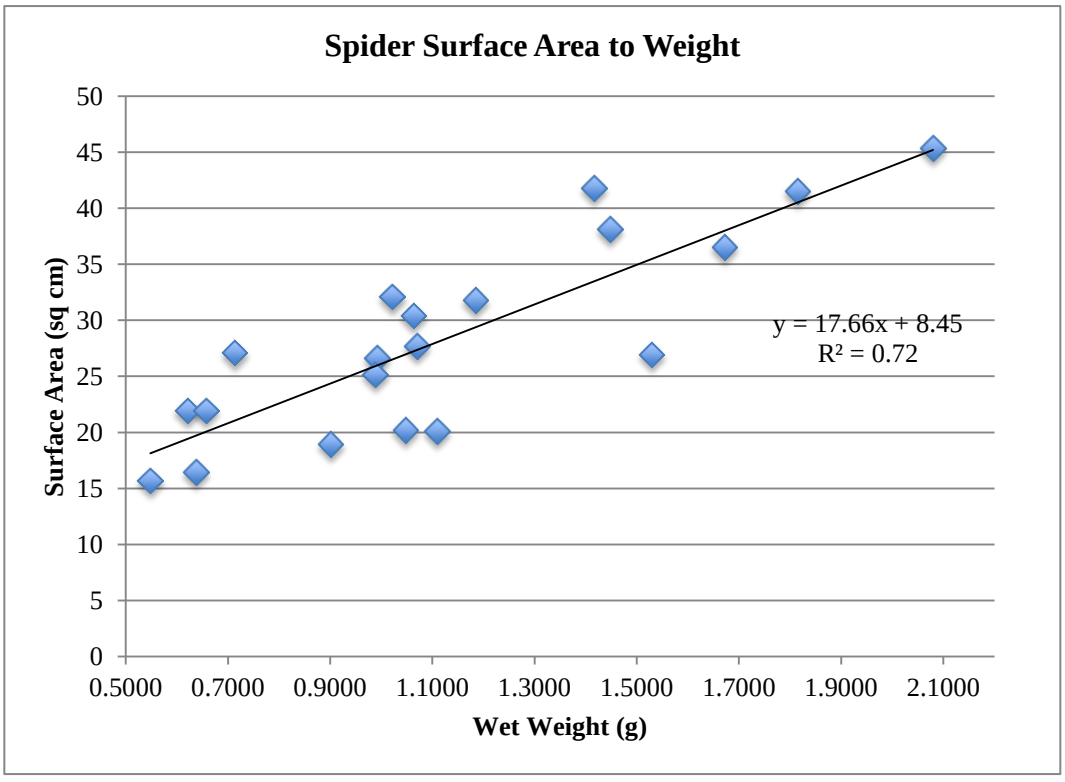

Fig. D-3. Spider weight to surface area determination

Table D-7: Cactus leaf data

Cactus					
Sample ID	Wet Weight (g)	Surface Area (sq cm)	Surface Area / Weight	Dry Weight (g)	Fractional water content
1	0.8997	5.67	6.30	0.0576	0.9360
2	2.2262	9.75	4.38	0.1846	0.9171
3	1.1805	6.49	5.50	0.0772	0.9346
4	1.2316	6.24	5.07	0.0940	0.9237
5	1.1690	5.42	4.64	0.0805	0.9311
6	2.4891	10.05	4.04	0.2096	0.9158
7	1.7684	7.31	4.13	0.1233	0.9303
8	0.8738	3.55	4.06	0.0523	0.9401
9	1.6852	7.24	4.30	0.1330	0.9211
10	1.1051	6.11	5.53	0.0996	0.9099
11	1.2335	6.54	5.30	0.0981	0.9205
12	1.0905	6.54	6.00	0.0753	0.9309
13	0.9056	5.31	5.86	0.0691	0.9237
14	0.6305	5.75	9.12	0.0464	0.9264
15	1.0519	6.14	5.84	0.0884	0.9160
16	0.8406	4.42	5.26	0.0615	0.9268
17	0.6403	5.57	8.70	0.0439	0.9314
18	1.4614	7.82	5.35	0.0982	0.9328
19	1.4633	7.84	5.36	0.1397	0.9045
20	0.8546	5.79	6.78	0.0563	0.9341
21	1.0849	5.69	5.24	0.0606	0.9441
22	1.3214	6.82	5.16	0.1052	0.9204
23	1.3279	6.29	4.74	0.0975	0.9266
24	0.8447	5.29	6.26	0.0677	0.9199
25	0.5102	4.71	9.23	0.0361	0.9292
26	1.0261	7.53	7.34	0.0681	0.9336
27	1.5384	8.49	5.52	0.1037	0.9326
28	1.1322	6.03	5.33	0.1020	0.9099
29	1.1349	7.15	6.30	0.0826	0.9272
30	0.9317	5.57	5.98	0.0646	0.9307
31	0.6246	4.61	7.38	0.0407	0.9348
32	0.7198	4.92	6.84	0.0548	0.9239
33	0.3659	2.07	5.66	0.0207	0.9434
34	0.7640	3.67	4.80	0.0507	0.9336
35	0.9014	6.07	6.73	0.0631	0.9300
Average	1.1151	6.13	5.83	0.0830	0.9271
Standard Dev.	0.4467	1.60	1.32	0.0396	0.0092

Table D-8: Cactus lipid extraction data

Cactus Lipid Extractions						
Sample ID	Sample Type	Sample Weight (g)	Pre Weight (g)	Post Weight (g)	Extraction Weight (g)	Lipid % / % Recovery
1	Cactus A	0.9295	109.8351	109.8716	0.0365	0.0393
2	Cactus B	1.0281	109.8171	109.8538	0.0367	0.0357
3	Cactus C	0.8620	124.6480	124.6822	0.0342	0.0397
4	Olive Oil	0.0875	114.2768	114.3651	0.0883	1.0091
5	Veggie Oil	0.0913	109.9491	110.0419	0.0928	1.0164
6	Blank		113.2922	113.2941	0.0019	
					Lipid % by dry weight	
					Average	0.0382
					Std Dev.	0.0022
	Cactus Dry Weight =			0.0729		
	Cactus Lipid % =			0.0382		
	Surface Area/Wet weight =			5.83		

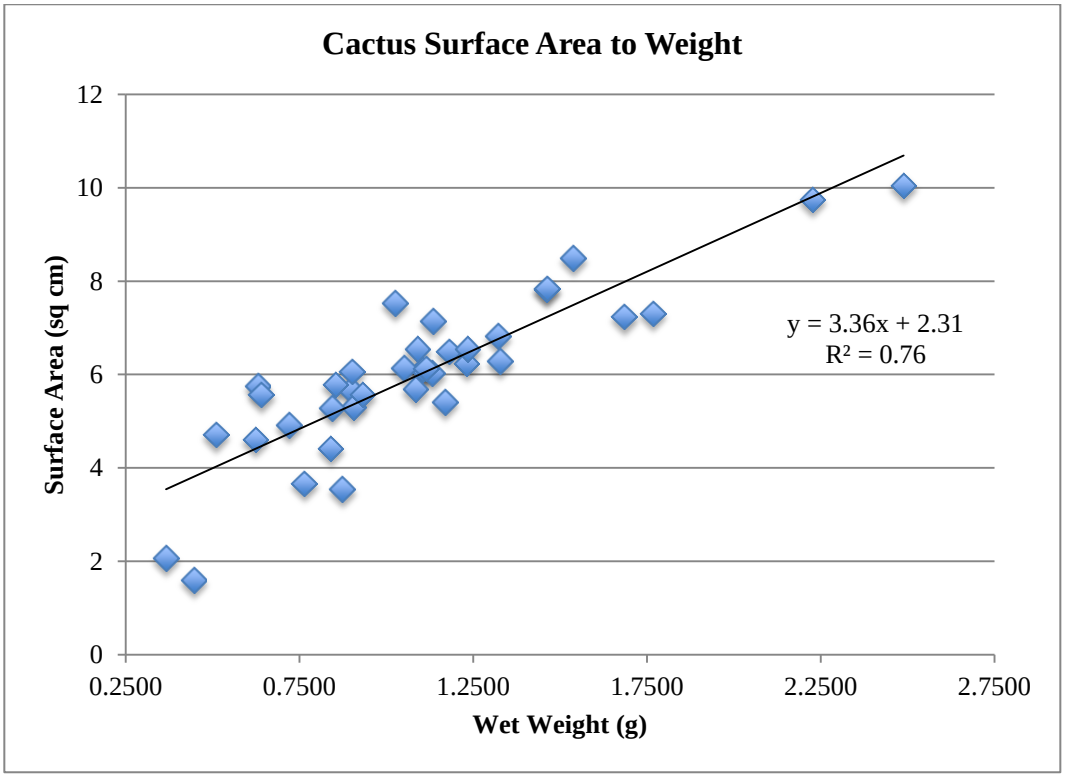

Fig. D-4. Cactus weight to surface area determination

APPENDIX E

FLOW THROUGH CHAMBER SUPPORTING MATERIAL

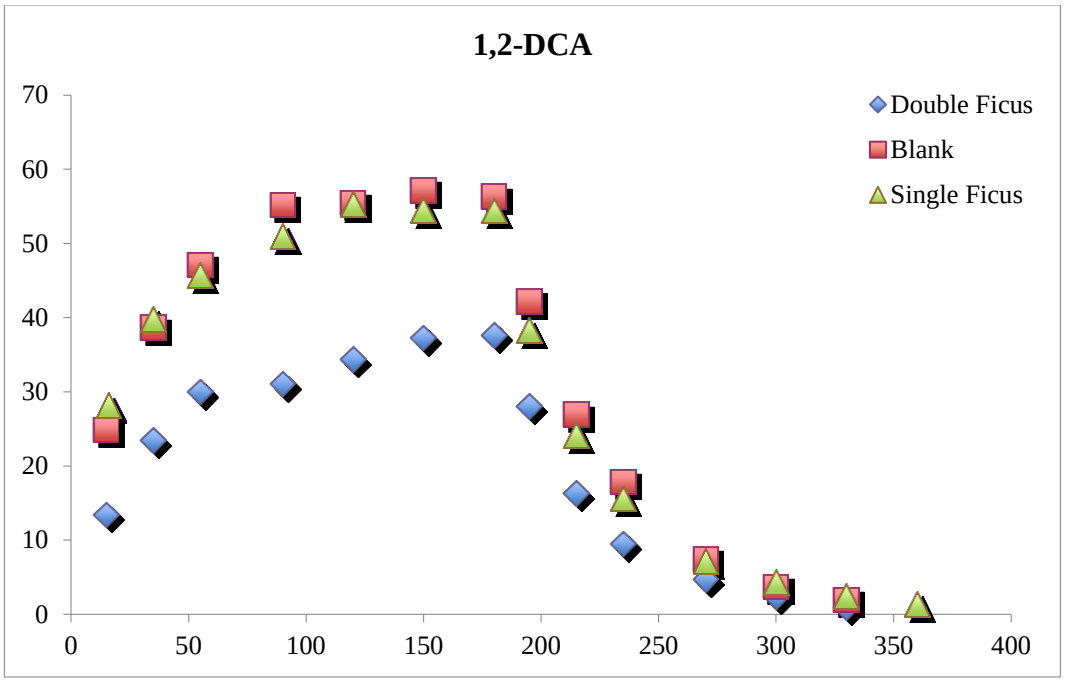

Fig. E-1: Effluent concentration time series plot determination of 1,2-DCA with single and double ficus mass compared to blank chamber

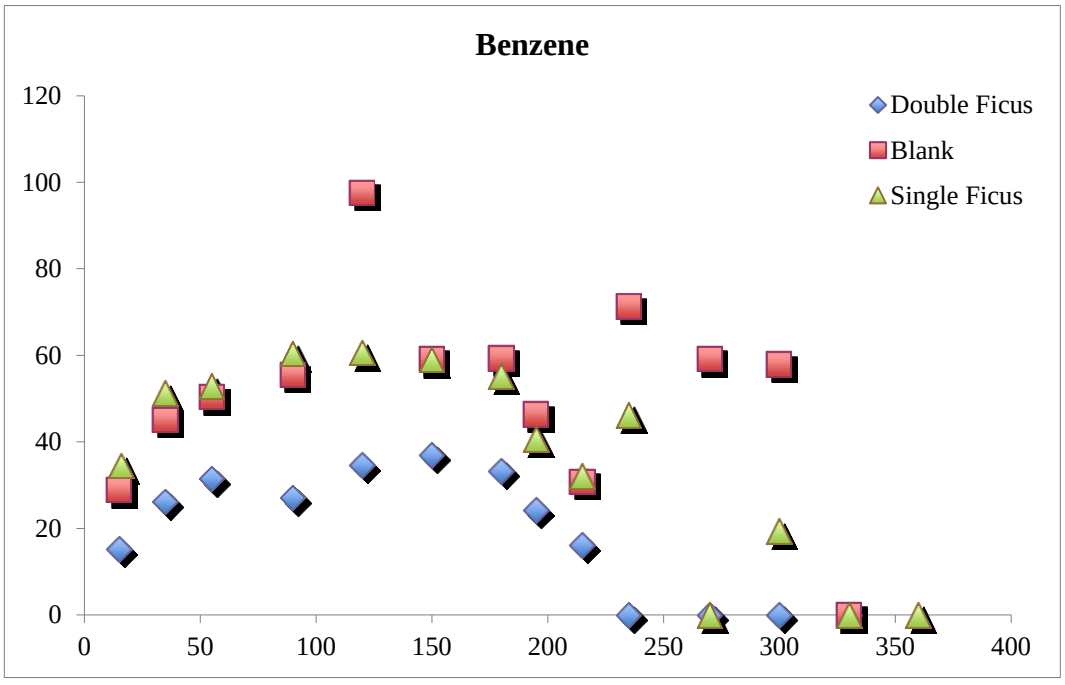

Fig. E-2: Effluent concentration time series plot determination of Benzene with single and double ficus mass compared to blank chamber

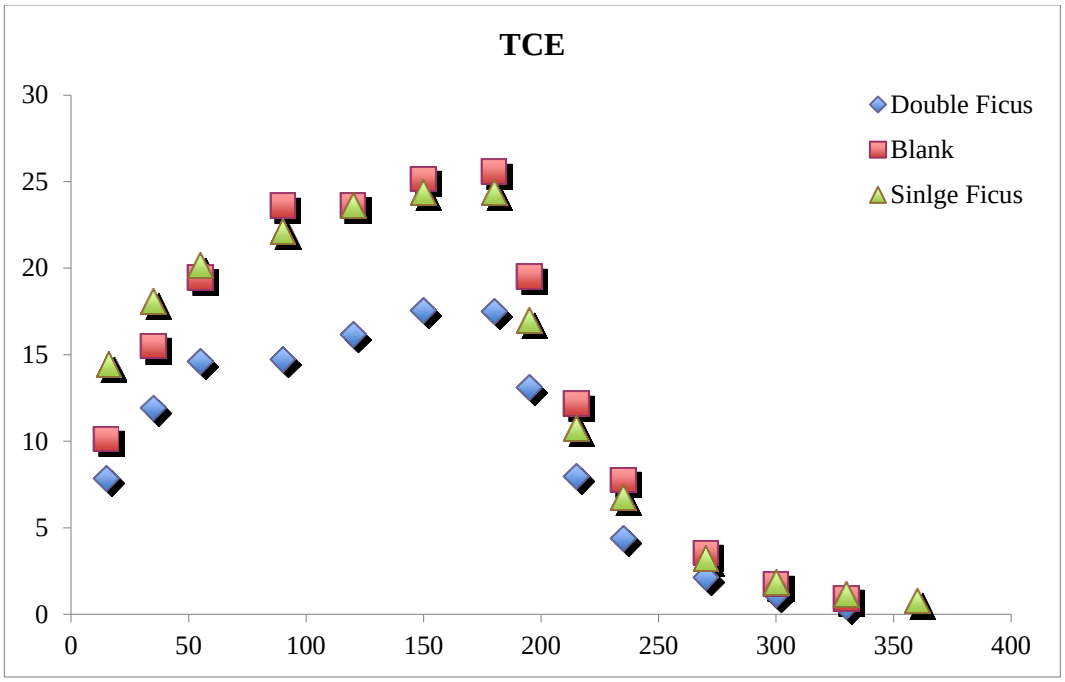

Fig. E-3: Effluent concentration time series plot determination of TCE with single and double ficus mass compared to blank chamber

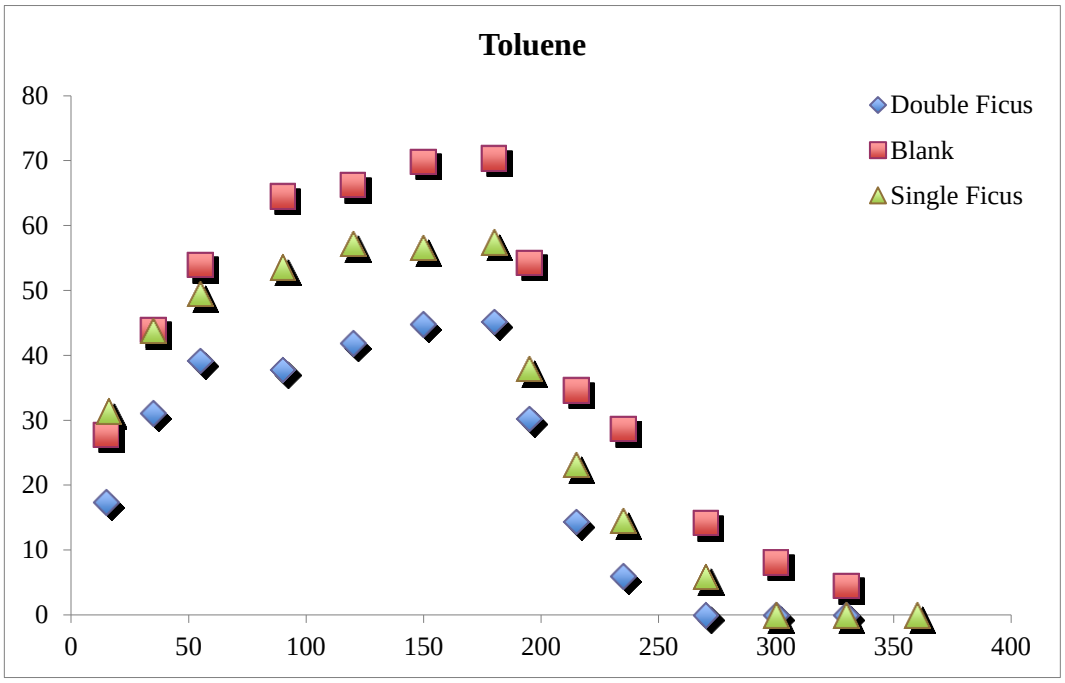

Fig. E-4: Effluent concentration time series plot determination of toluene with single and double ficus mass compared to blank chamber

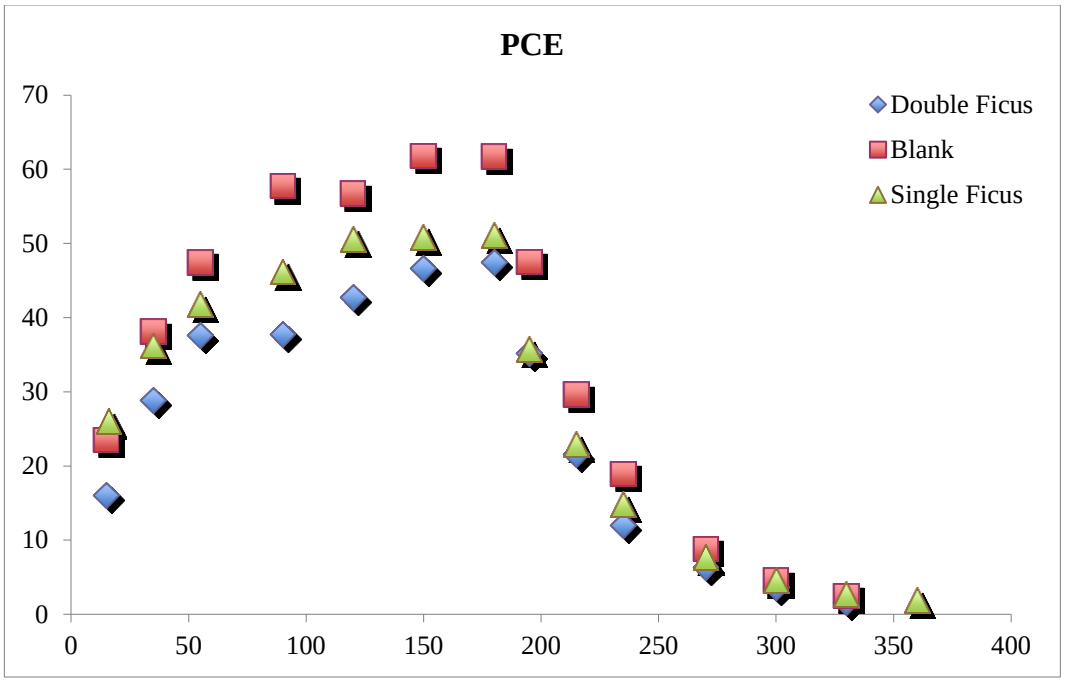

Fig. E-5: Effluent concentration time series plot determination of PCE with single and double ficus mass compared to blank chamber

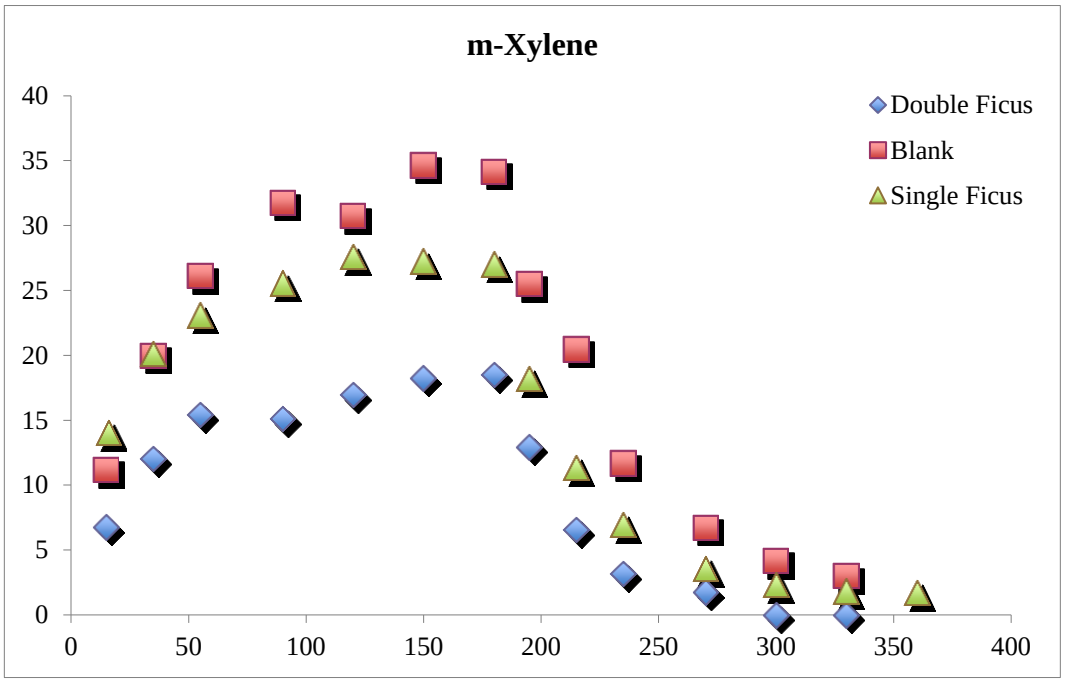

Fig. E-6: Effluent concentration time series plot determination of m-xylene with single and double ficus mass compared to blank chamber

APPENDIX F

STATIC HEADSPACE SUPPORTING MATERIAL

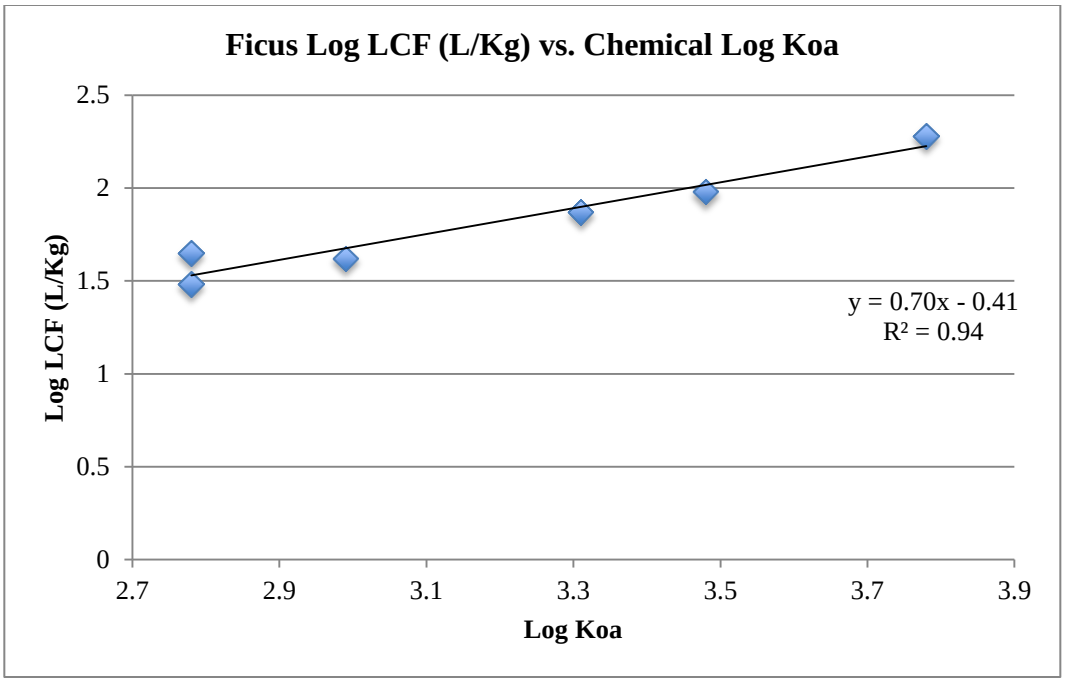

Fig. F-1. Static headspace ficus LCF vs Chemical Koa value

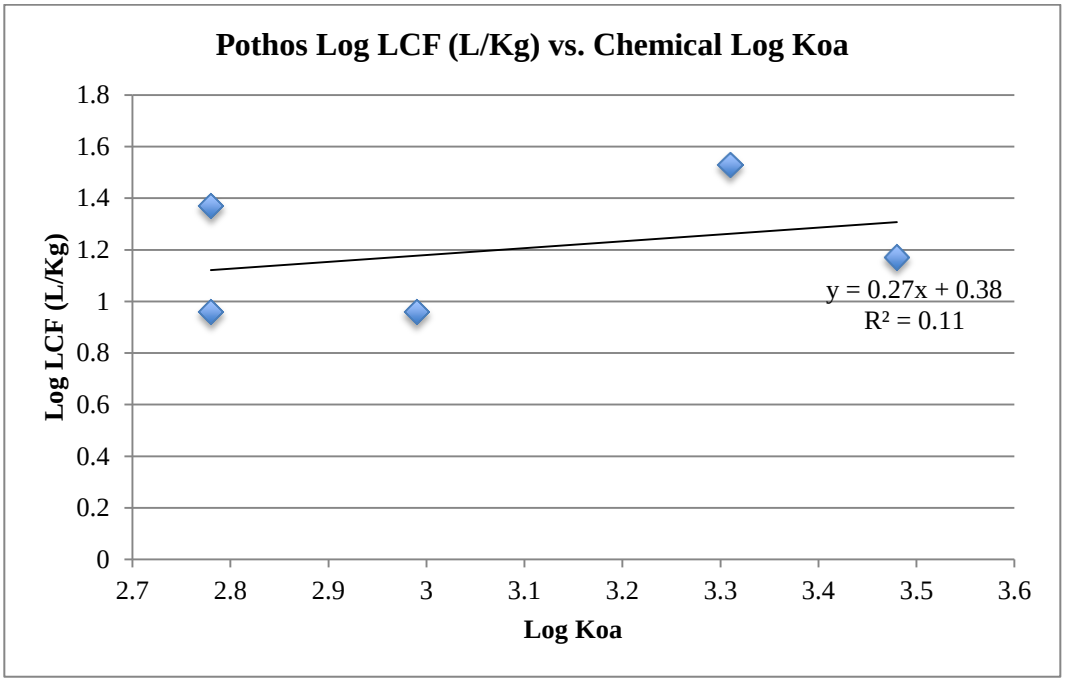

Fig. F-2. Static headspace pothos LCF vs Chemical Koa value

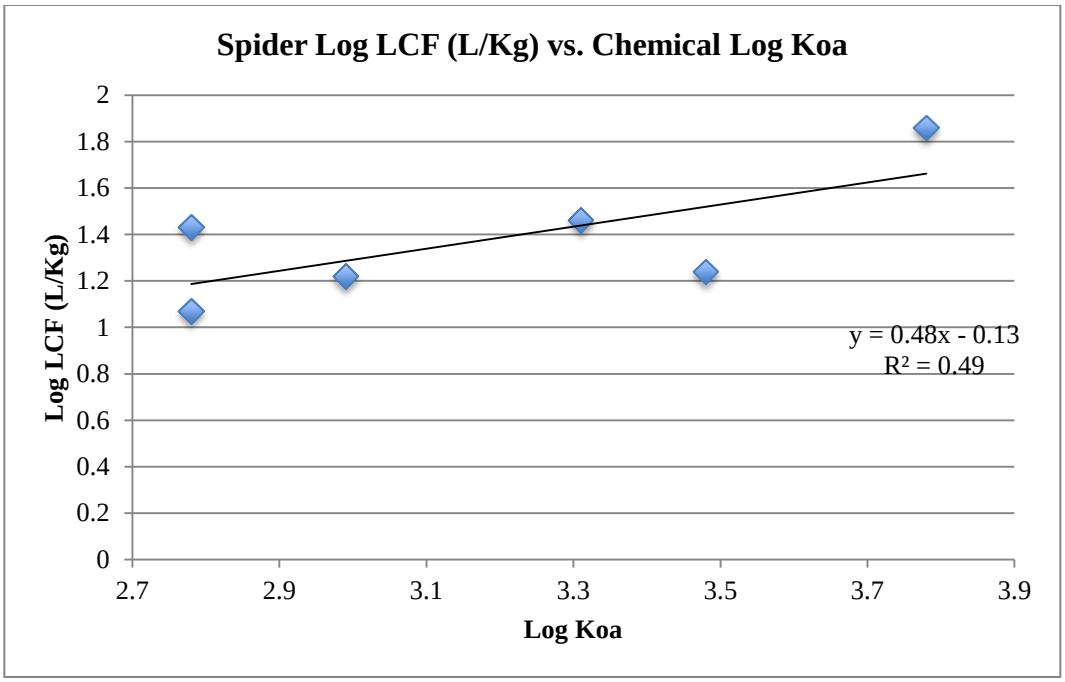

Fig. F-3. Static headspace spider LCF vs Chemical Koa value

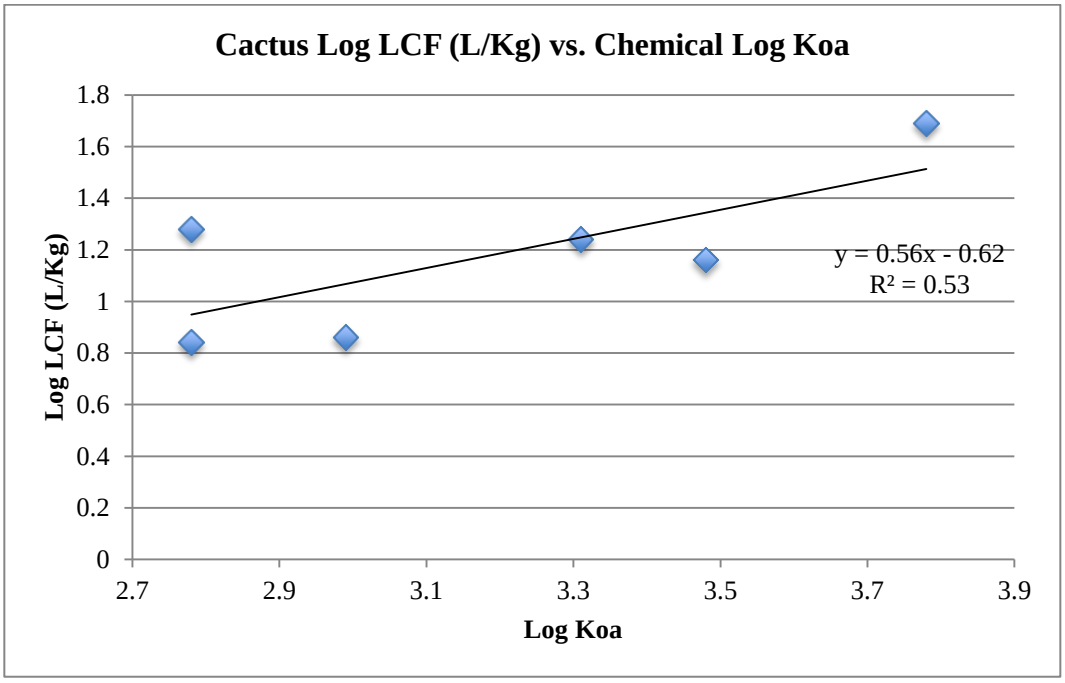

Fig. F-4. Static headspace cactus LCF vs Chemical Koa value